

JOURNAL OF THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS ON ORGANIC CHEMISTRY.

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BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Fractionation of Crude Petroleum by Capillary Diffusion. JOSEPH E. GILPIN and MARSHALL P. CRAM (*Amer. Chem. J.*, 1908, 40, 495—537).—It was observed by Day that when black vaselin is filtered through warm fuller's earth, the first product is liquid, whilst the succeeding portions become more and more viscous. This observation led to the discovery that a fractionation of crude petroleum can be effected in this way.

In the present investigation, tin tubes, $5\frac{1}{2}$ feet long, packed with fuller's earth have been employed, the lower ends of which were immersed in the petroleum. It has been found that a fractionation of the oil takes place, the fractions rising to the top of the tube being of lower sp. gr. than those at the bottom. The paraffin hydrocarbons collect in the former fractions, and the unsaturated hydrocarbons in the latter. When water is added in successive quantities to fuller's earth which contains petroleum, the oil which is first displaced differs in sp. gr. from that which is displaced later. The whole of the oil cannot be displaced with water; about one-third remains in the fuller's earth. E. G.

Method of Production of Olefines by Decomposition of Esters. ALBERT COLSON (*Compt. rend.*, 1908, 147, 1054—1059).—The author finds that the classical method for the preparation of ethylene is a particular case of a general reaction, since the esters of

organic or mineral acids decompose, at a sufficiently high temperature, into the corresponding acid and an olefine. Thus ethyl benzoate is unaltered when heated in sealed tubes at 300° ; at $305\text{--}310^{\circ}$, however, decomposition takes place, with formation of benzoic acid and ethylene. The action is most rapid at 330° ; after being heated for six hours at this temperature, the ester gave ten times its volume of hydrocarbon. Under the same conditions, amyl benzoate gave amylene. The yield of hydrocarbon is limited by the pressure of the gas, since, on allowing this to escape, a further quantity is obtained when the tube is re-heated. The benzoic acid has no influence on the reaction, which appears to be an irreversible one.

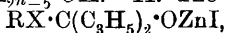
Ethyl stearate undergoes partial decomposition when distilled at 224° , but resists a temperature of 300° in the sealed tube; at 315° it furnishes stearic acid and ethylene. W. O. W.

Dehydration of Commercial Methyl Alcohol. JOSEPH GYR (*Ber.*, 1908, 41, 4322—4327. Compare Klason and Norlin, *Abstr.*, 1906, i, 921).—The author prepares pure methyl alcohol from the acetone-free alcohol by first heating for some time with freshly burnt lime, then the alcohol is left in contact with ignited potassium carbonate for several weeks, and finally distilled several times over metallic calcium. For the first distillation, 10 grams of shavings per litre of methyl alcohol are used, the later distillations requiring less. As the calcium only reacts slightly in the cold, the temperature is raised, and the reaction proceeds, but care must be taken that alcohol does not distil over at this stage. When the bulk of the calcium has been acted on, the alcohol is distilled, the first fraction, which has a disagreeable odour, being collected separately. When all the water has been removed, the calcium reacts energetically with methyl alcohol if the temperature be not under control, so that only small quantities of the metal are required for the final distillation. The distillation over calcium is continued until the initial esterification constant of phenylacetic acid reaches the value 3.556. In one experiment, Kahlbaum's methyl alcohol from methyl oxalate had $k=0.465$; after one distillation over lime and potassium carbonate, 2.094; after a first distillation over calcium, 3.032; after a second, 3.279; after the third, 3.556. Magnesium amalgam is not a suitable agent for drying methyl alcohol.

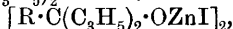
Pure methyl alcohol has $D_{15}^{15} 0.79647$ and b. p. $64.56^{\circ}/760$ mm. (compare Klason and Norlin, *loc. cit.*). 0.0524 volume % of water lowers the esterification constant of phenylacetic acid to 3.326, and 0.1254% to 2.976, so that the determination of this constant is even a better criterion than the density for determining whether the alcohol is pure. W. R.

Synthesis of Alcohols of the Series $C_nH_{2n-5}OH$. ALEXANDER N. REFORMATSKY (*Ber.*, 1908, 41, 4083—4102; *J. Russ. Phys. Chem. Soc.*, 1908, 40, 1182—1238).—The action of allyl iodide and zinc on esters of halogen derivatives of carboxylic acids in ethereal solution proceeds in three different directions, represented by the following equations, in which R represents a bivalent hydrocarbon radicle, R' a univalent

hydrocarbon radicle, and X , a halogen atom: I. (a) $RX \cdot COOR' + ZnI \cdot C_3H_5 = RX \cdot C(OZnI)(C_3H_5) \cdot OR'$; (b) $RX \cdot C(OZnI)(C_3H_5) \cdot OR' + ZnI \cdot C_3H_5 = RX \cdot C(C_3H_5)_2 \cdot OZnI + ZnI \cdot OR'$; (c) $RX \cdot C(C_3H_5)_2 \cdot OZnI + ZnI \cdot C_3H_5 = C_3H_5 \cdot R \cdot C(C_3H_5)_2 \cdot OZnI + ZnIX$; (d) $C_3H_5 \cdot R \cdot C(C_3H_5)_2 \cdot OZnI + H_2O = C_3H_5 \cdot R \cdot C(C_3H_5)_2 \cdot OH + ZnI \cdot OH$, the product obtained being an unsaturated, monohydric alcohol having the general formula $C_nH_{2n-5} \cdot OH$. II. The compound,

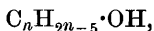


formed according to equation (b) above, reacts with the excess of zinc present, thus: $2RX \cdot C(C_3H_5)_2 \cdot OZnI + Zn = ZnX_2 +$



the latter being then decomposed by water, giving the tetra-allylglycol, $OH \cdot C(C_3H_5)_2 \cdot R \cdot R \cdot C(C_3H_5)_2 \cdot OH$. III. $RX \cdot C(C_3H_5)_2 \cdot OZnI + Zn + RX \cdot CO_2R' = ZnX_2 + CO_2R' \cdot R \cdot R \cdot C(C_3H_5)_2 \cdot OZnI$, which, with water, yields the ester of a diallylhydroxy-acid, $CO_2R' \cdot R \cdot R \cdot C(C_3H_5)_2 \cdot OH$; on hydrolysis, this ester yields either the free acid or the corresponding

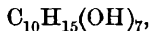
lactone, $O \begin{smallmatrix} \swarrow C(C_3H_5)_2 \cdot R \\ \searrow CO \end{smallmatrix} \text{---} R$. The proportion of the alcohol,



obtained diminishes, and that of the condensation products increases, as the molecular weight of the chloro-ester increases.

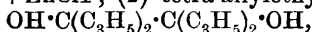
The alcohols, $C_nH_{2n-5} \cdot OH$, are colourless liquids with an odour resembling that of the terpenes, and are insoluble in water, but readily soluble in alcohols or ethers. They exhibit unexpected stability, for they do not oxidise appreciably in the air, although, when repeatedly distilled, they decompose to some extent, with formation of water. Their acetyl derivatives are obtained with difficulty, but the alcohols readily undergo bromination, which is, however, always accompanied by evolution of hydrogen bromide. They are readily oxidised by 1% potassium permanganate solution, yielding heptahydric alcohols. The boiling point and density of the alcohols rise as the molecular weight increases; the presence of an iso-radicle lowers the boiling point and also the yield of the alcohol.

Triallylcarbinol, $OH \cdot C(C_3H_5)_3$, prepared by the action of allyl iodide and zinc on ethyl chloro-formate, has b. p. $191-192^\circ$, $D_4^{21} 0.87829$, $D_4^{21} 0.8781$, $n_D^{21} 1.4680$. Bromination yields the *hexabromide*, $C_{10}H_{16}OBr_6$, which loses hydrogen bromide, giving the *compound*, $C_{10}H_{15}OBr_5$. Oxidation with 1% permanganate solution yields the *heptitol*,



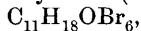
which could not be obtained pure, but yields a *hepta-acetyl* derivative, $C_{10}H_{15}(OAc)_7$, in the form of a dark brown syrup. Oxidation of triallylcarbinol with 3% permanganate solution yields oxalic and other acids. Attempts to prepare the methyl ether corresponding with the alcohol led to no definite results, as also did experiments made with the object of removing water from the alcohol and obtaining the corresponding hydrocarbon.

The triallylcarbinol, obtained as described above, is accompanied by: (1) crotonic acid, probably formed by isomeric change of vinylacetic acid, itself due to the reaction: $\dot{C}H_2 \cdot \dot{C}H \cdot CH_2I + Zn + Cl \cdot CO_2Et = CH_2 \cdot \dot{C}H \cdot CH_2 \cdot CO_2Et + ZnClI$; (2) tetra-allylethylene glycol,

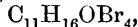


which is obtained as an odourless, yellow syrup, b. p. $160^{\circ}/12$ mm., and is being investigated further.

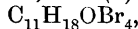
Diallylcrotonylcarbinol, $\text{OH}\cdot\text{C}(\text{C}_3\text{H}_5)_2\cdot\text{CH}_2(\text{C}_3\text{H}_5)$, prepared by the action of allyl iodide and zinc on ethyl bromo- or chloro-acetate, is a moderately viscous liquid, b. p. 217° , D_0^{18} 0.8823, D_4^{18} 0.88218, n_D^{18} 1.474. On bromination, it yields: (1) the *hexabromide*,



which gradually loses hydrogen bromide, giving $\text{C}_{11}\text{H}_{17}\text{OBr}_5$,

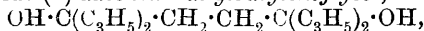


and lower brominated products; and (2) the *tetrabromide*,



which is a stable compound. Oxidation of the alcohol with 1% permanganate solution yields the *heptitol*, $\text{C}_{11}\text{H}_{17}(\text{OH})_7$, which was not obtained pure, and which, on acetylation, loses water and gives an *acetyl* derivative having the composition $\text{C}_{11}\text{H}_{17}\text{O}(\text{OAc})_5$. Attempts to remove H_2O from the alcohol, $\text{C}_{11}\text{H}_{18}\text{O}$, and thus obtain the hydrocarbon, $\text{C}_{11}\text{H}_{16}$, gave no definite result.

The action of allyl iodide and zinc on ethyl bromo- or chloro-acetate also yields (1) *ααδδ-tetra-allylbutyleneglycol*,

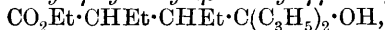


b. p. $200-213^{\circ}/10$ mm., which is being investigated, and (2) probably the ester, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{C}_3\text{H}_5)_2\text{OH}$.

Diallyl-α-allylethylcarbinol, $\text{OH}\cdot\text{C}(\text{C}_3\text{H}_5)_2\cdot\text{CHMe}\cdot\text{C}_3\text{H}_5$, prepared by the action of allyl iodide and zinc on ethyl α-bromopropionate, is a colourless oil, b. p. $223-224^{\circ}$, D_0^{22} 0.876193, D_4^{22} 0.876024, n_D^{22} 1.4692. On bromination, it yields the *hexabromide*, $\text{C}_{12}\text{H}_{20}\text{OBr}_6$, which loses hydrogen bromide, at first rapidly, giving the compound $\text{C}_{12}\text{H}_{19}\text{OBr}_5$, and subsequently more slowly. On oxidation with 1% permanganate solution, it gives the *heptitol*, $\text{C}_{12}\text{H}_{19}(\text{OH})_7$, the *hepta-acetyl* derivative of which, $\text{C}_{12}\text{H}_{19}(\text{OAc})_7$, was prepared. The action of allyl iodide and zinc on ethyl α-bromopropionate also yields the *lactone* of γ-hydroxy-

αβ-dimethyl-γγ-diallylbutyric acid, $\begin{array}{c} \text{CHMe}\cdot\text{C}(\text{C}_3\text{H}_5)_2 \\ \text{CHMe}-\text{CO} \end{array} > \text{O}$, b. p. $155-160^{\circ}/15$ mm.

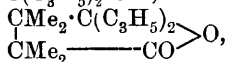
Diallyl-α-allylpropylcarbinol, $\text{OH}\cdot\text{C}(\text{C}_3\text{H}_5)_2\cdot\text{CHEt}\cdot\text{C}_3\text{H}_5$, prepared by the action of allyl iodide and zinc on ethyl α-bromobutyrate, is a colourless, oily liquid, b. p. $235-236^{\circ}$, D_0^{19} 0.88303, D_4^{19} 0.8817, n_D^{19} 1.471. On bromination, it yields the *bromide*, $\text{C}_{13}\text{H}_{18}\text{OBr}_4$, formed by the loss of 2HBr from the hexabromide. Oxidation by means of 1% permanganate solution yields the *heptitol*, $\text{C}_{13}\text{H}_{21}(\text{OH})_7$, which, on acetylation, undergoes dehydration and gives the *acetyl* derivative, $\text{C}_{13}\text{H}_{21}\text{O}(\text{OAc})_5$. *Ethyl γ-hydroxy-αβ-diethyl-γγ-diallylbutyrate*,



has b. p. $161-162^{\circ}$.

Diallyl-α-allylisopropylcarbinol, $\text{OH}\cdot\text{C}(\text{C}_3\text{H}_5)_2\cdot\text{CMe}_2\cdot\text{C}_3\text{H}_5$, prepared by the action of allyl iodide and zinc on ethyl α-bromoisobutyrate, is a colourless, oily liquid, b. p. 235° , D_0^{19} 0.8942, D_4^{19} 0.8928, n_D^{19} 1.4760. On bromination, it yields the *bromide*, $\text{C}_{13}\text{H}_{21}\text{OBr}_5$. Oxidation with 1% permanganate solution gives the *pentitol*, $\text{C}_{13}\text{H}_{21}\text{O}(\text{OH})_5$, the *penta-acetyl* derivative of which, $\text{C}_{13}\text{H}_{21}\text{O}(\text{OAc})_5$, was prepared. The action of allyl iodide and zinc on ethyl α-bromoisobutyrate also yields a

mixture of the ethyl ester of γ -hydroxy- $\alpha\alpha\beta\beta$ -tetramethyl- $\gamma\gamma$ -diallylbutyric acid, $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{C}(\text{C}_3\text{H}_5)_2\cdot\text{OH}$, and of its lactone,



b. p. 195—196°/15 mm.

T. H. P.

Methyl and Ethyl Esters of Thiophosphoric Acid. P. PISTSCHIMUKA (*Ber.*, 1908, 41, 3854—3859).—Alcohols react with phosphorus thiochloride, forming acid chlorides of the type $\text{PSCl}_2\cdot\text{OR}$, which, when treated with sodium alkyl oxides, yield neutral esters of thiophosphoric acid. The latter substances readily form additive compounds with salts, which decompose when heated; thus the additive compound, $\text{PS}(\text{OMe})_3\cdot 2\text{HgCl}_2$, when heated, decomposes thus: $\text{PS}(\text{OMe})_3\cdot 2\text{HgCl}_2 \rightarrow \text{PS}(\text{OMe})(\text{OHgCl})_2 + 2\text{MeCl}$.

Methyl thiophosphate forms with sodium methoxide the salt, $\text{PO}(\text{SNa})(\text{OMe})_2$, which, when treated with silver nitrate, yields the salt, $\text{PO}(\text{SAg})(\text{OMe})_2$; the latter substance may also be obtained by adding an alcoholic solution of silver nitrate to the methyl ester; it forms stellate groups of white needles, and must have the constitution given, since, when treated with methyl iodide, it does not yield methyl thiophosphate, but gives rise to an ester, $\text{PO}(\text{SMe})(\text{OMe})_2$, a liquid, b. p. 103°/12 mm., D_4^{20} 1.2685.

The following additive products were prepared: $\text{PS}(\text{OMe})_3\cdot 2\text{HgCl}_2$; $3\text{PS}(\text{OMe})_3\cdot 2\text{FeCl}_3$; $\text{PO}(\text{SHgCl})(\text{OEt})_2\cdot \text{HgCl}_2$; $\text{PS}(\text{OMe})(\text{OHgCl})_2$; $\text{PS}(\text{OMe})(\text{OTlCl})_2$, yellow scales; $\text{PO}(\text{SAg})(\text{OEt})_2$, white crystals, m. p. 82°; and $\text{PO}(\text{SNa})(\text{OEt})_2$.

Methyl thiophosphate, $\text{PS}(\text{OMe})_3$, is an oil with an odour somewhat like ozone, b. p. 82°/20 mm., D_4^{20} 1.2192.

The following acid chlorides were prepared: $\text{PSCl}_2\cdot\text{OMe}$, b. p. 70°/40 mm., D_4^{20} 1.4949; $\text{PSCl}_2\cdot\text{OEt}$, b. p. 68°/20 mm., D_4^{20} 1.3966; $\text{PSCl}_2\cdot\text{OPr}^a$, b. p. 84°/20 mm., D_4^{20} 1.3344; $\text{PSCl}_2\cdot\text{OPr}^b$, b. p. 91°/20 mm., D_4^{20} 1.2724; they are colourless liquids, and are not decomposed by alcohols or water.

W. H. G.

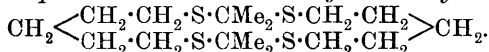
Constitution of Phytin. ERNST WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1908, 58, 118—121).—Phytin, the calcium magnesium salt of Posternak's anhydro-oxyethylenediphosphoric acid (*Abstr.*, 1903, ii, 680), is not appreciably affected by heating with saturated barium hydroxide solution at 180° or with 10% sodium hydroxide solution for one hundred hours, but when heated at 220—230° for twenty to twenty-four hours with 20% sodium hydroxide, it yields inositol and phosphoric acid. The compound is thus an inositolphosphoric acid. J. J. S.

The Lability of Lecithin. WOLFGANG HEUBNER (*Arch. exp. Path. Pharm.*, 1908, 59, 420—423).—The unstable nature of the lecithin molecule is shown by the fact that, after heating with alcohol, the platinum salt obtained is not pure choline platinichloride, but, in part, that of a base of lower molecular weight. The lecithin cadmium chloride also undergoes alteration in composition when recrystallised. Ovo-lecithin was employed.

W. D. H.

Pentamethylene Mercaptans and Multi-membered Cyclic Mercaptols and Disulphones. WILHELM AUTENRIETH and ALFRED GEYER (*Ber.*, 1908, 41, 4249—4256. Compare Abstr., 1899, i, 579, 580; 1902, i, 389).—*Pentamethylene mercaptan*, $\text{SH} \cdot [\text{CH}_2]_5 \cdot \text{SH}$, obtained by the action of an alcoholic solution of potassium hydrogen sulphide on α -dibromopentane (Braun, Abstr., 1904, i, 841), is a clear, colourless liquid, b. p. 108—109°/15 mm. or 123°/27 mm., and dissolves readily in organic solvents and in alkalis. The *lead* derivative, $\text{C}_5\text{H}_{10}\text{S}_2\text{Pb}$, forms a lemon-yellow, amorphous powder. The *dibenzoate*, $\text{C}_5\text{H}_{10}(\text{S} \cdot \text{COPh})_2$, crystallises from alcohol in slender needles, m. p. 45°. The ethers are readily obtained by the action of alkyl halides on the potassium salt, and when oxidised with permanganate yield the corresponding disulphones. *Pentamethylene- α -diethylsulphone*, $\text{C}_5\text{H}_{10}(\text{SO}_2\text{Et})_2$, crystallises from alcohol in glistening plates, m. p. 154°, and the corresponding *dibenzylsulphone*, $\text{C}_5\text{H}_{10}(\text{SO}_2 \cdot \text{C}_7\text{H}_7)_2$, has m. p. 162—163°.

By the action of hydrogen chloride on a dry ethereal solution of acetone and pentamethylene mercaptan, a cyclic compound is formed, which crystallises from alcohol or acetone in plates with a pearly lustre. It has m. p. 117—118°, a molecular weight 352, and is probably *cycloduplo-1 : 3-dithio-2 : 2-dimethylhexamethylene*,



When oxidised with acidified 5% permanganate solution, it yields the corresponding *cyclo-1 : 3-disulphone*, $\text{C}_{16}\text{H}_{32}\text{O}_8\text{S}_4$, which crystallises from aqueous acetone in slender needles, m. p. 270°.

The 2 : 2-*diethyl* derivative, $\text{C}_{20}\text{H}_{40}\text{S}_4$, obtained from diethyl ketone and pentamethylene mercaptan, crystallises from alcohol in needles, m. p. 113°, and yields a *disulphone*, $\text{C}_{20}\text{H}_{20}\text{O}_8\text{S}_4$, m. p. 260° (decomp.).

J. J. S.

Constitution of Disulphoxides. II. OSCAR HINSBERG (*Ber.*, 1908, 41, 4294—4297. Compare Abstr., 1908, i, 875).—The synthesis of ethyl disulphoxide from potassium ethanethiosulphonate and ethyl bromide would appear to be against the compound being symmetrical, but from Gutmann's results (Abstr., 1908, i, 972) the aryl thiosulphonates are probably of the constitution $\text{R} \cdot \text{SO} \cdot \text{S} \cdot \text{OM}$, and not $\text{R} \cdot \text{SO}_2 \cdot \text{SM}$, and therefore the symmetrical formula for disulphoxides is strengthened. Further evidence in support of this conclusion is furnished by the easy reduction of β -naphthyl disulphoxide to disulphide by sulphurous acid in the presence of a small quantity of hydriodic acid; neither sulphinic acid nor mercaptan could be detected.

W. R.

Total Asymmetric Synthesis. FRANZ HENLE and HERMANN HAAKH (*Ber.*, 1908, 41, 4261—4264).—In previous attempts to obtain asymmetric syntheses by means of circularly polarised light, reactions have been employed which are not affected by light, for example, the addition of hydrogen to benzoylformic acid. The authors have investigated the elimination of carbon dioxide from certain carboxylic acids, a reaction which is influenced to a consider-

able extent by light, but asymmetric synthesis was not observable. The substances employed were α -cyano- α -methylbutyric acid and dichloro-*s*-dimethylsuccinic acid (Abstr., 1892, i, 142).

Ethyl α -cyano- α -methylbutyrate, $\text{CN}\cdot\text{CMeEt}\cdot\text{CO}_2\text{Et}$, has b. p. 198° , and the corresponding acid, $\text{CN}\cdot\text{CMeEt}\cdot\text{CO}_2\text{H}$, obtained by hydrolysing the ester with 25% methyl alcoholic potash, has m. p. 39° .

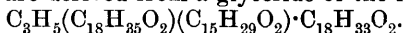
It is pointed out that it is not necessary that the light should be first plane polarised for this type of experiment. J. J. S.

Solid Constituents of Japanese Train Oil. H. OKADA (*Chem. Zeit.*, 1908, 32, 1199—1201).—Repeated extraction with ether and cooling the extract to -10° gave a solid product, which was purified by fractional dissolution in ether-alcohol mixtures of various strengths. This treatment led to a more or less complete separation of a substance, m. p. $34-35^\circ$, having a saponification number, an acid number, and an iodine value in very fair agreement with the mixed glyceride, $\text{C}_3\text{H}_5(\text{C}_{17}\text{H}_{33}\text{O}_2)_2\cdot\text{C}_{18}\text{H}_{33}\text{O}_2$ (Holde, Abstr., 1901, i, 577).

When saponified, this substance gave a liquid fatty acid having a molecular weight and saponification value in agreement with oleic acid; also a white, crystalline compound, m. p. $43-47^\circ$, which is possibly a mixture of stearic acid and *isocetic* acid ($\text{C}_{18}\text{H}_{36}\text{O}_2 + \text{C}_{15}\text{H}_{30}\text{O}_2$).

This mixture, when dissolved in alcohol and cooled by ice, deposited a crystalline mass, m. p. $56-59^\circ$, whilst from the mother liquor there was obtained a substance, m. p. $44-47^\circ$. After fractionally precipitating these substances by adding magnesium acetate to the alcoholic solutions, each was obtained in an apparently pure state, m. p. $57-59^\circ$ and $44-47^\circ$ respectively.

From the evidence at present available, the conclusion is drawn that these substances are derived from a glyceride of the form



J. V. E.

β -Cinenic Acid. HANS RUPE and H. ALTENBURG (*Ber.*, 1908, 41, 3952—3957).— β -Cinenic acid, first obtained by heating α -cinenic acid with dilute sulphuric acid, was held to be a stereoisomeride of the α -acid (Abstr., 1901, i, 578), because the addition of hydrogen bromide gave with the two acids ϵ -bromo- α -hydroxy- $\alpha\epsilon$ -dimethylheptioic acid. As the yield from the β -acid was very poor, the subject has been reinvestigated.

A more convenient method of separating the β - from the α -acid is by the action of hydrochloric acid on a methyl-alcoholic solution of the mixture. The α -acid gives a chlorinated ester boiling $30-35^\circ$ higher than the methyl β -cinenate formed simultaneously, and the pure β -acid is obtained by hydrolysis of the methyl ester, b. p. $127-128^\circ/12\text{ mm.}$, n_D^{20} 1.45083; *ethyl* ester, b. p. $92-93^\circ/12\text{ mm.}$; the *silver*, *lead*, *uranium*, and *copper* salts have also been prepared. The acid could not be obtained solid, nor does it react with hydroxylamine or semicarbazide.

It is now found that a good yield of the bromohydroxydimethylheptioic acid is obtained if the β -cinenic acid is heated with a

saturated solution of hydrobromic acid in a closed tube at 56° for two hours and then at the ordinary temperature for twenty-four hours. The stereoisomerism of the two acids is, therefore, proved. The β -acid is not converted into the α -isomeride on treatment with acetyl chloride.

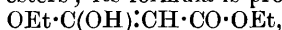
α -Cinenic acid crystallises with $1\text{H}_2\text{O}$ from alcohol in triclinic plates [$a:b:c = 0.7089:1:0.783$; $a = 106^{\circ}23'$, $\beta = 125^{\circ}5'$, $\gamma = 83^{\circ}10'$], m. p. 76° . W. R.

Decomposition of Ricinoleic Sulphuric Acid with Dilute Acids. ADOLF GRÜN and H. WETTERKAMP (*Zeitsch. Farb.-Ind.*, 1908, 7, 375—376. Compare Grün, Abstr., 1907, i, 111).—The authors have investigated the products formed by treating ricinoleic sulphuric acid (sulphoricinoleic acid) with dilute acids, and find that their observations are in many cases not in agreement with those recently published by Wagner (*ibid.*, 284). When an aqueous solution of this ester is boiled, it does not liberate sulphur dioxide, but yields *ricinoleic ricinoleate*, thus: $2\text{SO}_3\text{H}\cdot\text{O}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + \text{OH}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}_2\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}_2\text{H}$. The latter is a yellowish-brown, viscid oil, forming a grey *silver* salt, $\text{C}_{36}\text{H}_{65}\text{O}_5\text{Ag}$. The sulphuric ester decomposes more rapidly when heated with dilute mineral acids, the product formed in this case being a neutral substance, probably the *lactide* of ricinoleic acid, $\text{C}_{17}\text{H}_{32}\left\langle \begin{smallmatrix} \text{O}\cdot\text{CO} \\ \text{CO}\cdot\text{O} \end{smallmatrix} \right\rangle \text{C}_{17}\text{H}_{32}$.

The isomeric ricinelaidic sulphuric ester behaves in an analogous manner. W. H. G.

The Claisen Condensation. III. Mechanism of the Reaction. J. BISHOP TINGLE and ERNEST E. GORSLINE (*J. Amer. Chem. Soc.*, 1908, 30, 1874—1882).—A continuation of the work described in previous papers (Abstr., 1907, i, 498; 1908, i, 732). In order to ascertain whether in the formation of ethyl acetoacetate the sodium reacts directly with the ethyl acetate, or whether it reacts first with a trace of alcohol, experiments have been made with ethyl acetate carefully purified with phosphoric oxide and with calcium. The results show that the reaction with sodium takes place just as readily with this purified ester as with that prepared in the ordinary way. It has also been found that ethyl acetoacetate is readily formed from ethyl acetate and sodium in presence of ether. The velocity of the reaction is not reduced by the presence of the ether. It is evident, therefore, that ethyl acetate, entirely free from alcohol, reacts with sodium as readily as the ester containing a trace of alcohol.

Ethyl malonate, ethyl dimethylmalonate, and ethyl chloromalonate react with two, four, and one atoms of sodium respectively. These results indicate that ethyl malonate has a different structure from that of the other two esters; its formula is probably



whilst that of the dimethylmalonate is $\text{CMe}_2(\text{CO}_2\text{Et})_2$.

Experiments are described which show that the catalytic influence of ether and the tertiary bases in promoting the Claisen reaction is

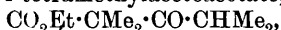
general, and that the effect appears to depend on the velocity with which the particular ketone and ester react; if this is relatively small, the catalytic effect is considerable.

A condensation compound has been obtained from benzophenone and ethyl oxalate. The fact that this ketone, which does not contain a $\text{CH}_3\cdot\text{CO}-$ or $\text{RCH}_2\cdot\text{CO}-$ group, reacts in this manner shows that the Claisen-Nef hypothesis of the mechanism of the condensation is erroneous. Attempts have been made to condense acetaldehyde with various esters in presence of sodium, but without success.

Benzophenone combines with two atoms of sodium; by the action of water on the sodium derivative, benzhydrol and benzopinacol are produced. E. G.

Action of Zinc on a Mixture of Esters of α -Bromoisobutyric and Carbonic Acids. M. L. SHDANOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1347—1367).—The action of zinc on a mixture of ethyl- α -bromoisobutyrate and ethyl carbonate yields, under all experimental conditions employed, ethyl dimethylmalonate, $\text{CMe}_2(\text{CO}_2\text{Et})_2$, b. p. 199.2—200.2°. Dimethylmalonic acid, $\text{CMe}_2(\text{CO}_2\text{H})_2$, crystallises from water in hexagonal, monoclinic prisms [*W. I. Lychitschky*: $\beta = 104^\circ 8'$], m. p. 185—186° (decomp.). The *silver*, $\text{C}_5\text{H}_6\text{O}_4\text{Ag}_2$, *barium*, $\text{C}_5\text{H}_6\text{O}_4\text{Ba}$, and *zinc*, $\text{C}_5\text{H}_6\text{O}_4\text{Zn}\cdot 3\text{H}_2\text{O}$, salts were prepared, the last crystallising from water in characteristic plates.

The ethyl dimethylmalonate formed was accompanied by small proportions of (1) ethyl tetramethylacetoacetate,



which, on hydrolysis with potassium hydroxide solution, yields alcohol and diisopropyl ketone; (2) ethyl trimethylglutarate.

When the proportions of the reacting substances are 1 atom of zinc, 2 mols. of ethyl α -bromoisobutyrate, and 1 mol. of ethyl carbonate, the reaction also gives rise to ethyl tetramethylacetonedicarboxylate (compare Petrenko-Kritschenko, Pissarjewsky, and Herschkowitsch, *Abstr.*, 1896, i, 135).

It is found that the action of zinc on ethyl α -bromoisobutyrate alone yields ethyl trimethylglutarate and ethyl tetramethylacetoacetate, so that in the formation of these products in the previous reaction the ethyl carbonate plays no part. T. H. P.

Ethyl Formylsuccinate and its Relationship with Aconic Acid. WILHELM WISLICENUS, EMIL BOKLEN, and FELIX REUTHE (*Annalen*, 1908, 363, 340—370. Compare *Abstr.*, 1900, i, 9).—It has been found possible to convert aconic acid into ethyl formylsuccinate to the extent of 80% of the theoretical yield by treating an alcoholic solution of the acid with hydrogen chloride, and thus to show the correctness of the view put forward previously, that ethyl formylsuccinate and aconic acid are respectively the ester and lactone of hydroxyitaconic acid (compare *Abstr.*, 1894, i, 127).

Ethyl formylsuccinate yields a *copper* salt, $(\text{C}_9\text{H}_{13}\text{O}_5)_2\text{Cu}$, which crystallises with $2\text{Et}\cdot\text{OH}$ in glistening, green needles; the alcohol-free salt has m. p. 132—133°; the *nickel* salt, $(\text{C}_9\text{H}_{13}\text{O}_5)_2\text{Ni}$, forms tufts of

bright green needles, m. p. 219—220°. The ester combines with phenylcarbimide, forming an *additive* product,

$\text{NHPH} \cdot \text{CO} \cdot \text{O} \cdot \text{CH} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, glistening, colourless prisms, m. p. 103—104°, and yields a *benzoyl* derivative, $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{Et}) : \text{CH} \cdot \text{OBz}$, long, colourless needles, m. p. 57—58°, b. p. 130—140°/24 mm.; the *p*-nitrobenzoyl derivative, $\text{C}_{16}\text{H}_{17}\text{O}_3\text{N}$, forms long, glistening needles, m. p. 104°.

An 80% yield of β -aldehydopropionic acid is obtained by heating the formylsuccinic ester with water under pressure at 120—130°; the phenylhydrazone phenylhydrazide of the aldehydo-acid has m. p. 188—189°; Perkin and Sprankling give m. p. 192° (Trans., 1899, 75, 16); the same compound is formed by the action of phenylhydrazine on aconic acid (compare Reitter and Bender, Abstr., 1905, i, 669). Ethyl formylsuccinate is converted by phenylhydrazine (1 mol.) into a substance which is probably *ethyl 1-phenyl-5-pyridazinone-4-carboxylate*, $\text{NPh} \left\langle \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{N} = \text{CH} \end{smallmatrix} \right\rangle \text{CH} \cdot \text{CO}_2\text{Et}$, pale yellow leaflets, m. p. 111—112°, since the corresponding *acid*, $\text{C}_{11}\text{H}_{10}\text{O}_3\text{N}_2$, small, slightly yellow prisms, m. p. 178—179°, when oxidised by potassium permanganate, is converted into an *acid*, $\text{NPh} \left\langle \begin{smallmatrix} \text{CO} \cdot \text{CH} \\ \text{N} = \text{CH} \end{smallmatrix} \right\rangle \text{C} \cdot \text{CO}_2\text{H}$ (?), obtained as a yellow powder, m. p. 181—182°; the *silver* salt, $\text{C}_{11}\text{H}_7\text{O}_3\text{N}_2\text{Ag}$, is a yellow powder.

Ethyl p-toluidino- γ -itaconate, $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CH} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, is prepared by the action of *p*-toluidine on ethyl formylsuccinate; it forms white crystals, m. p. 115—116°, and gives off alcohol when heated above 150°.

Ethyl formylsuccinate is reduced by "active" aluminium to ethyl itamalatate, and is converted by phosphorus pentachloride into *ethyl chloroitaconate*, $\text{CHCl} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, a colourless liquid with a pleasant, fruity odour, b. p. 125°/20 mm., which, when hydrolysed, yields a *chloroitaconic acid*, $\text{C}_5\text{H}_5\text{O}_4\text{Cl}$, obtained as small, colourless crystals, m. p. 150—151°, not identical with the chloroitaconic acid described by Swarts (*Jahresb.*, 1873, 584), since it is not decomposed when boiled with water; the two acids are possibly geometrical isomerides. The *methyl hydrogen* ester, $\text{CHCl} : \text{C}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ or $\text{CHCl} : \text{C}(\text{CO}_2\text{Me}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared by heating the acid just described with methyl alcohol in a closed tube at 130—140°, crystallises in colourless rhombohedra, m. p. 74—75°.

Ethyl aconate, $\text{CO} \left\langle \begin{smallmatrix} \text{O} \cdot \text{CH} \\ \text{CH}_2 \end{smallmatrix} \right\rangle \text{C} \cdot \text{CO}_2\text{Et}$, obtained by the action of ethyl iodide on silver aconate, is a colourless, almost odourless oil, b. p. 144—145°/18 mm. Methyl formylsuccinate has b. p. 112—115°/12 mm. (compare von Rothenburg, Abstr., 1894, i, 302); it yields a *copper* salt, $(\text{C}_7\text{H}_5\text{O}_5)_2\text{Cu} \cdot \text{H}_2\text{O}$, which crystallises in green needles or leaflets, m. p. 133—135°; the *anhydrous* salt is greenish-yellow, and has m. p. 144—145°. The green salt when boiled with methyl alcohol is converted into a *basic methoxide*,

$\text{CO}_2\text{Me} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Me}) : \text{CH} \cdot \text{O} \cdot \text{Cu} \cdot \text{OMe}$, which crystallises in stellate groups of small, blue prisms, m. p. 193—194°.

Phenylhydrazine (1 mol.) and aniline convert methyl formylsuccinate into the substance, $C_{12}H_{12}O_3N_2$, yellow scales, m. p. 133—134°, and *methyl anilinoitaconate*,

$NHPh \cdot CH : C(CO_2Me) \cdot CH_2 \cdot CO_2Me$,
tufts of microscopical needles, m. p. 91—93°, respectively.

Both ethyl and methyl formylsuccinate are converted by phenylhydrazine (2 mols.) into the substance, $C_{17}H_{16}O_2N_4$, m. p. 192—194° (decomp.), identical with that obtained by Reitter and Bender (*loc. cit.*) by the action of phenylhydrazine on methyl aconate. W. H. G.

Acetonedicarboxylic Acid from Calcium Sucrate. EDMUND O. VON LIPPMANN (*Ber.*, 1908, 41, 3981—3982. Compare Abstr., 1894, i, 105).—On opening a vessel in which calcium sucrate had been kept for many years, a pronounced odour of acetone was observed, and the contents yielded a substance which was identified as acetonedicarboxylic acid by its m. p., 136° (decomp. into acetone and carbon dioxide), and by its conversion into diphenyltetrahydropyrone (compare Petrenko-Kretschenko, Abstr., 1898, i, 142). C. S.

State in Solution of the Tartrates of Aliphatic and Aromatic Amines as Revealed by their Rotatory Power. JULES MINGUIN and HENRI WOHLGEMUTH (*Compt. rend.*, 1908, 147, 978—981. Compare Abstr., 1905, ii, 130; 1908, ii, 137).—The authors have measured the rotation of *M*/100 solutions of tartaric acid, and of its hydrogen and normal salts with propylamine, butylamine, diethylamine, and triethylamine, and of *M*/100 solutions of the normal salt containing an excess of the amine. The results verify Tschugaëff's rule (Abstr., 1898, i, 274, 495; 1899, ii, 3; Minguin and Bollemont, Abstr., 1903, i, 352), for all the hydrogen salts of the homologous series have the same rotatory power, as have also the normal salts, and show also that the normal salts are not dissociated in solution, since the rotation is not changed by the addition of excess of the amine.

Similar measurements made with the tartrates of the aromatic amines, aniline, *o*-, *m*-, and *p*-toluidines, methylaniline, dimethylaniline, and diethylaniline show that these amines do not form normal salts, and that the hydrogen salts are dissociated in solution.

The *hydrogen tartrates* of *aniline*, *o*-, *m*-, and *p*-*toluidines*, *methylaniline*, and a *naphthylamine* have m. p. 172°, 154°, 149°, 182°, 92°, and 172° respectively. M. A. W.

Nitrogen Pentoxide as a Nitrating Agent. G. E. GIBSON (*Proc. Roy. Soc. Edin.*, 1908, 28, 705—707).—Tartaric acid dinitrate is more advantageously prepared by substituting nitrogen pentoxide for the ordinary nitrating mixture of fuming nitric acid and concentrated sulphuric acid, whereby subsequent treatment of the product with water is no longer necessary.

Finely-powdered tartaric acid is mixed with slightly more nitrogen pentoxide than is indicated by the equation $C_4H_4O_4(OH)_2 + 2N_2O_5 = C_4H_4O_4(NO_3)_2 + 2HNO_3$, and is kept over solid sodium hydroxide in an evacuated desiccator until practically free from nitric acid. The dinitrate is separated from unchanged tartaric acid by extracting with

dry ether; the solvent is removed by evaporating below 40°, and finally by placing in a vacuum over concentrated sulphuric acid. Tartaric acid dinitrate prepared by this method is a white, crystalline powder, and is obtained in 81% of the theoretical yield.

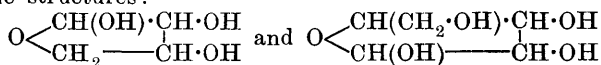
Details of a convenient method of preparing large quantities of nitrogen pentoxide from nitric acid and phosphoric anhydride are also given. J. V. E.

Humic Substances of Coals. OCTAVE BOUDOUARD (*Compt. rend.*, 1908, 147, 986—988).—The author has analysed the humic acid extracted by means of potassium hydroxide solution from seven varieties of coal, both before and after artificial oxidation. The results of the fourteen analyses show that the chemical constitutions of the humic substances thus obtained correspond with one or other of the formulæ: (1) $C_{18}H_{14}O_6$ (Berthelot and André, *Abstr.*, 1891, 1089); (2) $C_{18}H_{18}O_9$ (Malaguti), (3) $C_{18}H_{14}O_9$, (4) $C_{18}H_{14}O_{11}$, and that the effect of oxidising the coal is to diminish the carbon and increase the hydrogen and oxygen content of the humic substance yielded by the coal. M. A. W.

Action of Ammonia on Methyl Ethyl Ketone. WILHELM TRAUBE (*Arch. Pharm.*, 1908, 246, 666—675. Compare *Abstr.*, 1908, i, 362).—A reply to Thomae (*ibid.*, 762). T. A. H.

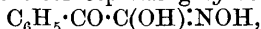
Certain Aldehydic Compounds. ANGELO ANGELI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 360—366).—The authors have examined members of the following classes of compounds to ascertain whether they yield hydroxamic acids when treated with benzenesulphohydroxamic acid in presence of sodium hydroxide: (1) hydroxyaldehydes; (2) ketoaldehydes; (3) aldehydes containing nitrogen. The general results are that this reaction is not given by any of the aldehydes formed by the action of chloroform in presence of alkali or by aromatic hydroxyaldehydes, although the ethers corresponding with the latter do yield hydroxamic acids.

With the aliphatic hydroxyaldehydes, the presence of a hydroxyl group in the γ -position prevents the formation of a hydroxamic acid. Thus, whilst glycollaldehyde and glyceraldehyde yield hydroxamic acids, *d*-erythrose and *l*-arabinose do not; these sugars probably have the structures:



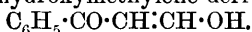
respectively, the latter configuration being also justified by the ease with which *l*-arabinose yields furfuraldehyde. Dextrose also does not yield a hydroxamic acid.

Phenyglyoxal gives the corresponding *hydroxamic acid*,



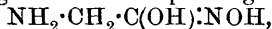
which separates from benzene in crystals, m. p. 128°.

Formylacetophenone does not yield a hydroxamic acid, and must be regarded as a hydroxymethylene derivative,



Neither levulinaldehyde nor *d*-glucosone yields a hydroxamic acid.

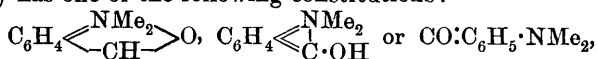
Aminoacetaldehyde gives the corresponding *hydroxamic acid*,



the *picrate* of which is obtained as a yellow precipitate, m. p. 108° (decomp.).

δ-Aminovaleraldehyde does not give a hydroxamic acid (compare Rimini, Abstr., 1901, i, 450).

p-Dimethylaminobenzaldehyde does not form a hydroxamic acid, and probably has one of the following constitutions :



the aromatic residue containing two double linkings as is the case with the quinones.

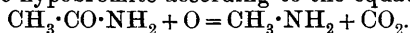
Pyrrole and indole aldehydes do not give hydroxamic acids (compare Abstr., 1907, i, 551). T. H. P.

Colloidal Properties and Spontaneous Gelatination of Starch. EUGÈNE FOUARD (*Compt. rend.*, 1908, 147, 931—933).—A pseudo-solution of starch at 15° gradually becomes opalescent and finally sets (compare Abstr., 1908, ii, 503). The molecular aggregates which are first coagulated are those with the largest rotatory power, as not only does the quantity of dissolved matter gradually diminish during several months, but also its specific rotatory power.

During extraction of starch grains and before coagulation begins, however, the larger molecular aggregates are slowly being broken down into smaller ones with low rotatory power. The hyperbolic equation representing the rate of coagulation is supposed to be the resultant of the two opposing changes. The heat transfer during these reversible changes must be very small, a supposition which is confirmed by the continuous circulation of starchy matter in living cells. R. J. C.

Constitution of Sodium Cellulose. O. MILLER (*Ber.*, 1908, 41, 4297—4304. Compare Abstr., 1908, i, 78).—Polemical. A reply to Viewig (Abstr., 1908, i, 857). W. R.

Theory of the Preparation of Methylamine from Solutions of Acetylbroamide. MAURICE FRANÇOIS (*Compt. rend.*, 1908, 147, 983—986 *).—The author suggests that in the preparation of methylamine by Hofmann's method the bromine in the alkaline solution of bromine and acetamide is present as hypobromite and not as acetylbroamide, and the reaction consists in the oxidation of the acetamide by the hypobromite according to the equation :



In support of this theory, experiments are described which show (1) that the bromine in a solution of acetamide bromine and potassium hydroxide in molecular proportions can be estimated by the usual methods for determining hypobromous acid ; (2) that methylamine can be prepared by heating a solution containing potassium hypobromite and acetamide.

* and *J. Pharm. Chim.*, 1909, 29, 5—9.

The bromine in a solution of acetamide and bromine in the presence of excess of calcium carbonate (Abstr., 1908, i, 956) is present partly as hypobromite and partly as free bromine, and the mixture has all the properties of Hofmann's acetyl bromamide.

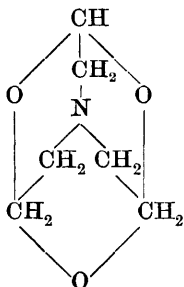
M. A. W.

Additive Compounds of Selenium Dioxide. F. CARNEVALI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 385—389).—When tetramethyl- or tetraethyl-ammonium chloride is added to a concentrated aqueous solution of a large excess of selenium dioxide containing hydrochloric acid, and the liquid evaporated to a syrup and allowed to cool in a vacuum over potassium hydroxide, an additive compound of selenium dioxide with tetramethyl- or tetraethyl-ammonium chloride of the composition $\text{SeO}_2 \cdot 2\text{NMe}_4\text{Cl}$ or $\text{SeO}_2 \cdot 2\text{NEt}_4\text{Cl}$ is deposited. Both these compounds form slightly yellow, deliquescent crystals, and are completely hydrolysed by water, to which they impart an acid reaction. Under the influence of light, they gradually decompose, giving small quantities of selenium (compare Muthmann and Schäfer, Abstr., 1893, ii, 318).

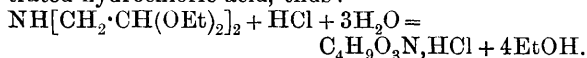
T. H. P.

Diacetalylamine and Triacetalylamine. LUDWIG WOLFF and RICHARD MARBURG (*Annalen*, 1908, 363, 169—220).—The authors have made a reinvestigation of diacetalylamine (diacetalamine, Wolff, Abstr., 1888, 809), with the object of ascertaining if the product obtained from it by the action of acids, which is probably iminodiacetaldehyde, can be converted into pyrazine by means of hydroxylamine. Diacetalylhydrazine was also examined with the same end in view, and the hitherto unknown triacetalylamine has also been prepared and examined. Di- and tri-acetalylamine, nitroso-acetalylamine, and diacetalylhydrazine are all much more sparingly soluble in hot water than in cold. The elimination of the acetal groups is best effected by means of concentrated hydrochloric acid.

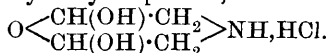
Triacetalylamine is decomposed by hot concentrated hydrochloric acid, thus: $\text{N}[\text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_3 + 3\text{H}_2\text{O} = \text{C}_6\text{H}_9\text{O}_3\text{N} + 6\text{EtOH}$, with the formation of a well-crystallised, monoacid, tertiary base to which is assigned the constitution (annexed) of a trimorpholine.



Diacetalylamine is decomposed by cold concentrated hydrochloric acid, thus:

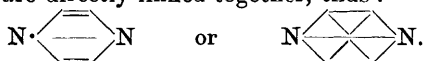
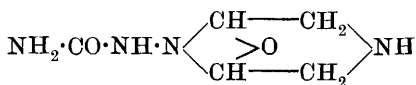


The salt formed (from which the base could not be prepared in a pure state) is regarded as the hydrochloride of dihydroxymorpholine,



This, when treated with hydrogen sulphide, yields dihydroxythiomorpholine hydrochloride; with phenylhydrazine acetate it yields the bisphenylhydrazone of iminodiacetaldehyde, $\text{NH}(\text{CH}_2 \cdot \text{CH} \cdot \text{N} \cdot \text{NHPh})_2$;

with semicarbazide it gives the hydrochloride of morpholylsemicarbazone, annexed formulæ, which with dilute hydrochloric acid is slowly converted at the ordinary temperature into pyrazine and carbamide with loss of water, and with hydrazine or hydroxylamine it furnishes products extremely soluble in water, which pass into pyrazine at 0°. These reactions lead to the conclusion that in pyrazine the two nitrogen atoms are directly linked together, thus :



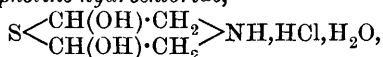
Diacetalyldiazine also yields pyrazine when treated with hydrochloric acid, but the mechanism of this reaction is obscure, owing to the occurrence of a second reaction which has not yet been explained.

By using a modification of the process previously described for the preparation of acetalylamine (Wolff, *loc. cit.*, Abstr., 1893, i, 612), a mixture of di- and tri-acetalylamines with some acetalylamine is obtained, which is separated by fractional distillation. *Triacetalylamine*, $\text{N}[\text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_3$, is a yellow liquid of a faintly aromatic odour. It has b. p. 175°/11 mm. (without decomposition), 302—304°/745 mm. (slight decomp.), D_4^{20} 0.957, and n_D^{20} 1.4322. It dissolves in 25 parts of water at 0° and 76 parts at 19°. The *platinichloride* forms brownish-red to orange needles, m. p. 136° (decomp.); the *aurichloride* and *mercurichloride* are oils. *Trimorpholine*, $\text{C}_6\text{H}_9\text{O}_3\text{N}$, forms large, colourless, monoclinic crystals, which turn yellow at 180° and decompose at 210—220°. The base is very slowly attacked by hydroxylamine with the formation of a small amount of glyoxime. The *hydrochloride*, decomp. 255—260°, *mercurichloride*, decomp. above 260°, *aurichloride*, decomp. 220°, *picrate*, m. p. 210° (decomp.), *nitrate*, decomp. 240°, *oxalate*, decomp. above 220°, *methiodide*, decomp. above 270°, *methochloride*, decomp. 308°, and the following double salts of the latter: *mercury*, m. p. 270°, *gold*, m. p. 290°, and *platinum*, decomp. above 270°, are described. The *ammonium* base, prepared from the methiodide, forms a white, leafy, crystalline mass, m. p. 76—78°.

Diacetalyldiazine is a liquid of faint aromatic odour, b. p. 133°/9 mm., 260—262°/745 mm., decomposing slightly at the latter temperature. It has D_4^{20} 0.938 and n_D^{20} 1.4248. It forms a *benzoyl* and an *acetyl* derivative, b. p. 290°. The *hydrogen oxalate*, by means of which the base can be separated from triacetalyldiazine, forms colourless leaves, m. p. 174—175° (decomp.). The *nitroso-derivative*, $\text{NO} \cdot \text{N}[\text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_2$, is a pale greenish-yellow oil of a faint, agreeable odour, b. p. 162°/13 mm., D_4^{20} 1.014, n_D^{20} 1.4397. It does not give Liebermann's reaction. On reduction with zinc dust and acetic acid, it yields *diacetalyldiazine*, $\text{NH}_2 \cdot \text{N}[\text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_2$, a colourless, viscid oil of faint aromatic odour, b. p. 149°/10 mm., D_{15}^{17} 0.972, which gives a viscid *benzoyl* derivative, and forms a viscid compound with *p*-nitrobenzaldehyde. The *hydrochloride*, white needles, m. p. 75—76°, and *hydrogen oxalate*, small, white needles, m. p. 104—105°, are

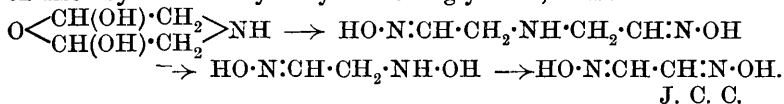
described. *Diacetalylsemicarbazide*, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N}[\text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_2$, forms small, white needles, m. p. 96°.

Dihydroxymorpholine hydrochloride forms white, microscopic needles or tablets, m. p. 124°. The corresponding *aurichloride* crystallises in small, brownish-yellow prisms or tablets, m. p. 130° (decomp.). *Dihydroxythiomorpholine hydrochloride*,



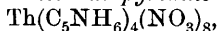
forms colourless or pale yellow prisms, m. p. 113—114° (decomp.). The *bisphenylhydrazone* of *iminodiacetaldehyde* crystallises in pale yellow, quadratic tablets or in small prisms, m. p. 114°. The *hydrochloride*, colourless, microscopic needles, m. p. 134—135°, *nitrate*, pale yellow, crystalline powder, m. p. 140°, and *picrate*, deep red, crystalline powder, m. p. 132—133° (decomp.), are described. *Morpholylsemicarbazone* is an amorphous mass. The *nitrate*, $\text{C}_5\text{H}_{10}\text{O}_2\text{N}_2 \cdot \text{HNO}_3 \cdot 2\text{H}_2\text{O}$, a brownish-white, crystalline powder, m. p. 178° (decomp.), *picrate*, crystallising with $2\text{H}_2\text{O}$, yellow needles or leaflets, m. p. 153—154° (decomp.), *hydrochloride*, crystallising with $2\text{H}_2\text{O}$, white powder, decomp. at 187—190°, *mercurichloride*, aggregates of colourless prisms, m. p. 168—169° (decomp.), and *aurichloride* are described. By treating morpholylsemicarbazone with boiling 20% hydrochloric acid, pyrazine is obtained; the aurichloride, m. p. 247° (decomp.), on crystallisation from boiling water loses HCl , yielding the salt, $\text{C}_4\text{H}_4\text{N}_2 \cdot \text{AuCl}_3$, golden-yellow leaflets, m. p. 212—214° (compare Abstr., 1893, i, 612).

Pyrazine may be prepared in a 78% yield direct from diacetalylamine by treating the hydrochloride with hydroxylamine hydrochloride. By the action of hydroxylamine hydrochloride on dihydroxymorpholine, a 70% yield of pyrazine is obtained, together with a small amount of glyoxime, which is also formed directly from diacetalylamine and hydroxylamine; it is therefore probable that in the interaction between dihydroxymorpholine and hydroxylamine the dioxime of iminoacetaldehyde is first formed, which is then hydrolysed and oxidised by excess of hydroxylamine to glyoxime, thus:



Double Nitrates and Double Sulphates of the Rare Earths.

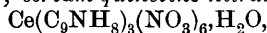
A. KOLB [with G. MELZER, A. MERCKLE, and C. TEUFEL] (*Zeitsch. anorg. Chem.*, 1908, 60, 123—133. Compare Wyruboff, Abstr., 1908, ii, 385). —The double nitrates were prepared by evaporating aqueous solutions of the components and recrystallising from absolute alcohol. *Thorium diethylamine nitrate*, $\text{Th}(\text{NH}_2\text{Et}_2)_2(\text{NO}_3)_6$, occurs in transparent, rhombic crystals, m. p. very low. *Thorium pyridine nitrate*,



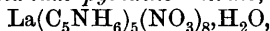
forms colourless, pointed leaflets, m. p. 135°. The corresponding *quinoline* compound, $\text{Th}(\text{C}_9\text{NH}_8)_4(\text{NO}_3)_8$, also forms colourless, spear-shaped crystals, m. p. 135°. Thorium nitrate reacts with antipyrine as free base even in the presence of excess of nitric acid. When 1 mol. of thorium nitrate and 4 mols. of antipyrine interact in nitric

acid solution, the compound, $2\text{Th}(\text{NO}_3)_4 \cdot 5\text{C}_{11}\text{H}_{12}\text{ON}_2$, is formed; in the absence of acid, the same compound with $4\text{H}_2\text{O}$ is obtained. When 8 mols. of antipyrine are used, the compound, $\text{Th}(\text{NO}_3)_4 \cdot 4\text{C}_{11}\text{H}_{12}\text{ON}_2$, is obtained, and the same compound is formed when solid thorium nitrate (2 grams) is added to fused antipyrine (6 grams).

Cerium pyridine nitrate, $\text{Ce}(\text{C}_5\text{NH}_6)_5(\text{NO}_3)_8 \cdot \text{H}_2\text{O}$, forms large, colourless plates, m. p. 82.5° ; *cerium quinoline nitrate*,

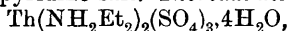


prismatic crystals, m. p. 165° ; *cerium piperidine nitrate*, lustrous, rhombic crystals; *lanthanum pyridine nitrate*,

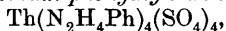


colourless, monoclinic crystals, m. p. 91.5° ; *lanthanum quinoline nitrate*, $\text{La}(\text{C}_9\text{NH}_8)_3(\text{NO}_3)_6 \cdot \text{H}_2\text{O}$, m. p. 153° .

The majority of the double sulphates were prepared by boiling the solid rare earth sulphate with an aqueous solution of the other sulphate until a clear solution was obtained; the separation of the double salt was in some cases brought about by the addition of absolute alcohol. *Thorium pyridine sulphate*, $\text{Th}(\text{C}_5\text{NH}_6)_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$, occurs in colourless, microscopic leaflets, and is readily split up into its components by water. *Thorium quinoline sulphate*, $\text{Th}(\text{C}_9\text{NH}_8)_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$, behaves in all respects like the pyridine salt. *Thorium diethylamine sulphate*,

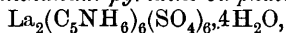


and *thorium ethylamine sulphate*, $\text{Th}(\text{NH}_3\text{Et})_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$, occur in colourless crystals. *Thorium phenylhydrazine sulphate*,



occurs in small, slightly yellow crystals, which are very stable.

Cerium pyridine sulphate, $\text{Ce}_2(\text{C}_5\text{NH}_6)_6(\text{SO}_4)_6 \cdot 3\text{H}_2\text{O}$, needles, *cerium quinoline sulphate*, probably $\text{Ce}_2(\text{SO}_4)_3 \cdot 6\text{C}_9\text{NH}_7 \cdot 4\text{H}_2\text{SO}_4 \cdot 17\text{H}_2\text{O}$, *cerium hydrazine sulphate*, lustrous crystals, *cerium hydroxylamine sulphate*, microscopic leaflets, *lanthanum pyridine sulphate*,



lustrous, columnar crystals, *lanthanum quinoline sulphate*, small, columnar crystals, and *lanthanum hydrazine sulphate*, small leaflets, have also been prepared. G. S.

Organic Mercury Compounds. EINAR BIILMANN (*Ber.*, 1908, 41, 4340—4341. Compare Schrauth and Schoeller *Abstr.*, 1908, i, 617).—A claim for priority: the alkyl mercuridimalonates have been obtained previously (*Abstr.*, 1902, i, 665). W. R.

Nitration of Toluene. ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 248—256. Compare *Abstr.*, 1905, i, 272; Nölting and Wild, *Abstr.*, 1885, 973; Loesner, *Abstr.*, 1895, i, 214; Holdermann, *Abstr.*, 1906, i, 439; Friswell, *Abstr.*, 1908, i, 332).—An investigation on the composition of the product obtained when toluene is nitrated at various temperatures by adding nitric acid (D 1.475) to the hydrocarbon. The percentages of the isomeric mononitrotoluenes present in the nitration product were ascertained by determining its density and initial solidifying point and comparing with mixtures of known composition. In this way, it was found that the product obtained by nitrating at -30° , 0° , 30° , and 60° contained

41.7, 40.9, 39.9, and 38.5% of *p*-nitrotoluene; 55.6, 56.0, 56.9, and 57.5% of *o*-nitrotoluene, and 2.7, 3.1, 3.2, and 4.0% of *m*-nitrotoluene respectively.

W. H. G.

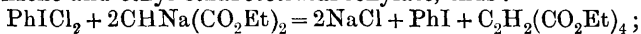
Nitration of *p*-Chlorotoluene. ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 257—260. Compare preceding abstract).—The initial solidifying points and densities of mixtures of 4-chloro-2-nitrotoluene (solidifying point 38.2°, D^{80} 1.2559) and 4-chloro-3-nitrotoluene (solidifying point 5.8°, D^{80} 1.2296) have been determined; mixtures containing 57.0, 44.7, 34.8, 29.8, 24.1, 17.5, 14.1, and 6.6% of the former compound commence to solidify at 9.7°, 1.4°, -6.3°, -7.2°, -4.1°, -0.5°, 0.4°, and 4.5° respectively; mixtures having D^{80} 1.2477 and 1.2364 contain respectively 57 and 17.5% of 4-chloro-2-nitrotoluene.

Since the product obtained by acting on *p*-chlorotoluene at 0° with about four times its weight of nitric acid (D 1.48) commences to solidify at 10.2° and has D^{80} 1.2481, it must contain 58% of 4-chloro-3-nitrotoluene and 42% of 4-chloro-2-nitrotoluene. The product obtained by nitrating at 30° and 60° contains polynitro-4-chlorotoluenes.

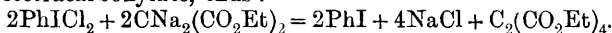
W. H. G.

Some Reactions of Phenyl Iodochloride and Iodosobenzene Acetate. HERBERT HENRY HODGSON (*Proc. Camb. Phil. Soc.*, 1908, 14, 547—556).—Unsuccessful attempts have been made to prepare compounds containing the grouping :C:I:C: or :C>I:C: , possibly because suitable conditions for isolating the substances were not employed.

Phenyl iodochloride interacts with ethyl sodiomalonate, forming iodobenzene and ethyl ethanetetra-carboxylate, thus:



and with ethyl disodiomalonate, forming iodobenzene and ethyl ethylenetetra-carboxylate, thus:



The action of phenyl iodochloride is, therefore, analogous to that of iodine on the sodium derivatives of ethyl malonate (compare Bischoff, *Abstr.*, 1885, 244; 1896, i, 469; Blank and Samson, *Abstr.*, 1899, i, 484). Similarly, iodine acts on ethyl sodiocyanoacetate, forming ethyl dicyanosuccinate, which is obtained in good yield. Iodosobenzene acetate behaves like phenyl iodochloride towards ethyl sodio- and disodio-malonate.

Phenyl iodochloride and iodosobenzene acetate react with ethyl sodiocyanoacetate in a similar manner, yielding iodobenzene and ethyl dicyanosuccinate.

Diphenyliodonium iodide and ethyl sodiomalonate apparently do not interact either at the ordinary temperature or at 100°. W. H. G.

Chlorides of Aromatic Sulphinic Acids. THOMAS P. HILDITCH and SAMUEL SMILES (*Ber.*, 1908, 41, 4113—4116).—The reaction between phenolic ethers, thionyl chloride, and aluminium chloride takes place in three stages (Smiles and Le Rossignol, *Trans.*, 1906, 89, 696; 1908, 93, 745; Knøevenagel and Kenner, *Abstr.*, 1908, i,

970), but hitherto the aromatic sulphinyl chloride produced in the first step has not been isolated. The authors have now obtained aromatic sulphinyl chlorides by the action of an excess of thionyl chloride on the sulphinic acids at the ordinary temperature. *Benzenesulphinyl chloride*, PhSOCl , has m. p. 38° . *p-Toluenesulphinyl chloride*, $\text{C}_7\text{H}_7\cdot\text{SOCl}$, has m. p. $54-58^\circ$. *4-Methoxytoluene-3-sulphinyl chloride* has m. p. $70-73^\circ$. C. S.

Preparation of Diphenylmethane. ALEXANDER M. NASTUKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1376—1379).—The author has investigated further the interaction of benzene and formaldehyde in presence of concentrated sulphuric acid (compare Abstr., 1904, i, 242). For the preparation of diphenylmethane, the glacial acetic acid employed may be replaced by water, provided that the proportions of formaldehyde and sulphuric acid are suitably adjusted.

T. H. P.

Fluorene Perhydride: Reply to Spiegel. JULIUS SCHMIDT and ERNST FISCHER (*Ber.*, 1908, 41, 4227—4230).—In view of Spiegel's statement (Abstr., 1908, i, 331) that, contrary to Schmidt and Mezger's view (*ibid.*, i, 16) of the non-existence of Liebermann's fluorene perhydride (Abstr., 1889, 719), the compound can actually be prepared, the authors have repeated Liebermann and Spiegel's work and maintain that the substance obtained is really the decahydride.

J. C. C.

Preparation of 9:10-Dihydrophenanthrene. JULIUS SCHMIDT and ERNST FISCHER (*Ber.*, 1908, 41, 4225—4226).—Willstätter and Mayer's method of reduction with platinum and hydrogen (Abstr., 1908, i, 383) is very suitable for the preparation of dihydrophenanthrene. A brisk stream of pure hydrogen is led into a boiling ethereal solution of phenanthrene in the presence of platinum black. After six to eight hours, the solution is filtered and evaporated, when the residue consists of almost pure 9:10-dihydrophenanthrene. The reduction may also be carried out at the ordinary temperature, but in this case requires about two days (for 5 grams of phenanthrene).

J. C. C.

Hydrogenation of Triphenylmethane. Tricyclohexylmethane. MARCEL GODCHOT (*Compt. rend.*, 1908, 147, 1057—1059).—The ultimate reduction product obtained by submitting triphenylmethane to the hydrogenisation process of Sabatier and Senderens (Abstr., 1901, i, 459) is *tricyclohexylmethane*, $\text{CH}(\text{C}_6\text{H}_{11})_3$, a colourless liquid with an aromatic odour, b. p. $140^\circ/20\text{ mm.}$, D^{13}_4 0.8406. This compound is sparingly soluble in alcohol and acetic acid, but very soluble in ether and benzene; these solutions are not fluorescent. It develops a brown coloration with sulphuric acid, and yields hydrogen bromide and a bromo-derivative with bromine. *Phenyldicyclohexylmethane*, $\text{C}_{19}\text{H}_{28}$, b. p. $210-212^\circ/20\text{ mm.}$, D^{13}_4 0.9894, was obtained at an intermediate stage in the preparation, but not in a state of purity.

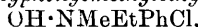
W. O. W.

The Action of Dichloroacetic Acid on Aniline and its Homologues. GUSTAV HELLER (*Ber.*, 1908, 41, 4264—4266. Compare Abstr., 1904, i, 730).—A reply to Ostromisslensky (Abstr., 1908, i, 82, 888). It has not been found possible to isolate phenylmesatin from the products obtained by the action of dichloroacetic acid on aniline; the chief product is the diamino-acid, m. p. 98°. The author does not agree with Ostromisslensky's view that the compound $C_{14}H_{14}O_2N_2$ is dianilinoacetic acid, as it is immediately decomposed by cold dilute alkalis.

J. J. S.

A New Kind of Asymmetry in the Nitrogen Atom. JAKOB MEISENHEIMER (*Ber.*, 1908, 41, 3966—3976).—It is theoretically possible to have two forms of a quinevalent nitrogen compound in which there are four different radicles, related as object and image, but so far all attempts to resolve such compounds have resulted in failure. Further, this possibility exists in the amino-oxides, and experiments were undertaken with the object of resolving methylethylaniline oxides into optical isomerides.

Methylethylaniline, on being stirred for three days with hydrogen peroxide at 60—70°, is converted into the oxide, which is purified by conversion into the picrate. This, on treatment with hydrochloric acid, yields racemic *hydroxyphenylmethylethylammonium chloride*,



which crystallises in colourless, hygroscopic needles from a mixture of alcohol and ether; m. p. 122—124° (decomp.). The compound is strongly acid; its *picrate*, $C_{15}H_{16}O_8N_4$, has m. p. 147—148° (decomp.). The free base obtained from the chloride by baryta is a very hygroscopic solid, and decomposes slowly. The chloride on treatment with silver *d*-bromocamphorsulphonate is resolved into two optical antipodes, the *l*-hydroxyphenylmethylethylammonium-*d*-bromocamphorsulphonate, $C_{19}H_{28}O_5NBrS$, being the less soluble, decomp. 167—168°, $[a]_D + 50^\circ$, $[M]_D$ 231—235°; the *d*-salt has m. p. 151—153° (decomp.), $[a]_D + 68^\circ$, $[M]_D$ 311—315°.

The *d*-picrate, m. p. 147—148° (decomp.), when treated with hydrochloric acid and ether, is converted into the *d*-chloride, which crystallises in hygroscopic prisms, m. p. 90—95°, $[M]_D + 32^\circ$. The *l*-chloride, obtained in a similar manner, has $[M]_D - 41^\circ$, the calculated value from the bromocamphorsulphonate being $\pm 40^\circ$.

If the active chlorides be decomposed by baryta water free from carbonate, the bases are obtained, and the $[M]_D$'s of the solutions decrease from -41° to -25° and $+32^\circ$ to $+20^\circ$ respectively, a result probably not due to racemisation, as the original value is re-obtained on acidification with hydrogen chloride. Further, these values are not altered after three days. The free bases are obtained as very hygroscopic oils after removal of the barium chloride, and have not yet been isolated in the solid condition. It is, therefore, uncertain whether they possess the formula: $O:NMeEtPh$ or $NMeEtPh(OH)_2$.

W. R.

3:5-Dibromoaceto-*p*-toluidide and its Nitro-derivatives. FRANZ KUNCKELL (*Ber.*, 1908, 41, 4111—4112).—Ulffers and

von Janson's 3:5-dibromoaceto-*p*-toluidide (Abstr., 1894, i, 719) is conveniently obtained by heating aceto-*p*-toluidide with somewhat less than the calculated quantity of bromine in chloroform for four hours at 90—100°. With fuming nitric acid, it yields 3:5-*dibromo-2-nitroaceto-p-toluidide*, m. p. 238°, whilst in the presence of concentrated sulphuric and fuming nitric acids, 3:5-*dibromo-4:6-dinitroaceto-p-toluidide*, m. p. 265—267°, is obtained, from which boiling aniline eliminates one atom of the halogen. C. S.

cycloHexanol. G. CHAVANNE and Mlle. B. VAN ROELEN (*Bull. Soc. chim. Belg.*, 1908, 22, 410—413. Compare Mascarelli, Abstr., 1907, ii, 602, 936; 1908, i, 527).—Cryoscopic determinations of the molecular weights, using *cyclohexanol* as a solvent, are rendered difficult by the smallness or absence of the phenomenon of superfusion, and by the slow rate of crystallisation. Experiments made with nineteen organic compounds show that the latter can be divided into two groups: (1) including aromatic hydrocarbons composed of several nuclei or having complex side-chains, such as naphthalene, *m*-xylene, *p*-xylene, cymene, diphenyl, and acenaphthene, which produce a molecular depression of 61—62 (water, 1·85); and (2) all other types of organic compound which either do not obey the Blagden-Rüdorff law, or give molecular depressions less than 61. Thus nitrobenzene gives the value 53, toluene 40, chloroform 25, ethyl alcohol 34·5, methyl alcohol 28, lactic acid 40, isobutyric acid 33, *cyclohexanone* 31, *cyclohexene* 23, and *cyclohexane* 11. The conclusion is drawn that the normal molecular depression for *cyclohexanol* is 61·5. Substituting this value in van't Hoff's formula ($K=0\cdot02T^2/L$) gives 2·8 Cal. as the value for the heat of fusion (L), whilst a direct determination of the latter constant gives the value 3 Cal.

The anomalous results obtained in cryoscopic determinations with *cyclohexanol* may be due either to the associating power of this solvent or to its capacity for forming solid solutions.

cycloHexanol easily loses water with the production of *cyclohexene*; thus when heated at 80° with an equal molecular quantity of methyl sulphate, 40 grams of the alcohol give 26 grams of *cyclohexene*. Similarly, when boiled over alumina or silica, the vapour of *cyclohexanol* is wholly converted into *cyclohexene* and water. E. H.

2:4-Dinitro- α -naphthol. FRITZ ULLMANN and WALTER BRUCK (*Ber.*, 1908, 41, 3932—3939).—A continuation of the work of Ullmann and Náday (Abstr., 1908, i, 525). The interaction of *p*-toluenesulphonyl chloride, diethylaniline, and 2:4-dinitro- α -naphthol furnishes at the ordinary temperature the dinitronaphthyl ester of *p*-toluenesulphonic acid, and at a higher temperature 1-chloro-2:4-dinitronaphthalene. Both compounds react readily with bases, giving the corresponding α -naphthylamine derivatives, and the reactions proceed so smoothly that it is unnecessary to isolate the intermediate compounds in the preparation of the latter.

1-Chloro-2:4-dinitronaphthalene crystallises in large, yellow needles, m. p. 146·5° (corr.). 2:4-Dinitro- α -naphthyl *p*-toluenesulphoante, $C_{10}H_5(NO_2)_2\cdot O\cdot SO_2\cdot C_7H_7$, forms large, pearly, almost colourless leaflets, m. p. 159·5° (corr.).

By warming a mixture of dinitronaphthol, pyridine, and toluene-sulphonyl chloride, there is formed 2:4-dinitro- α -naphthylpyridinium toluenesulphonate, $C_{27}H_{17}O_7N_3S$, in shining leaflets, m. p. 205° (decomp.). When either the ester or the chloro-derivative mentioned above is treated with ammonia, 2:4-dinitro- α -naphthylamine is produced, and with dimethylamine there is formed 2:4-dinitro- α -naphthyl-dimethylamine, $C_{10}H_5(NO_2)_2 \cdot NMe_2$, which crystallises in orange-red needles, m. p. 88° .

2:4-Dinitro- α -naphthylbenzylamine, $C_{10}H_5(NO_2)_2 \cdot NH \cdot CH_2Ph$, prepared by warming chlorodinitronaphthalene with benzylamine in alcoholic solution, forms orange-red needles, m. p. 139° (corr.). Phenyl-2:4-dinitro- α -naphthylamine, $C_{10}H_5(NO_2)_2 \cdot NHPh$, prepared either from the ester or the chloro-derivative, or from dinitronaphthol without the isolation of the intermediate compound, crystallises in large, orange-red, glistening plates, m. p. 180° (corr.).

On reduction with zinc dust, alcohol, and ammonium chloride, it yields phenyl-2:4-diamino- α -naphthylamine, white, felted needles, m. p. 190° (corr.), which on distillation with lead oxide gives 6-aminonaphthaphenazine.

2-Hydroxyphenyl-2:4-dinitro- α -naphthylamine,
 $C_{10}H_5(NO_2)_2 \cdot NH \cdot C_6H_4 \cdot OH$,

prepared by condensing the ester with *o*-aminophenol, forms orange-red, felted needles, m. p. 178° (corr.). 2:4-Dinitro- α -naphthyl methyl ether, prepared by the action of sodium methoxide on the chloro-derivative, forms yellow needles, m. p. 97° .

The ethyl ether is obtained in a similar manner.

J. C. C.

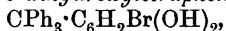
Action of Chlorine, Bromine, and Nitric Acid on *p* Hydroxy-tetraphenylmethane. THEODOR ZINCKE and E. WUGK (*Annalen*, 1908, 363, 284—301. Compare this vol., i, 23).—3:5-Dibromo-*p*-hydroxytetraphenylmethane, $CPh_3 \cdot C_6H_2Br_2 \cdot OH$, prepared by brominating the parent substance, crystallises in white needles or leaflets, m. p. 168° ; it forms a sodium salt and an acetate, $C_{27}H_{20}O_2Br_2$, white needles, m. p. 177° , and on treatment with bromine, it yields penta-bromo-*p*-hydroxytetraphenylmethane, $C(C_6H_4Br)_3 \cdot C_6H_2Br_2 \cdot OH$, in which the three added bromine atoms are probably in the para-position. This compound forms small, white crystals, m. p. 267 — 271° ; it forms an acetate, $C_{27}H_{17}O_2Br_5$, small, white needles, and, possibly, a per-bromide, which was not, however, obtained pure.

3:5-Dichloro-*p*-hydroxytetraphenylmethane, $CPh_3 \cdot C_6H_2Cl_2 \cdot OH$, prepared by chlorinating the parent substance, crystallises in small, white needles, m. p. 135° ; the acetate, $C_{27}H_{20}O_2Cl_2$, forms large, white needles, m. p. 180° .

3-Nitro-*p*-hydroxytetraphenylmethane, $CPh_3 \cdot C_6H_3(NO_2) \cdot OH$, prepared by adding nitric acid, D 1.4, to a solution of the parent substance in glacial acetic acid, or by adding sodium nitrite to an ethereal solution containing water and acetic acid, forms yellow leaflets or dark yellow, compact crystals, m. p. 183 — 184° ; the alkali salts are brownish-red; the acetate, $C_{27}H_{21}O_4N$, forms small, yellow needles, m. p. 152° . 3-Bromo-5-nitro-*p*-hydroxytetraphenylmethane, $CPh_3 \cdot C_6H_3Br(NO_2) \cdot OH$, prepared by adding sodium nitrite to a glacial acetic acid solution of

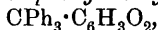
the dibromo-compound or by warming the latter solution with nitric acid, crystallises in yellow needles, m. p. 188° ; it forms brownish-red alkali salts; the acetate, $C_{27}H_{20}O_4NBr$, crystallises in white needles, m. p. $169-170^{\circ}$.

6-Bromo-4-triphenylmethyl-o-benzoquinone, $CPh_3 \cdot C_6H_2O_2Br$, prepared by adding nitric acid, D 1.5, to a glacial acetic acid solution of dibromo-*p*-hydroxytetraphenylmethane at 40° , crystallises in red needles with a golden lustre, m. p. 230° ; on reduction with hydriodic acid, it yields 3-bromo-4:5-dihydroxytetraphenylmethane,



which crystallises in almost white needles, m. p. 175° ; the diacetate forms leaflets, m. p. $135-136^{\circ}$. 6-Chloro-4-triphenylmethyl-o-benzoquinone, $CPh_3 \cdot C_6H_2O_2Cl$, prepared similarly from the dichloro-compound, crystallises in red needles with a golden lustre, m. p. 229° ; at the same time is formed chloronitro-*p*-hydroxytetraphenylmethane, large, yellow crystals, m. p. 154° . On reduction, the quinone furnishes 3-chloro-4:5-dihydroxytetraphenylmethane, $CPh_3 \cdot C_6H_2Cl(OH)_2$, crystallising in white needles, m. p. $190-191^{\circ}$; it is oxidised by nitric acid to the quinone, and forms an acetate.

3:4-Dihydroxytetraphenylmethane, $CPh_3 \cdot C_6H_3(OH)_2$, prepared by the condensation of triphenylcarbinol with catechol, crystallises in white needles and leaflets, m. p. $262-263^{\circ}$; with bromine it yields 3-bromo-4:5-dihydroxytetraphenylmethane; it forms a diacetyl derivative, white needles, m. p. $197-198^{\circ}$, and when oxidised with nitric acid, D 1.5, it gives 4-triphenylmethyl-o-benzoquinone,



crystallising in dull red needles with a green, metallic lustre, m. p. 217° . J. C. C.

Styphnic Acid. FRITZ ULLMANN and WALTER BRUCK (*Ber.*, 1908, 41, 3939-3940).—Styphnic acid combines with 1 mol. of diethylaniline to form a salt, which crystallises in yellow needles, m. p. 159° . When styphnic acid, diethylaniline, and *p*-toluenesulphonyl chloride are warmed together, the diethylaniline salt of 2:4:6-trinitro-3-hydroxyphenyl *p*-toluenesulphonate, $OH \cdot C_6H(NO_2)_3 \cdot O \cdot SO_2 \cdot C_7H_7 \cdot NEt_2Ph$, is obtained. This forms small, yellow plates, m. p. 164° (decomp.); on boiling with alcoholic hydrogen chloride, styphnic acid is regenerated, and when treated with aniline it yields 2:4:6-trinitro-3-hydroxydiphenylamine, $OH \cdot C_6H(NO_2)_3 \cdot NHPh$, crystallising in orange-yellow needles, m. p. 162° (corr.). J. C. C.

Action of Bromine on the Alkyl and Aryl Derivatives of Di-*p*-hydroxydiphenylmethane. THEODOR ZINCKE (*Annalen*, 1908, 363, 246-283).—The author has extended his work on the action of bromine and alkyl and aryl derivatives of di-*p*-hydroxydiphenylmethane (Zincke and Krügener, *Abstr.*, 1904, i, 401; Zincke and Grütters, *Abstr.*, 1906, i, 172; Zincke, *ibid.*, 737; Zincke and Goldemann, *Abstr.*, 1908, i, 780) to the cases of di-*p*-hydroxy-di- α -phenylethane, -tri- α -phenylethane, -tetraphenylmethane, and -triphenylmethane.

[With K. HENKE.]—Four, six, or eight atoms of bromine can be introduced into the molecule of di-*p*-hydroxydi- α -phenylethane (prepared

according to Lunjak's method, Abstr., 1904, i, 495). The resulting compounds are normal phenols and soluble in alkali. By the action of sodium nitrite in glacial acetic acid solution, an atom of bromine is replaced by the nitro-group. 3:5:3':5'-*Tetrabromodi-p-hydroxydi- α -phenylethane*, $\text{CHMe}(\text{C}_6\text{H}_2\text{Br}_2\cdot\text{OH})_2$, prepared by the action of bromine on the parent phenol dissolved in glacial acetic acid, forms nodular crystals, m. p. 140—141°; the *diacetate*, $\text{C}_{18}\text{H}_{14}\text{O}_4\text{Br}_4$, crystallises in white leaflets, m. p. 130—131°. 3:3'-*Dibromo-5:5'-dinitrodi-p-hydroxydi- α -phenylethane*, $\text{C}_{14}\text{H}_{10}\text{O}_6\text{N}_2\text{Br}_2$, is prepared by adding solid sodium nitrite to a solution of the tetrabromo-compound in glacial acetic acid; it forms compact, yellow crystals, m. p. 172°, and yields a sparingly soluble red salt with alkali; the *diacetate* forms yellowish white, compact crystals, m. p. 174—175°. When the tetrabromo-compound is heated with bromine and carbon tetrachloride in a sealed tube at 100°, there is formed 3:5:6:3':5':6'-*hexabromodi-p-hydroxydi- α -phenylethane*, $\text{C}_{14}\text{H}_8\text{O}_2\text{Br}_6$, in white leaves or compact crystals, m. p. 169—170°; the *diacetate*, $\text{C}_{18}\text{H}_{12}\text{O}_4\text{Br}_6$, crystallises in white needles, m. p. 182—183°. 2:5:2':5'-*Tetrabromo-3:3'-dinitrodi-p-hydroxydi- α -phenylethane*, $\text{C}_{14}\text{H}_8\text{O}_6\text{N}_2\text{Br}_4$ (constitution not quite certain), formed by the action of sodium nitrite on a solution of the hexabromo-derivative in glacial acetic acid, crystallises in yellow needles, m. p. above 145° (decomp.); the *diacetate*, $\text{C}_{18}\text{H}_{12}\text{O}_8\text{N}_2\text{Br}_4$, forms yellow needles, m. p. 123°.

2:3:5:6:2':3':5':6'-*Octabromodi-p-hydroxydi- α -phenylethane*, $\text{C}_{14}\text{H}_6\text{O}_2\text{Br}_8$, prepared by heating the hexabromo-compound with bromine at 160—180°, crystallises in large, transparent prisms or in colourless, stout needles, m. p. 227—228°; the *diacetate*, $\text{C}_{18}\text{H}_{10}\text{O}_4\text{Br}_8$, forms compact, white needles, m. p. 205—206°. 2:3:6:2':3':6'-*Hexabromo-5:5'-dinitrodi-p-hydroxydi- α -phenylethane*, $\text{C}_{14}\text{H}_6\text{O}_6\text{N}_2\text{Br}_6$, prepared by the action of sodium nitrite on a glacial acetic acid solution of the octabromo-compound, crystallises in yellow leaflets, m. p. 233° (decomp.); the *diacetate*, $\text{C}_{18}\text{H}_{10}\text{O}_8\text{N}_2\text{Br}_6$, is a crystalline powder, m. p. 252—254°.

Of the three bromo-derivatives of di-*p*-hydroxydi- α -phenylethane, only the tetrabromo-compound undergoes fission under the influence of bromine; the reaction proceeds at the ordinary temperature, with the formation of $\alpha\beta$ -3:5-tetrabromo- ψ -*p*-ethylphenol, m. p. 124° (Zincke and Lisse, Abstr., 1902, i, 615) and 2:3:4:6-tetrabromophenol (m. p. 112—113° instead of 118° and 120°, as given in the literature); the *acetate* of the latter forms white leaflets or stout needles, m. p. 104—105°.

Tetrabromodi-*p*-hydroxydi- α -phenylethane, when treated in glacial acetic acid solution with nitric acid, D 1·4, gives 2:6-dibromo-4-nitrophenol and a *substance*, $\text{C}_8\text{H}_5\text{O}_6\text{N}_2\text{Br}$, crystallising in yellow needles, m. p. 102—103°, which is, perhaps, a bromodinitroethyl-*p*-benzoquinone; if, however, the tetrabromo-derivative is added to nitric acid, D 1·5, there are formed 2-bromo-4:6-dinitrophenol and 2:6-dibromo-*p*-benzoquinone.

Hexabromodi-*p*-hydroxydi- α -phenylethane is decomposed by nitric acid, D 1·4, into a quinone-like substance, which could not be purified, and a small amount of 2:3(or 2:5)-*dibromo-5(or 3)-nitro-p-ethyl-*

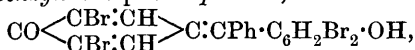
phenol, $C_8H_5O_3NBr_2$, crystallising in yellow needles, sintering at 145° , m. p. 160° (decomp.); the *acetate*, $C_{10}H_9O_4N_2Br_2$, forms yellow needles, m. p. $96-98^\circ$.

Octabromodi-*p*-hydroxydi- α -phenylethane is decomposed by nitric acid, D 1.4, but only a small amount of a *substance*, crystallising in yellow leaflets, m. p. 233° (decomp.), and giving a yellowish-red, sparingly soluble alkali salt, could be isolated; it is suggested that the substance may be 2 : 5 : 6-tribromo-5-nitro-4-hydroxyacetophenone.

[With W. WOLLENBERG.]—3 : 5 : 3' : 5'-*Tetrabromodi-p-hydroxytriphenylmethane*, $CHPh(C_6H_2Br_2 \cdot OH)_2$, prepared by the action of bromine on a chloroform solution of di-*p*-hydroxytriphenylmethane (Rusanoff, Abstr., 1889, 1188), crystallises in colourless needles or prisms, m. p. $160-161^\circ$; the *diacetate* forms white leaflets, m. p. 165° . The tetrabromo-compound is decomposed by nitric acid, D 1.5, into 2 : 6-dibromo-4-nitrophenol and benzaldehyde, and with sodium nitrite it yields 3 : 3'-dibromo-5 : 5'-dinitrodi-*p*-hydroxytriphenylmethane,



small, yellow needles, m. p. 161° , forming sparingly soluble, red alkali salts. α -3 : 5 : 3' : 5'-*Pentabromodi-p-hydroxytriphenylmethane perbromide*, $CBrPh(C_6H_2Br_2 \cdot OH)_2 \cdot Br_2$, prepared by adding a slight excess of bromine to a glacial acetic acid solution of di-*p*-hydroxytriphenylmethane, forms dark red crystals with a green, metallic lustre, which, on boiling with acetone, yield 3 : 5 : 3' : 5'-*tetrabromo-4'-hydroxyphenylbenzylidene-p-benzoquinone*,



a micro-crystalline, dark brownish-red powder, remaining unmelted at 270° , and decomposing at a higher temperature; the *sodium* salt forms small, dark green needles with a metallic lustre. The quinone is reduced by hydriodic acid to tetrabromodi-*p*-hydroxytriphenylmethane; when boiled with acetone, water, and alkali hydroxide, it yields 3 : 5 : 3' : 5'-*tetrabromodi-p-hydroxytriphenylcarbinol*, $CPh(C_6H_2Br_2 \cdot OH)_2 \cdot OH$, a white, amorphous powder, and with methyl alcohol and sulphuric acid it forms the corresponding *methyl ether*, $CPh(C_6H_2Br_2 \cdot OH)_2 \cdot OMe$, a white, amorphous powder (compare Zincke and Krügener, *loc. cit.*; Zincke and Birschel, Abstr., 1908, i, 781). The perbromide described above readily loses bromine when triturated with acetone, yielding the ψ -form of α -3 : 5 : 3' : 5'-*pentabromodi-p-hydroxytriphenylmethane*, $CBrPh \cdot (C_6H_2Br_2 \cdot OH)_2$, which is also obtained by treating the corresponding quinone with acetic-hydrobromic acid; it forms slender, white needles. When the quinone is treated with hydrochloric acid, the ψ -form of α -chloro-3 : 5 : 3' : 5'-*tetrabromodi-p-hydroxytriphenylmethane* is obtained in slender, white needles.

[With E. WUGK.]—3 : 5 : 3' : 5'-*Tetrabromodi-p-hydroxytri- α -phenylethane*, $CMePh(C_6H_2Br_2 \cdot OH)_2$, prepared by mixing glacial acetic acid solutions of bromine and di-*p*-hydroxytri- α -phenylethane (m. p. $187-188^\circ$; *diacetate*, white needles, m. p. 179°), forms compact, colourless crystals, m. p. 194° ; the *diacetate* crystallises in white leaflets, m. p. $96-98^\circ$. With nitric acid, D 1.5, the compound yields 6-bromo-2 : 4-dinitrophenol.

p-Hydroxydiphenylmethylecarbinol, $CMePh(C_6H_4 \cdot OH) \cdot OH$, obtained

on one occasion by the condensation of phenol with acetophenone, forms compact, white crystals, m. p. 186—187°; the *diacetate* crystallises in white needles, m. p. 178°. The carbinol yields with bromine a *tribromo*-derivative, $C_{14}H_{11}O_2Br_3$, forming white needles, m. p. 194°, and it condenses readily with phenol with the production of di-*p*-hydroxytri- α -phenylethane.

3 : 5 : 3' : 5'-Tetrabromodi-*p*-hydroxytetraphenylmethane,
 $CPh_2(C_6H_2Br_2 \cdot OH)_2$,

prepared by brominating di-*p*-hydroxytetraphenylmethane (Mackenzie, *Trans.*, 1901, 79, 1209), crystallises in compact, white needles, m. p. 202°; the *diacetate*, $C_{29}H_{20}O_4Br_4$, forms compact, white needles, m. p. 190°. When boiled with nitric acid, D 1.5, the tetrabromo-compound yields 6-bromo-2 : 4-dinitrophenol. and with sodium nitrite it gives 3 : 3'-dibromo-5 : 5'-dinitrodi-*p*-hydroxytetraphenylmethane,

$CPh_2[C_6H_2Br(NO_2) \cdot OH]_2$,

yellow, glistening leaflets or transparent, brownish-yellow, rhombic tablets, m. p. 196—197°; the *diacetate*, $C_{29}H_{20}O_8N_2Br_2$, forms small, white needles, m. p. 166°.

Hexabromodi-*p*-hydroxytetraphenylmethane,

$C(C_6H_4Br)_2(C_6H_2Br_2 \cdot OH)_2$,

prepared by the action of bromine on the tetrabromo-compound, crystallises in stout, white needles, m. p. 286—290°; it forms a *sodium* salt and an *acetate*, white leaflets, m. p. 170°. J. C. C.

Formation of Benzyl Ether. RUDOLF WEGSCHEIDER (*Ber.*, 1908, 41, 4341).—The formation of benzyl ether from benzyl alcohol and a little sulphuric acid, regarded by Meisenheimer (*Abstr.*, 1908, i, 417) and Schroeter and Sondag (*Abstr.*, 1908, i, 497) as new, was first observed by the author (*Abstr.*, 1900, i, 657). W. R.

Action of Phosphorus Pentachloride and Pentabromide on Mercaptans. WILHELM AUTENRIETH and ALFRED GEYER (*Ber.*, 1908, 41, 4256—4258. Compare Vogt, *Annalen*, 1861, 119, 148).—Phenyl and benzyl mercaptans react with phosphorus pentachloride or pentabromide at -15° , giving quantitative yields of the corresponding disulphides, phosphorus trihalide, and hydrogen halide, for example: $2PhSH + PCl_5 = S_2Ph_2 + PCl_3 + 2HCl$. J. J. S.

Phytosterol from South African Rubber. N. H. COHEN (*Arch. Pharm.*, 1908, 246, 592—593).—The phytosterol previously described (*Abstr.*, 1908, i, 884) as similar to Schulze's *ischolesterol* has now been carefully compared with Schulze's original preparation, and corresponding derivatives of the two substances have also been examined. The results show that the two are identical. T. A. H.

Electrolytic Dissociation Constants of cycloAliphatic Acids. NICOLAI D. ZELINSKY and N. IZGARYSCHEFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1379—1388).—The authors have measured the dissociation constants for a number of cyclic acids, the following being the values of *K* obtained. *cyclo*Hexanecarboxylic (hexahydrobenzoic) acid, 0.00134; 1-methyl*cyclo*hexane-2-carboxylic (hexahydro-*o*-toluic)

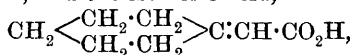
acid, solid *trans*-modification, 0.00205, liquid *cis*-modification, 0.00164; 1-methylcyclohexane-3-carboxylic (hexahydro-*m*-toluic) acid, 0.00128; 1-methylcyclohexane-4-carboxylic (hexahydro-*p*-toluic) acid, 0.00111; 1-methylcyclohexane-1-carboxylic acid, 0.00069; cyclohexaneacetic (hexahydrophenylacetic) acid, 0.00236; 1-methylcyclohexane-3-acetic acid, 0.00159; cyclohexanepropionic (β -hexahydrophenylpropionic) acid, 0.00134. It will be seen that a methyl group in the ortho-position increases the constant of hexahydrobenzoic acid to 1.5 times its value for the *trans*-acid and to 1.25 times in the case of the *cis*-acid, which is hence the weaker of the two; similar results were obtained by Smith (Abstr., 1898, ii, 284) with the *cis*- and *trans*-modifications of hexahydrophthalic and hexahydroterephthalic acids. In the case of maleic, fumaric, crotonic, and isocrotonic acids, however, Ostwald (Abstr., 1889, 818) found that the *cis*-forms have constants much greater than those of the corresponding *trans*-isomerides. A methyl group in the para-position lowers the dissociation constant in the ratio 1.2:1, whilst in the meta-position it is practically without influence.

Comparison of the above numbers with the values of K for benzoic (0.00600) and *o*- (0.0120), *m*- (0.00514), and *p*-toluic (0.00515) acids shows that the presence of the extra six hydrogen atoms in the hexahydrogenated acids weakens the corresponding aromatic acids to extents varying from 3.3 to 5.8 times. The hexahydrogenation of phenylacetic acid lowers its constant only 2.3 times, whilst with β -hexahydrophenylpropionic acid the weakening influence of the six hydrogen atoms and the strengthening action of the phenyl group compensate one another, so that the acid has the same constant as propionic acid. The weakening action of a methyl group in the meta-position is shown by the constant of 1-methylcyclohexane-3-acetic acid.

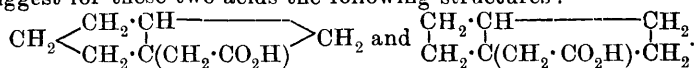
The value of K for the *trans*-form of 3:5-dimethylcyclohexane-carboxylic acid is 0.00109, and for the corresponding *cis*-modification, 0.00107. The insertion of two methyl groups in the meta-positions hence lowers the constant of cyclohexanecarboxylic acid in the ratio 1.25:1, although one such group is almost without influence.

A methyl group attached to the same carbon atom as the carboxyl group causes considerable lowering in the constant, which for 1:3-dimethylcyclohexanecarboxylic acid has the value 0.000630.

cyclo- Δ^1 -Hexeneacetic acid, $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH} \end{array} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, has the constant 0.00249, and the isomeric acid,



the constant 0.00260. Since unsaturated acids in general have high dissociation constants, whilst the above numbers are about the same as the value (0.00236) found for hexahydrophenylacetic acid, the authors suggest for these two acids the following structures:



The value of K for cyclopropanecarboxylic acid is 0.00150; cyclobutanecarboxylic acid, 0.00180; cyclopentanecarboxylic acid, 0.00124;

3-methylcyclopentanecarboxylic acid, 0.00107; 2-ethylcyclopentanecarboxylic acid, 0.00111; cycloheptanecarboxylic acid, 0.00122; vinylacetic acid, 0.00465.

In the series of non-substituted cycloaliphatic acids, the constant of an acid with an even number of carbon atoms is greater than the constants of the two neighbouring acids with odd numbers of carbon atoms.
T. H. P.

Quantitative Estimation of the Products of Nitration of *m*-Chloro- and *m*-Bromo-benzoic Acid. ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 260—266).—The composition of the product obtained on nitrating *m*-chloro- or *m*-bromo-benzoic acid has again been determined, because the results previously obtained by two different methods did not agree very closely (compare Abstr., 1900, i, 638; 1901, i, 591). The method adopted in this investigation was to extract the nitration product with water, care being taken to keep the solution saturated with 3-chloro- or 3-bromo-2-nitrobenzoic acid, and to titrate the solution so obtained with standard alkali. It was found that the product formed by nitrating *m*-chlorobenzoic acid at 0° and -30° contained 92 and 93% of 3-chloro-6-nitrobenzoic acid and 8 and 7% of 3-chloro-2-nitrobenzoic acid respectively. The corresponding bromobenzoic acid gave under similar conditions 87 and 89% of 3-bromo-6-nitrobenzoic acid and 13 and 11% of 3-bromo-2-nitrobenzoic acid respectively.

W. H. G.

***o*-Bromophenyl- and α -Bromophenyl-acetamide.** JOAN POPOVICI (*Ber.*, 1908, 41, 4052).—In reply to Steinkopf and Benedek (Abstr., 1908, i, 981), it is pointed out that *o*-bromophenylacetamide (m. p. 186—187°) has been prepared previously (*Diss.*, 1906) by the hydrolysis of *o*-bromobenzyl cyanide.

J. J. S.

Desylanthranilic Acid. ROMUALD WECKOWICZ (*Ber.*, 1908, 41, 4144—4147).—*Desylanthranilic acid*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CHPh}\cdot\text{COPh}$, m. p. 231—232°, is obtained by heating equal molecular quantities of anthranilic acid and benzoin. The silver, calcium, barium, magnesium, and zinc salts are mentioned. The acetyl derivative, $\text{C}_{23}\text{H}_{19}\text{O}_4\text{N}$, has m. p. 198—200°, and the oxime, $\text{C}_{21}\text{H}_{18}\text{O}_3\text{N}_2$, has m. p. 185—186°. By nitration by concentrated sulphuric and nitric acids, a tetranitro-*desylanthranilic acid*, $\text{C}_{21}\text{H}_{13}\text{O}_{11}\text{N}_5$, is obtained, which sinters and darkens at 85°, and decomposes at 105—130°. *Desylanthranilic acid* and phenylhydrazine react in acetic acid to form a yellow, crystalline substance, $\text{C}_{33}\text{H}_{27}\text{N}_5$, m. p. 229—230°, which is insoluble in alkalis or dilute acids.

C. S.

Intramolecular Rearrangement of Phthalamic Acids. III. J. BISHOP TINGLE and H. F. ROLKER (*J. Amer. Chem. Soc.*, 1908, 30, 1882—1894).—In earlier papers (Abstr., 1907, i, 692, 1044), it has been shown that phthalanil is formed by the action of aniline on phthalanilic acid at a comparatively low temperature. A study has now been made of the action of pyridine, quinoline, ethylaniline, diphenylamine, aniline, α - and β -naphthylamine, and

benzylamine on phthalanilic, *o*-, *m*-, and *p*-tolylphthalamic, *m*- and *p*-nitrophenylphthalamic, and α - and β -naphthylphthalamic acids.

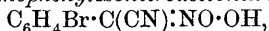
Pyridine and quinoline reacted with all these acids with formation of the corresponding phthalimide. Ethylaniline also gave the phthalimides, except in the case of β -naphthylphthalamic acid, which failed to react under the conditions of the experiment. Diphenylamine did not effect any change. Aniline gave phthalanil with each of the acids; it also yielded some phthalanilic acid with the three tolylphthalamic acids, and some *phenyl-p-tolylphthalamide*, m. p. 168°, with the *p*-tolyl derivative. α -Naphthylamine failed to produce any change with the α - and β -naphthyl- and *p*-nitrophenyl-phthalamic acids, but with the other compounds it gave α -naphthylphthalamic acid, mixed in two cases with *m*- and *p*-tolylphthalamide respectively. A comparison of these results with those produced by aniline shows that the phenyl and naphthyl groups are mutually replaceable in the system $R \cdot NH_2 \rightleftharpoons R' \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H$. The velocity appears to be greatest when R is $C_{10}H_7$. β -Naphthylamine reacted in a similar manner to α -naphthylamine. *o*-, *m*-, and *p*-Toluidine were each treated only with the particular phthalamic acid yielded by the individual amine, and the product consisted of *o*-, *m*-, and *p*-tolylphthalamide respectively. The efficiency of these amines in producing the imide is less than that of quinoline, pyridine, and ethylaniline. *m*- and *p*-Nitroanilines failed to react with *m*- and *p*-nitrophenylphthalamic acids respectively. Benzylamine formed salts with *m*-tolyl-, *m*-nitrophenyl-, and α - and β -naphthyl-phthalamic acids; in the case of the *m*-nitrophenyl and α -naphthyl compounds some dibenzylphthalamide was produced.

These results show that the change of the phthalamic acids into phthalimides, $R \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H \rightarrow C_6H_4 \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} NR$, depends on (1) the nature of R, the stability of the acid increasing as R becomes more negative; (2) the temperature, increase of temperature facilitating the transformation; (3) the nature of the amine, the activity being greater the more positive the amine; and (4) the nature of the solvent. Alcohol (95%) is very active in favouring the transformation, and it is suggested that this is due to salt-formation.

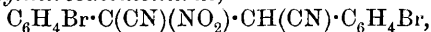
The following compounds are described: *m*-Tolylphthalamic acid, m. p. 159—161°, needles or plates. *p*-Tolylphthalamic acid, m. p. 160°, white, lustrous flakes. *m*-Nitrophenylphthalamic acid, m. p. 202°, and the corresponding *p*-derivative, m. p. 186°. *m*-Tolylphthalamide has m. p. 170—172°. Benzylamine *m*-tolylphthalamate and quinoline and benzylamine *m*-nitrophenylphthalamates are also described. E. G.

Condensation of Ethyl Nitrate and *p*-Bromobenzyl Cyanide. WILHELM WISLICENUS and HEINRICH ELVERT (*Ber.*, 1908, 41, 4121—4133. Compare *Abstr.*, 1905, i, 284).—The reaction between ethyl nitrate, *p*-bromobenzyl cyanide, and sodium ethoxide in alcohol-etheral solution yields sodium *p*-bromophenylisonitroacetonitrile, $C_6H_4Br \cdot C(CN) : NO \cdot ONa$, which crystallises in colourless leaflets and decomposes above 300°

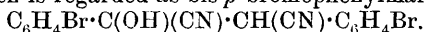
The *potassium* salt, which darkens at 200° and has m. p. $254-256^{\circ}$ (decomp.), is obtained in better yield by using potassium ethoxide; the *copper*, *barium*, and *silver* salts are described. From a 5% aqueous solution of the sodium salt and dilute sulphuric acid in a freezing mixture, *p*-bromophenylisonitroacetonitrile,



m. p. 64° (decomp.), is obtained, which is less unstable than the compounds described previously (*loc. cit.*). By spontaneous decomposition, it yields water and oxides of nitrogen, together with one or more of three other substances, $\alpha\beta$ -bis-*p*-bromophenyl- α -nitrosuccinonitrile, $\alpha\beta$ -bis-*p*-bromophenylmaleonitrile (*pp'*-dibromo-*aa'*-dicyanostilbene), and *p*-bromobenzoic acid, according to the temperature. *Bis-p*-bromophenylnitrosuccinonitrile,



m. p. $130-134^{\circ}$, obtained together with dibromodicyanostilbene by the slow decomposition of *p*-bromophenylisonitroacetonitrile at a low temperature, or by warming the benzene solution of the precipitate obtained by acidifying the aqueous solution of the sodium salt with dilute sulphuric acid, separates from alcohol in colourless needles, and develops a purplish-red colour with phenol and concentrated sulphuric acid. When heated above its m. p., it loses 1 mol. HNO_2 , and forms the second of the three substances mentioned above, whilst by repeated crystallisation from alcohol it is changed into a *substance*, m. p. 162° , which is regarded as *bis-p*-bromophenylmalonitrile,



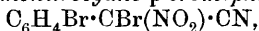
pp'-Dibromo-*aa'*-dicyanostilbene, $\text{C}_6\text{H}_4\text{Br}\cdot\text{C}(\text{CN})\cdot\text{C}(\text{CN})\cdot\text{C}_6\text{H}_4\text{Br}$, m. p. $214-215^{\circ}$, is obtained by warming a benzene or ethereal solution of *p*-bromophenylisonitroacetonitrile until the evolution of nitric oxide ceases, and quantitatively by treating the sodium salt with dilute sulphuric acid at the ordinary temperature; it separates from benzene in colourless prisms, and is hydrolysed by 10% alcoholic potassium hydroxide, giving a product which by acidification yields *bis-p*-bromophenylmaleic anhydride, m. p. $208-210^{\circ}$, and a little *p*-bromobenzoic acid. When an acidified solution of sodium *p*-bromophenylisonitroacetonitrile is distilled with steam, the chief product of the decomposition is *p*-bromobenzoic acid.

When sodium *p*-bromophenylisonitroacetonitrile and excess of sodium nitrite in aqueous solution are slowly treated with dilute sulphuric acid at 0° , *p*-bromoisonitrosobenzyl cyanide is obtained, which is hydrolysed by dilute sodium hydroxide, yielding *p*-bromophenyloximinodiacetic acid, $\text{C}_6\text{H}_4\text{Br}\cdot\text{C}(\text{NOH})\cdot\text{CO}_2\text{H}$, m. p. $160-161^{\circ}$. Methyl iodide reacts with an alcoholic solution of sodium *p*-bromophenylisonitroacetonitrile at 100° to form *p*-bromo-oximinobenzyl cyanide, and with the silver salt at the ordinary temperature, yielding the *methyl* ether, $\text{C}_6\text{H}_4\text{Br}\cdot\text{C}(\text{CN})\cdot\text{NO}\cdot\text{OMe}$, m. p. 110° .

Boiling dilute sodium hydroxide converts sodium *p*-bromophenylisonitroacetonitrile into sodium *p*-bromophenylisonitromethane, from which Hantzsch and Schultze's *p*-bromophenylisonitromethane (*Abstr.*, 1896, i, 672) is obtained by acidification; at $150-160^{\circ}$ the action of the alkali hydroxide results in the formation of *pp'*-dibromostilbene, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\text{Br}$, m. p. $208-210^{\circ}$, which forms a *dibromide*,

$C_{14}H_{10}Br_4$, m. p. 235—240° (decomp.). Reduction of sodium *p*-bromophenylisonitroacetonitrile by zinc and sodium hydroxide yields *amino-p-bromophenylacetic acid*, $C_6H_4Br \cdot CH(NH_2) \cdot CO_2H$, which crystallises in colourless leaflets, sublimes at 265°, and is soluble in dilute acids or alkalis.

Bromine acts on a cold solution of sodium *p*-bromophenylisonitroacetonitrile to form *bromonitrocyano-p-bromophenylmethane*,

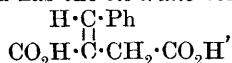


which is unstable, and by warming yields *p*-bromobenzoyl cyanide, $C_6H_4Br \cdot CO \cdot CN$, m. p. 65—66°, from which phenylhydrazine in ether produces *p-bromobenzoylphenylhydrazine*, $C_6H_4Br \cdot CO \cdot N_2H_5Ph$, m. p. 198—200°, which gives the Bülow reaction. The hydrolysis of *p*-bromobenzoyl cyanide by concentrated hydrochloric acid yields *p-bromobenzoylformamide*, $C_6H_4Br \cdot CO \cdot CO \cdot NH_2$, m. p. 128—129°, which is converted by boiling water containing a little sodium hydroxide into *p-bromobenzoylformic acid*, $C_6H_4Br \cdot CO \cdot CO_2H$, m. p. 108°, which responds to Claisen's test for benzoylformic acid.

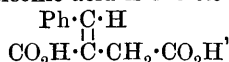
C. S.

Indoneacetic Acids. IV. Configuration of Phenylitaconic and Phenylaticonic Acids. HANS STOBBE and OTTO HORN (*Ber.*, 1908, 41, 3983—3988. Compare Abstr. 1902, i, 542; 1904, i, 503; 1906, i, 361).—The method of determining the configuration of stereoisomeric substituted itaconic acids by cold concentrated sulphuric acid, whereby the *cis-trans*-modification merely anhydrides, whilst the *cis*-isomeride “indonises,” has been applied to γ -phenylitaconic and γ -phenylaticonic acids, which Fittig has shown to be stereoisomerides (Abstr., 1904, i, 418).

γ -Phenylitaconic acid has the *cis-trans*-configuration



since it is converted by sulphuric acid at 0° into the *anhydride*, m. p. 164°. γ -Phenylaticonic acid is the *cis*-modification,



since with 99% sulphuric acid at -12° it yields the three following indone derivatives. 1-Indone-2-acetic acid, $C_6H_4 \begin{array}{c} < CH \\ CO \end{array} > C \cdot CH_2 \cdot CO_2H$,

m. p. 99°, crystallises in yellow needles or prisms, and forms a yellow *semicarbazone*, m. p. 199° (decomp.). The *lactone* of 3-hydroxy-1-

hydrindone-2-acetic acid, $C_6H_4 \cdot \begin{array}{c} CH \cdot O \\ CO - CH \cdot CH_2 \end{array} > CO$, m. p. 123°, forms

colourless needles, and yields with 10% sodium hydroxide the golden-yellow sodium salt of 1-indone-2-acetic acid. Bimolecular 1-indone-2-acetic acid, $C_{22}H_{16}O_6$, m. p. 229°, is colourless, and gives a colourless solution with 10% sodium hydroxide, which turns bluish-violet and finally brown by warming; the cooled solution on acidification gives a substance, m. p. 135° (decomp.). Formulæ are suggested for the bimolecular acid, in which the absence of colour indicates that fewer chromophores are present than in the yellow unimolecular acid.

C. S.

Electrolysis of Santonin and of its Derivatives. ERNESTO PANNAIN (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 499—500).—The electrolysis of santonin in aqueous acetic acid solution yields santonone, the carbonyl group of the santonin being reduced, and two molecules condensed with elimination of water. Under similar conditions, benzophenone yields benzopinacone. The experiments are being extended to various santonin derivatives, and to artemesin, camphor, purine derivatives, etc. T. H. P.

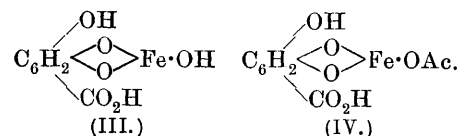
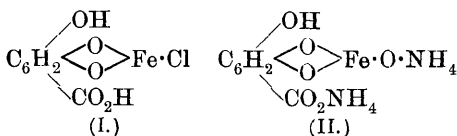
Equilibria among the Stereoisomerides of Santonin. MARIO LEVI-MALVANO and ANTONIO MANNINO (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 484—494).—The authors have prepared melting-point curves for the following pairs of santonin derivatives.

iso- and *l*-Acetyl-desmotroposantonin: the curve here consists of three branches with two eutectic points, thus confirming the existence of racemic acetyl-desmotroposantonin. The reciprocal solubilities of the racemic form in the two active forms are practically equal. Theoretically, the compound with the lower melting point, in this case the racemic modification, should be the more soluble, and this phenomenon, which is general in a binary system, has been verified in several instances where the difference between the melting points is greater than in the present case.

Acetyl-desmotroposantonin and acetyl-*l*-desmotroposantonin: in this case the two stereoisomerides give only mixtures, the solubility curve of acetyl-desmotroposantonin consisting of two branches, the first of which resembles a solid solution curve.

Acetyl-desmotroposantonin and acetyl-*isodesmotroposantonin* yield only mixtures, as also do desmotroposantonous and *isodesmotroposantonous* acids. T. H. P.

Complex Salts of Gallic Acid. Ferrigallic Inks. T. SILBERMANN and H. OZOROVITZ (*Chem. Zentr.*, 1908, ii, 1024—1025; from *Bul. Soc. Sci. Bucuresci*, 1908, 17, 43—57).—Aqueous solutions of gallic acid yield a blue precipitate with ferric chloride which is probably *chloroferrigallic acid* (I); it dissociates readily into gallic acid and ferric chloride



when treated with acid, when warmed, or when kept for some time.

The addition of ammonia or alkalis to chloroferrigallic acid produces a precipitate which is soluble in excess of the precipitant, giving an intensely reddish-yellow solution. The compound with ammonia,

ammonium ammonoxyferrigallate (II), is obtained by precipitating with alcohol; it forms a shining black, brittle mass containing $4\text{H}_2\text{O}$, and is very soluble in cold water, giving an intense violet-blue solution. Ammonia turns this solution somewhat red; alkalis, brownish-yellow; and acetic acid produces a dark blue coloration.

Alcohol added to the dissociated yellow solution of chloroferrigallic acid causes the precipitation of *hydroxyferrigallic acid* (III), a blue, flocculent substance. It appears to be the intermediate compound between (I) and (II), and may also be prepared by shaking freshly precipitated ferric hydroxide with a solution of gallic acid. The blue solution obtained from substance (II) with acetic acid contains acetylferrigallic acid (IV), and by heating this solution, hydroxyferrigallic acid is precipitated, which is converted into soluble chloro- or acetyl-ferrigallic acid when treated with hydrogen chloride or acetic acid respectively. A neutral ammonium gallate solution when shaken with ferric hydroxide yields the deep red, sparingly soluble ammonium hydroxyferrigallate, which, in presence of hydrogen chloride, gives the insoluble blue acid (III), and with ammonia the neutral, soluble salt (II).

Compounds having two or more hydroxyl groups, or one hydroxyl and one carboxyl group, in the ortho-position give similar complex iron ammonium salts, which are soluble in water with a more or less blood-red colour, and are precipitated by alcohol from such solutions.

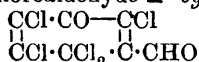
The complex iron ammonium salt of tannin is slightly soluble in water, insoluble in 10—15% alcohol; catechol and pyrogallol give a blood-red-coloured solution, from which alcohol causes a reddish-violet precipitate to separate.

Methylenedigallic acid yields a blood-red salt which is soluble in water, alcohol precipitating it in the form of a greyish-black powder. Salicylic acid gives a less intense orange-red solution, from which alcohol causes a red substance to separate.

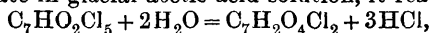
Besides ammonia and alkali hydroxides, complex salts are obtained with alkali carbonates and other salts of alkaline reaction, also alkaline earth hydroxides and organic bases. Aniline gives with gallic acid and ferric chloride a sparingly soluble salt, which resembles in colour those of the alkali salts rather than the ammonium salt. Further, it is found that ferrous salts behave in a similar manner to ferric salts; for instance, ferrous sulphate with gallic acid and ammonia gives a deep red solution, from which alcohol causes precipitation.

Nearly every salt of a multivalent metal is capable of forming complex salts with gallic acid and alkali. J. V. E.

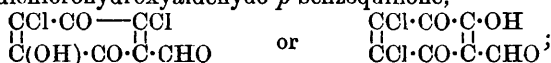
Pentachloro- and Heptachloro-*m*-hydroxybenzaldehyde. THEODOR ZINCKE and W. BROEG (*Annalen*, 1908, 363, 221—245).—The authors have investigated the properties of aldehydotrichloroquinodichloride [pentachloroaldehydo- Δ^2 -cyclohexadienone],



(Biltz and Kammann, *Abstr.*, 1902, i, 162); its aldehydic nature is confirmed by the formation of a methylal and a diacetate. With potassium acetate in glacial acetic acid solution, it reacts thus:



forming dichlorohydroxyaldehydo-*p*-benzoquinone,

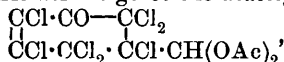


this with sulphurous acid yields a trihydroxy-derivative, which with acetic anhydride gives a penta-acetyl derivative, and with aniline it forms a compound, $\text{OH}\cdot\text{C}_6\text{O}_2\text{Cl}(\text{NHPh})\cdot\text{CH:NPh}$.

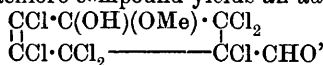
On chlorination, the above pentachloro-compound gives heptachloro-aldehydo- Δ^2 -cyclohexen-1-one, $\begin{array}{c} \text{CCl} \cdot \text{CO} - \text{CCl}_2 \\ | \quad | \\ \text{CCl} \cdot \text{CCl}_2 \cdot \text{CCl} \cdot \text{CHO} \end{array}$, which on reduction furnishes tetrachloro-*m*-hydroxybenzaldehyde; with sodium hydrogen sulphite, pentachlorophenol, and with concentrated sulphuric acid in glacial acetic acid solution, tetrachloro-*p*-benzoquinone. The heptachloro-compound on heating yields the compound $\text{C}_{12}\text{O}_2\text{Cl}_8$ (Zincke and Schaum, *loc. cit.*), m. p. 320° .

The *dimethyl* ether of pentachloroaldehydo- Δ^2 -cyclohexadienone, $\text{C}_9\text{H}_7\text{O}_5\text{Cl}_5$, forms small, colourless needles, m. p. 108° . The corresponding *diacetyl* compound crystallises in small, white needles, m. p. $186-187^\circ$. 2:6-Dichloro-5-hydroxy-3-aldehydo-*p*-benzoquinone forms glistening, yellow leaflets, m. p. $197-198^\circ$ (decomp.), which, under the influence of light, rapidly turn copper-red and finally greyish-green. The *potassium* salt forms small, dark red needles. The *dianilide*, $\text{C}_{19}\text{H}_{13}\text{O}_2\text{N}_2\text{Cl}$, forms orange-red crystals, m. p. 250° . 2:4-Dichloro-3:5:6-trihydroxybenzaldehyde, prepared by reducing the hydroxyquinone with sulphurous acid, forms small, yellow crystals, m. p. 192° ; the *penta-acetyl* derivative crystallises in small, white needles, m. p. 143° . On warming the hydroxyquinone with dilute potassium hydroxide, 6-chloro-2:5-dihydroxy-3-aldehydo-*p*-benzoquinone, $\text{C}_7\text{H}_3\text{O}_5\text{Cl}$, is obtained; it forms small, brown crystals sintering at 195° ; the *potassium* and *sodium* salts form red needles.

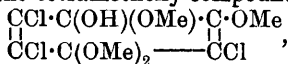
Heptachloroaldehydo- Δ^2 -cyclohexen-1-one forms glistening crystals containing $1\frac{1}{2}\text{H}_2\text{O}$, m. p. $107-112^\circ$ (evolving water); with alcohol and sulphuric acid it yields the *ethyl* ether, $\begin{array}{c} \text{CCl} \cdot \text{CO} - \text{CCl}_2 \\ | \quad | \\ \text{CCl} \cdot \text{CCl}_2 \cdot \text{CCl} \cdot \text{CH}(\text{OH}) \cdot \text{OEt} \end{array}$, colourless needles, m. p. $110-111^\circ$ (losing alcohol), the *acetyl* derivative of which forms white needles, m. p. 92° , and with acetic anhydride and sulphuric acid it gives the *diacetyl* derivative,



white leaves, m. p. 171° . With methyl alcohol in presence of sodium methoxide the heptachloro-compound yields an *additive* compound,



transparent leaflets, m. p. $98-100^\circ$, which with excess of sodium methoxide furnishes the tetramethoxy-compound, probably:



m. p. $150-152^\circ$ (Zincke and Schaum, *Abstr.*, 1894, i, 232, give $142-143^\circ$); the *silver* salt is a yellowish-white, amorphous powder.

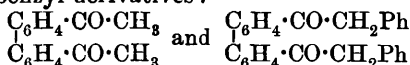
J. C. C.

Phenanthrene Series. XXV. Phenanthrene Derivatives from 9:9-Dichloro-10-phenanthrene. JULIUS SCHMIDT and HERMANN LUMPP (*Ber.*, 1908, 41, 4215-4225).—The authors have investigated the reactions of 9:9-dichloro-10-phenanthrene; the substance is best prepared by the action of phosphorus pentachloride on phenanthraquinone (Lachowicz, *Abstr.*, 1883, 666; 1884, 82), but

it is also formed by treating phenanthraquinone with chlorine in presence of red phosphorus. It crystallises in yellowish-white prisms, m. p. 168—169°. 9-Chloro-10-hydroxyphenanthrene is best prepared by treating the preceding compound with tin and hydrochloric acid; it forms white prisms, m. p. 121° (Lachowicz gives 122—123°); the *picrate*, cinnabar-red prisms, m. p. 169—170°, *acetate*, yellow prisms, m. p. 145—147°, and *benzoate*, pale yellow prisms, m. p. 165—166°, are described. On reduction with zinc dust and glacial acetic acid, chlorohydroxyphenanthrene yields 10-hydroxyphenanthrene, and when heated with aqueous ammonia it gives di-9-hydroxyphenanthryl-10-amine (Schmidt and Kämpf, Abstr., 1902, i, 757), which has m. p. 230° (decomp.), and not 168—170° as previously given. This substance exhibits phototropism in ethereal solution. When boiled with acetic anhydride it furnishes phenanthroxazine (Bamberger and Grob, Abstr., 1901, i, 280). Chlorohydroxyphenanthrene, on sulphonation, gives rise to a *disulphonic acid*, which forms glistening, dark brown leaflets containing 10H₂O; the *barium* salt crystallises in dark green leaflets with 4½H₂O. 3-Nitrophenanthraquinone is obtained in a 30% yield by boiling chlorohydroxyphenanthrene with nitric acid, D 1.35; this is an important improvement on the previous methods of preparation (Abstr., 1908, i, 995), and it is hoped to employ this substance for the synthesis of further scission products of the opium alkaloids.

J. C. C.

Diacetophenone, Dideoxybenzoin, and Dibenzil. THEODOR ZINCKE and W. TROPP (*Annalen*, 1908, 363, 302—312).—The authors have previously shown (Abstr., 1908, i, 786) that the ditertiary alcohols prepared from phenanthraquinone by the aid of organo-magnesium compounds are oxidised by chromic acid to diketones; the reactions of the methyl and benzyl derivatives:

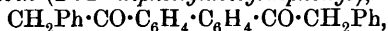


have now been further investigated.

oo'-Diacetophenone (2 : 2'-diacetyldiphenyl), C₆H₄Ac·C₆H₄Ac, prepared by oxidising a glacial acetic acid solution of dihydroxydimethyl-

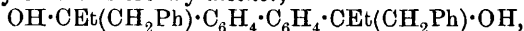
dihydrophenanthrene, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{CMe} \cdot \text{OH} \\ \text{C}_6\text{H}_4 \cdot \text{CMe} \cdot \text{OH} \end{array}$, with chromic acid, crystallises in small, glistening leaflets or colourless prisms, m. p. 84°; the *dioxime*, C₁₆H₁₆O₂N₂, crystallises in compact, colourless needles, m. p. 212° (decomp.); the *bisphenylhydrazone*, C₂₈H₂₆N₄, forms large, pale yellow crystals, m. p. 178°. By the action of magnesium ethyl bromide, the ketone yields a ditertiary alcohol, OH·CMeEt·C₆H₄·C₆H₄·CMeEt·OH, crystallising in colourless prisms, m. p. 119—120°, and on reduction with zinc dust and hydrochloric acid the parent compound is regenerated.

oo'-Dideoxybenzoin (2 : 2'-diphenylacetyldiphenyl),

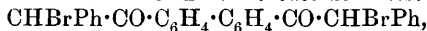


prepared by oxidising dihydroxydibenzyl-dihydrophenanthrene with chromic acid, crystallises in glistening leaflets, m. p. 139—140°; the *dioxime*, C₂₈H₂₄O₂N₂, forms colourless needles, m. p. 108—111°; the *bisphenylhydrazone*, C₄₀H₃₄N₄, crystallises in pale yellow, glistening

leaflets, m. p. 188—189°. By the action of magnesium ethyl bromide, the ketone yields a ditertiary alcohol,



crystallising in colourless tablets, m. p. 130—131°; the *acetate* forms colourless leaflets, m. p. 126—128°. Dideoxybenzoin is readily reduced by zinc dust in acid or alkaline solution to the parent compound; with bromine it forms a *dibromo*-derivative,



white leaflets, m. p. 195° (decomp.), and with phosphorus pentachloride the corresponding *dichloro*-derivative is obtained in white leaflets, m. p. 196—200° (decomp.).

isoNitrosodideoxybenzoin, $\text{OH} \cdot \text{N} \cdot \text{CPh} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CPh} \cdot \text{N} \cdot \text{OH}$, prepared by adding amyl nitrite to an alcoholic solution of dideoxybenzoin, crystallises in stellate clusters of white needles, m. p. 196°; it forms a pale yellow *sodium* salt. When an acetic acid solution of the *isonitroso*-compound is warmed with dilute hydrochloric acid, there is formed *oo'*-*dibenzil*, $\text{COPh} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{COPh}$, which crystallises in sulphur-yellow, rhombic tablets and columns, m. p. 120°; it condenses with 2 mols. of *o*-phenylenediamine to a *diquinoxaline*, $\text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \cdot \text{CPh}$, m. p. above 300°. J. C. C.

Quinonoid Derivatives of Diphenyl. I. WILHELM SCHLENK [with ANGELO KNORR] (*Annalen*, 1908, 363, 313—339).—The object of this investigation was to prepare the diphenyl analogues of *p*-benzoquinone-di-imine, -chloroimine, and -dichlorodi-imine. It has been found possible to isolate the chloroimine and dichlorodi-imine of diphenoquinone; all attempts to prepare the corresponding imines by gentle reduction of these chloroimines have, up to the present, been unsuccessful (compare Willstätter and Kalb, Abstr., 1905, i, 361; 1906, i, 996).

It has long been known that coloured, complex compounds are formed when benzidine is treated with various oxidising agents (compare Zinin, *J. pr. Chem.*, 1845, 36, 98; Claus and Risler, Abstr., 1881, 605; Lauth, Abstr., 1891, 457; Willstätter and Kalb, *loc. cit.*; Barsilowsky, Abstr., 1905, i, 549; Moir, Trans., 1907, 91, 1305; Proc., 1906, 22, 258). It is now shown that these substances are *meri*quinoned-i-immonium salts. The behaviour of some of these salts when dissolved in water or alcohol supports the view recently put forward by Kehrman with reference to the constitution of these compounds (compare Abstr., 1908, i, 699); thus *meri*diphenoquinone-tetramethyldi-immonium chloride (compare Lauth, *loc. cit.*) is not dissociated to any marked degree in aqueous solution, whilst *meri*-ditoluquinoned-i-immonium chloride is partly, and *meri*dichloroditoluquinoned-i-immonium chloride is completely, dissociated in dilute alcoholic solution.

A general method for preparing halogen derivatives of benzidine and the tolidines is described, namely, treating the diamine, suspended in concentrated hydrochloric or hydrobromic acid, with chlorine or bromine respectively; the halogen enters the positions ortho to the

amino-groups; consequently, *p*- and *m*-tolidine yield tetrahalogenated derivatives, whilst only dihalogenated compounds are derived from *o*-tolidine.

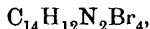
The compound first obtained by Claus and Risler (*loc. cit.*) by the action of sodium hypochlorite on an aqueous solution of benzidine containing hydrochloric acid is shown to be *diphenquinonedichloro-ti-imine*, $\text{ClN}:\text{C}_6\text{H}_4=\text{C}_6\text{H}_4:\text{NCl}$; it is a dark reddish-brown, amorphous powder, and, when heated rapidly, explodes slightly at about 135° ; it also forms microscopic, red needles, which explode at $155\text{--}160^\circ$. It is decomposed with explosive violence by concentrated sulphuric or nitric acid, and is reduced by stannous chloride to benzidine. *Ditoluquinonedichlorodi-imine*, $\text{C}_{14}\text{H}_{12}\text{N}_2\text{Cl}_2$, prepared in a similar manner from *o*-tolidine, crystallises in tufts of ruby-red needles, which explode slightly at about 163° . *p*-*Diphenquinonechloroimine*, $\text{O}:\text{C}_6\text{H}_4:\text{C}_6\text{H}_4:\text{NCl}$, prepared from 4-amino-4'-hydroxydiphenyl, is an olive-brown powder, which rapidly decomposes, forming a black, humous mass.

3:3'-*Dichloro-o-tolidine*, $\text{C}_{14}\text{H}_{14}\text{N}_2\text{Cl}_2$, prepared by the action of chlorine on *o*-tolidine hydrochloride suspended in concentrated hydrochloric acid, crystallises in white needles, m. p. $160\text{--}161^\circ$; the *sulphate*, $\text{C}_{14}\text{H}_{14}\text{N}_2\text{Cl}_2 \cdot 2\text{H}_2\text{SO}_4$, forms microscopic needles. The *hydrochloride* forms white needles, m. p. about 152° , and is converted by ferric chloride in aqueous alcoholic solution into *meridichloroditoluquinonedi-immonium chloride*, $(\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{MeCl} \cdot \text{C}_6\text{H}_2\text{MeCl} \cdot \text{NH}_2, \text{NH}:\text{C}_6\text{H}_2\text{MeCl}:\text{C}_6\text{H}_2\text{MeCl}:\text{NH})$, $2\text{HCl} \cdot 2$ or $3\text{H}_2\text{O}$,

obtained as a bronzy, dark blue powder; the *sulphate* forms microscopical, bronzy, dark blue needles. Similar *dibromo*-derivatives were prepared. *meriDitoluquinonedi-immonium chloride*, $\text{C}_{28}\text{H}_{30}\text{N}_4$, 2HCl , obtained from *o*-tolidine, is a bronzy, violet-black powder.

3:5:3':5'-*Tetrachlorobenzidine*, $\text{C}_{12}\text{H}_8\text{N}_2\text{Cl}_4$, crystallises in white, felted needles, m. p. $226\text{--}227.5^\circ$; the *tetra-acetyl* derivative,

$\text{C}_{20}\text{H}_{16}\text{O}_4\text{N}_2\text{Cl}_4$, forms white needles, m. p. $265\text{--}266^\circ$. *Tetrabromo-m-tolidine*,

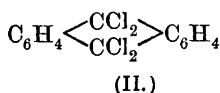
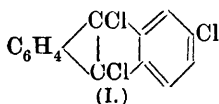


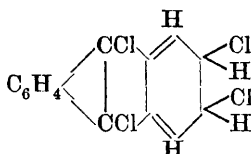
is a heavy, white, crystalline powder, m. p. $229\text{--}230^\circ$; the *tetra-acetyl* derivative, $\text{C}_{22}\text{H}_{20}\text{O}_4\text{N}_2\text{Br}_4$, crystallises in leaflets, m. p. $259\text{--}263^\circ$.

W. H. G.

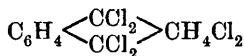
Action of Phosphorus Pentachloride on Anthraquinone.

DAN RADULESCU (*Chem. Zentr.*, 1908, ii, 1032—1033; from *Bul. Soc. Sti. Bucuresti*, 1908, 17, 29—40).—When treated with a mixture of phosphorus pentachloride (2 mol.) and phosphorus oxychloride (4 mol.), anthraquinone yields trichloroanthracene (I), together with small quantities of isomeric dichloroanthracene dichloride (α and β), as well as higher chlorinated products.





(III.)



(IV.)

The small quantity of 9:10-dichloroanthracene β -dichloride (III) that is found is considered to be the intermediate product between the 9:10-dichloride (II) and trichloroanthracene (I).

When anthraquinone is treated at 175–180° with phosphorus pentachloride (3 to 3½ mols.), there is produced trichloroanthracene and dichloroanthracene tetrachloride (IV), which is probably present in two stereoisomeric modifications.

9:10-Dichloroanthracene 9:10-dichloride, $C_{14}H_8Cl_4$ (II), called the α -dichloride, forms red or bluish-cream-coloured, prismatic crystals, m. p. 139°, at which temperature it decomposes into trichloroanthracene. When heated in a current of carbon dioxide at 170–180°, it gives trichloroanthracene, and when heated for a short time above the m. p., small quantities of the so-called β -dichloride are produced.

9:10-Dichloroanthracene 2:3-dichloride, $C_{14}H_8Cl_4$ (III), called the β -dichloride, crystallises in long, greenish-yellow needles, which decompose from 150°, giving trichloroanthracene. It is a very unstable substance, readily losing hydrogen chloride, and when dissolved in chloroform exhibits a blue fluorescence.

Trichloroanthracene, $C_{14}H_7Cl_3$ (I), forms dark red or pale yellow needles, m. p. 172°, which dissolve without decomposition in strong sulphuric acid, giving a malachite-green coloration; when warmed or kept, this colour disappears. So intense is it that a drop of an acetic acid solution of trichloroanthracene diluted 1/10,000 gives a green colour with 2 c.c. of concentrated sulphuric acid. On the addition of acetic acid, this green-coloured solution when not very dilute becomes decolorised, and develops a violet-blue fluorescence. This reaction is found to be a general one for all 9:10-halogen substituted products of anthracene.

9:10-Dichloroanthracene 2:3:9:10-tetrachloride, $C_{14}H_8Cl_6$ (IV) (compare Schwarzer, Abstr., 1877, ii, 493), exists in two, probably stereoisomeric, modifications, α , and γ . The α -tetrachloride crystallises in silky needles, m. p. 185° (decomp.), with formation of trichloroanthracene.

The γ -tetrachloride forms transparent, strongly refracting, prismatic crystals, m. p. 149° (decomp.), yielding trichloroanthracene.

Schwarzer's reaction (*loc. cit.*).—When chlorine is passed into a 0.25–3.5% chloroform solution of anthracene, it is found that 9:10-dichloroanthracene is first produced, then dichloroanthracene α -tetrachloride, and finally a stable compound, m. p. 280°, which crystallises in cream-coloured needles.

J. V. E.

Constituents of Essential Oils. Constitution of Umbellulone. FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 3988–3994).—Previous work of the author, culminating in a representation of the

constitution of umbellulone (Abstr., 1908, i, 92), has been severely criticised by Tutin (Trans., 1908, 93, 252) on the ground that the author employed impure umbellulone, from some constituent of which, other than umbellulone, homotanacetonedicarboxylic acid was produced. The author has therefore distilled 1000 grams of crude oil of *U. Californica*, and obtained a fraction, b. p. 92—94°/10 mm., D^{20} 0.950, n_D 1.4872, and α_D -37°30' (100 mm. tube). This fraction has been treated with semicarbazide hydrochloride (rather more than 2 mols.) in alcoholic solution, whereby two products have been obtained: (a) *Umbellulone semicarbazone*, $C_{11}H_{17}ON_3$, is almost insoluble in water, separates from methyl alcohol in snow-white crystals, decomposes at 240—243°, and yields, with the calculated quantity of dilute sulphuric acid, umbellulone, having b. p. 92.5—93°/10 mm., D^{20} 0.950, n_D 1.48325, and α_D -36°30' (100 mm. tube); (b) semicarbazido-umbellulone semicarbazone, $C_{12}H_{24}O_2N_6$, is soluble in hot water, and is separated completely from the solution by ammonium sulphate, decomposes above 200°, according to the rate of heating, yielding the normal semicarbazone (decomp. 240°), and by treatment with the calculated quantity of sulphuric acid yields umbellulone, having b. p. 92—94°/10 mm., n_D 1.4825, and α_D -37°.

From either of these regenerated umbellulones, β -dihydroumbellulol, β -dihydroumbellulone, benzylidene- β -dihydroumbellulone, and homotanacetonedicarboxylic acid have been prepared in succession, having properties practically identical with those described previously (*loc. cit.*); thus proving that Tutin's objections are invalid.

The author's formula for umbellulone is supported by the fact that umbellulone is converted quantitatively at 280° into thymol. C. S.

Ethereal Oil from *Salvia sclarea*. THOMAS F. HARVEY (*Chemist and Druggist*, 1908, 73, 393).—The author gives analyses of four samples of Dalmatian and one of Spanish oil, from which it appears that pinene, cineol, thujone, borneol, and probably camphor are the normal constituents of Dalmatian oil.

There seems to be a considerable variation in the constituents and properties of oil obtained from different sources; Dalmatian oil derived from *Salvia officinalis*, and Syrian oil from *Salvia triloba*, differ from Spanish oil obtained from a different variety of *Salvia*.

Oil from Dalmatia may be taken as typical; it has D 0.915—0.930, α_D +4° to +25°, n_D^{20} 1.4618—1.4645; it is soluble in 1 vol. and more of 80% alcohol; acid number, 1.3—2.2; ester number, 6.7—12.6; saponification number, 6—18, and total content of borneol, 9.5—14.8.

J. V. E.

Carbonaceous Substances and Bitumens. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1327—1334).—Asphalte always contains more hydrogen than coal or carbonaceous substances, and may be regarded as hydrogenated coal. This view is confirmed by a study of the products of dry distillation of asphalte. Pit coal and brown coal, on dry distillation, give highly unsaturated cyclic compounds, consisting of variously substituted benzenes and of

compounds containing less hydrogen, such as naphthalene, anthracene, chrysene, etc. With asphalte, more highly hydrogenated compounds would be expected on dry distillation, and this is found to be the case. The liquid hydrocarbons obtained in this way give, on distillation, fractions which closely resemble, in density, external appearance, and in their proportions, the fractions obtained on distilling natural naphtha. The lower fractions are remarkably stable towards the action of reagents; thus they are not appreciably attacked by sulphuric acid, nitric acid, or potassium permanganate, and they do not yield benzene nitro-derivatives when treated with a nitrating mixture. This behaviour, together with the density, points to the predominance of naphthenes in the decomposition products of asphalte. In addition, in the absence of aromatic hydrocarbons, which in naphtha may have a secondary origin, the liquid hydrocarbon fraction of asphalte differs from naphtha in the low density of the distillation residue; this is probably to be explained by the presence in naphtha of more or less asphalte, which raises the density of its residue.

The hydrogenated nature of asphalte is confirmed by the character of the distillation products, which are partly hydrogenated aromatic hydrocarbons and partly saturated hydrocarbons. The resemblance, which in some cases amounts to identity, between the decomposition products of naphtha and asphalte indicates an undoubted genetic relationship between the two substances.

T. H. P.

Chemistry of Condurango Bark. KONRAD KUBLER (*Arch. Pharm.*, 1908, 246, 620—660. Compare Tanret, *Abstr.*, 1885, 552; Bocquillon, *J. Pharm. Chim.*, 1891, [v], 24, 485, and Carrara, *Abstr.*, 1891, 1387; 1892, 1352).—The principal constituents found in the bark, apart from dextrose and other usual components of plants, were the glucoside, condurangin, and a new polyhydric alcohol, conduritol.

Condurangin was isolated by extraction of the bark with alcohol and defecation of the alcoholic extract with acetone and chloroform. The glucoside was finally purified by fractional precipitation of its solution in alcohol with ether. Thus obtained it is an amorphous, bright yellow, slightly hygroscopic powder, soluble in water, chloroform, or alcohol, and insoluble in ether. It is bitter and optically inactive. Analyses of different preparations lead to the formula $C_{40}H_{60}O_{16}$. The glucoside contains two methoxyl groups. It is hydrolysed slowly in the cold, and more rapidly on heating with dilute sulphuric acid, yielding dextrose and an amorphous powder, which appears to be a mixture of at least four substances, and yields some cinnamic acid on treatment with alcoholic potassium hydroxide. Condurangin forms a clear solution with water, but this becomes opalescent or, in the case of strong solutions, gelatinous on heating, but returns to its normal condition on cooling.

Conduritol, $C_6H_{10}O_4$, m. p. 142—143°, occurs in the by-products of the purification of the crude glucoside, crystallises from hot alcohol in colourless prisms, is optically inactive, and has an intensely sweet taste. It does not reduce Fehling's solution or ammoniacal silver solution. The *tetrabenzoyl* derivative is amorphous, and the corresponding *phenylurethane*, m. p. 120°, is a colourless, tasteless powder.

Conduritol reacts in aqueous solution with bromine to form a dibromide, $C_6H_{10}O_4Br_2$, m. p. 196° , and a monobromo-compound, $C_6H_{11}O_5Br$, m. p. 175° . When heated with hydrochloric acid, conduritol yields, as one product, catechol. Oxidation experiments gave no results of value. It is thought that the alcohol and the monobromo-compound, referred to above, may be represented by the formulæ

$$\begin{array}{c} \text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{OH} \\ | \qquad | \\ \text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{OH} \end{array} \text{ and } \begin{array}{c} \text{CHBr}\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{OH} \\ | \qquad | \\ \text{OH}\cdot\text{CH}\text{---}\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{OH} \end{array}$$

On steam distillation, the bark yields 0.3% of volatile oil, sp. gr. 0.9741, b. p. 140° , $[\alpha]_D + 6.724^\circ$, having an intense, not unpleasant, aromatic odour, and consisting, in part, of higher fatty acids.

T. A. H.

Constituents of Vincetoxicum Root. KONRAD KUBLER (*Arch. Pharm.*, 1908, 246, 660—663).—This root has been examined in comparison with Condurango root (see preceding abstract), to which it is closely allied botanically. Vincetoxin was isolated by Tanret's method (*Abstr.*, 1885, 552), and, after purification by precipitation from its solution in chloroform by means of ether, was obtained as a colourless, amorphous powder, m. p. 182° (decomp.), $[\alpha]_D - 75^\circ$ in water, having the composition $C_{50}H_{32}O_{20}$. On treatment with hydriodic acid, it yielded methyl iodide equivalent to 10.4% of methoxyl. On hydrolysis with dilute sulphuric acid, dextrose was formed, and a brown, amorphous substance, which did not furnish cinnamic acid when treated with alcoholic potassium hydroxide. The root also contains 3% of sucrose and some dextrose.

T. A. H.

"Kawar" Root. RUDOLF BOEHM and KONRAD KUBLER (*Arch. Pharm.*, 1908, 246, 663—666).—This Asclepiadaceous root, stated to be used in the Transvaal as a remedy for cancer, was examined by the method described under "Condurango" bark (see two preceding abstracts). It contained a volatile oil, choline, a sugar yielding a phenylosazone, m. p. 215° , and a glucoside, *kawarin*. This last is an almost colourless, amorphous powder, soluble in water or chloroform, and insoluble in ether, has m. p. 188° (decomp.), is optically inactive, and its aqueous solution, like that of condurangin, when heated becomes cloudy and gelatinous, but returns to its normal state on cooling. When hydrolysed with dilute sulphuric acid, the glucoside yields about 22% of a dextrorotatory, fermentable sugar, and an amorphous product, insoluble in water, which does not yield cinnamic acid when treated with potassium hydroxide in alcohol. No formula is assigned to kawarin, but it contains 58.7—59.0% of carbon, 8.37—8.53% of hydrogen, and 9.0—9.1% of methoxyl.

T. A. H.

Quantitative Control in Chlorophyll Research. V. BRDLIK (*Compt. rend.*, 1908, 147, 990—993).—The control is spectrophotometric, the ratio of the coefficient of extinction to the amount of dissolved substance being regarded as increasing with the purity of

the chlorophyll preparation. The measurements are best carried out on band II ($\lambda=615$) in dilute benzene solution. Band IV ($\lambda=536$) is due to partial decomposition of the chlorophyll. G. B.

1- and 2-Methylcoumarone. JOHANNES BOES (*Chem. Zentr.*, 1908, ii, 1185; from *Apoth. Zeit.*, 1908, 23, 599).—After repeated fractionation of the distillate separated from the product of resinifying methylcoumarone by sulphuric acid, a substance is obtained having b. p. 185—198°. This gives a picrate which crystallises from alcohol in yellow needles, m. p. 79—80°, but is not a simple substance, giving when decomposed a practically colourless, pleasant-smelling oil, b. p. 189—195°, which exhibits the properties of coumarone. That a phenol and not a cresol is produced is shown by the formation of phenyl phenylcarbamate, m. p. 126°. The suggestion is made that the allylene products in coal-tar react, for the most part, with phenol, forming coumarone compounds. J. V. E.

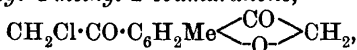
Homologues of Coumaranone and their Derivatives. KARL FRIES and G. FINCK (*Ber.*, 1908, 41, 4271—4284).—Stoermer's method of condensing phenoxyacetic acid by phosphoric oxide to form coumaranone gives poor yields (*Abstr.*, 1897, i, 528), and cannot therefore be used as a general method. Neither is Friedländer's method of obtaining coumaranone from ethyl coumaranonecarboxylate (*Abstr.*, 1897, i, 424) feasible. The simplest theoretical method, namely, the withdrawal of the elements of hydrogen haloid from ω -halogen- o -hydroxyacetophenones, has not been used up till now extensively, owing to the difficulty in obtaining the required acetophenones (compare Nencki, *Abstr.*, 1894, i, 85). These may be obtained easily from the chloroacetyl derivatives of the phenols.

The *chloroacetyl* derivatives of *p*-cresol, *m*-cresol, and *m*-4-xylenol, obtained quantitatively by heating the phenol with chloroacetyl chloride for four hours at 135° and subsequent fractional distillation under reduced pressure, have m. p. 32°, b. p. 162°/45 mm., b. p. 153°/30 mm., and b. p. 173°/45 mm. respectively. The *anilino*-compound from the *p*-tolyl chloroacetate, $C_6H_4Me \cdot O \cdot CO \cdot CH_2 \cdot NHPh$, crystallises from petroleum in slightly yellow needles, m. p. 109°.

These chloroacetyl compounds, when heated with aluminium chloride, undergo isomeric change into *o*-hydroxy-derivatives; thus the chloroacetyl derivative of *p*-cresol gives ω -chloro-2-hydroxy-5-methylacetophenone, $OH \cdot C_6H_3Me \cdot CO \cdot CH_2Cl$. It is obtained by heating at 140° for four hours, and then the product is distilled in steam and crystallised from petroleum; it forms long prisms, m. p. 65°; the alkaline solution becomes red, owing to chemical change. The yield is 90%; the *acetate* has m. p. 59°. ω -Chloro-2-hydroxy-4-methylacetophenone, $C_9H_9O_2Cl$, obtained in a similar manner from *m*-tolyl chloroacetate in 50% yield, crystallises from petroleum in prisms, m. p. 101°, and the ω -chloro-2-hydroxy-3:5-dimethylacetophenone, $C_{10}H_{11}O_2Cl$, is not obtained so easily from the isomeric chloroacetylxylenol; it separates from petroleum in needles, m. p. 92°. Interaction of chloroacetyl chloride, phenol, and aluminium chloride does not lead to such

good results as when the reaction is carried out in the two stages, as more than one chloroacetyl radicle is introduced into the nucleus; thus 3:5-dichloroacetyl-*p*-cresol (annexed formula) is obtained along with the monochloroacetyl compound by heating *p*-cresol with excess of chloroacetyl chloride and aluminium chloride; it separates from glacial acetic acid in slender needles, m. p. 168°; its acetyl derivative has m. p. 117°.

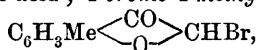
When these ω -chloro-*o*-hydroxymethylacetophenones are heated with alcoholic sodium acetate, the corresponding methylcoumaranones are obtained; the 4-methyl-, 5-methyl-, and 4:6-dimethyl-coumaranones have m. p.'s 54°, 85°, and 75° respectively, and are slightly yellow (Stoermer and Bartsch, Abstr., 1901, i, 94, only obtained these as oils). 6-Chloroacetyl-4-methyl-2-coumaranone,



separates from glacial acetic acid in slightly yellow crystals, m. p. 173°; its alkaline solution has a blood-red colour, and is easily oxidised.

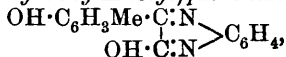
1-*p*-Nitrobenzylidene-4-methyl-2-coumaranone, $\text{C}_{16}\text{H}_{11}\text{O}_4\text{N}$, obtained by the condensation of aldehyde and coumaranone in the presence of alcoholic hydrogen chloride, crystallises in yellow needles, m. p. 208°; the corresponding *o*-nitrobenzylidene compound crystallises in red needles, m. p. 156°.

These methylcoumaranones are easily brominated in an acetic acid solution of hydrochloric acid; 1-bromo-4-methyl-2-coumaranone,



forms thick, red crystals, m. p. 86°; 1:1-dibromo-4-methyl-2-coumaranone, $\text{C}_9\text{H}_6\text{O}_2\text{Br}_2$, forms light yellow needles, m. p. 107°, and, on treatment with lead oxide, 2-hydroxy-5-methylbenzoylformic acid is obtained. 1:1-Dichloro-4-methyl-2-coumaranone, $\text{C}_9\text{H}_6\text{O}_2\text{Cl}_2$, crystallises in colourless leaflets, m. p. 62°. Bromomethylcoumaranone and silver acetate, when heated in glacial acetic acid, give 1-acetoxy-4-methyl-2-coumaranone, $\text{C}_{11}\text{H}_{10}\text{O}_4$, which forms long, yellow prisms, m. p. 74°. Experiments designed to remove the acetyl radicle by hydrolysis have so far been without the desired result.

1-Oximino-4-methylcoumaranone, $\text{C}_9\text{H}_7\text{O}_3\text{N}$, obtained from the methylcoumaranone and nitrous acid, crystallises from methyl alcohol in yellow leaflets, m. p. 187°, and when heated at 60° with hydrochloric acid it is converted into 6-hydroxy-*m*-toluoylformic acid, $\text{C}_9\text{H}_8\text{O}_4$, crystallising from petroleum in almost colourless needles, m. p. 105°. This acid behaves somewhat differently from its lower homologue, as on heating the dry acid, long, yellow prisms of probably 4-methyldiketocoumaran, $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CO}$, are produced in impure condition (compare Schad, Abstr., 1893, i, 279). The anil of 6-hydroxy-*m*-toluoylformic acid, $\text{C}_{15}\text{H}_{18}\text{O}_3\text{N}$, crystallises in yellow needles, m. p. 80°. Condensation of the hydroxytoluoylformic acid with *o*-phenylenediamine yields 2-hydroxy-3-(4'-hydroxy-*m*-tolyl)quinoxaline,



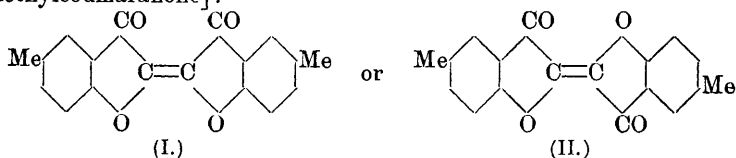
crystallising in yellow needles, m. p. above 300°.

By a similar series of experiments, the following derivatives of 5-methylcoumaranone have been prepared: 1-bromo-5-methylcoumaranone, $C_9H_7O_2Br$, forms light yellow crystals, m. p. 90° ; 1:1-dichloro-5-methylcoumaranone, $C_9H_6O_2Cl_2$, almost colourless crystals, m. p. 96° ; 1-oximino-5-methylcoumaranone, $C_9H_7O_3N$, slightly yellow leaflets, m. p. 185° (decomp.); 3-hydroxy-p-toluoylformic acid, $C_9H_8O_4$, colourless leaflets, m. p. 100° when free from water, otherwise 64° ; and 2-hydroxy-3-(3'-hydroxy-p-tolyl)quinoxaline, $C_{15}H_{12}O_2N_2$, yellow needles, m. p. above 300° .

The solutions of the two o-hydroxybenzoylformic acids in glacial acetic acid, benzene, or petroleum are intensely yellow, but their aqueous solutions are only slightly coloured. W. R.

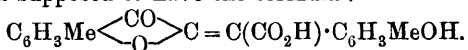
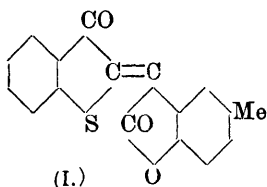
Oxygen Isologues of Homologous Indirubins. KARL FRIES and G. FINCK (*Ber.*, 1908, 41, 4284—4294).—Oxidation of the methylcoumaranones (preceding abstract) with hydrogen peroxide, potassium ferricyanide, etc., in alkaline solution takes place readily. The yellow or red, amorphous products so obtained could not, however, be prepared in a crystalline condition. Oxidation of 4-methylcoumaranone by air gives a yellow product, which, on recrystallisation, yields the compound, $C_{18}H_{14}O_4$. This compound is much more readily obtained by heating ω -chloro-2-hydroxy-5-methylacetophenone with a 5% sodium ethoxide solution for half an hour; it separates from benzene in small, yellow needles, m. p. 215° (decomp.). On heating in glacial acetic acid, it yields the compound $C_{18}H_{14}O_3$, which forms yellow leaflets, and an orange compound, $C_{18}H_{12}O_4$, the former being the less soluble. The constitution of the compounds $C_{18}H_{14}O_4$ and $C_{18}H_{14}O_3$ has not yet been elucidated, but the compound $C_{18}H_{12}O_4$ has also been obtained (1) by the condensation of 4-methylcoumaranone and 6-hydroxy-m-toluoylformic acid in the presence of sulphuric acid (the hydroxy-acid may be assumed to condense first to the lactone, 4-methyldiketocoumaran), (2) by heating an acetic acid solution of methylcoumaranone and dibromomethylcoumaranone, (3) by heating bromomethylcoumaranone in acetic acid.

These reactions, which do not occur in xylene solution, show that this compound, m. p. 264° , is a "bismethylcoumaranindigo" [bismethylcoumaranone]:

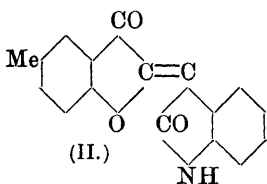


The question whether the compound was symmetrical or not was decided by condensing 4-methylcoumaranone with 5-methyldiketocoumaran and 5-methylcoumaranone with 4-methyldiketocoumaran. If the compound is an oxygen isologue of indigotin, then the two condensations should give rise to identical products, but it was found that two isomeric compounds, $C_{18}H_{12}O_4$, were obtained; this is held to prove that formula II is the correct one, and that the compound is "1:2'-bis-(4-methylcoumaran)indigo" [bis-4-methyl-

coumaranone], and therefore an oxygen isologue of indirubin. All the bismethylcoumaranones prepared are well-characterised, orange compounds, which sublime in a vacuum, and are stable towards cold alkalis. 1:2-*Bis-5-methylcoumaranone* has m. p. 279°; 4:5'-*dimethyl-1:2'-biscoumaranone*, m. p. 286°, and 5:4'-*dimethyl-1:2'-biscoumaranone*, m. p. 258°. These oxygen isologues of dimethylindirubin are quickly dissolved by alcoholic potassium hydroxide, and coloured, crystalline dipotassium salts are precipitated, hydrolysed by water, and, on acidification with acetic acid, a yellow, insoluble acid is precipitated, which is quickly reconverted into the dimethylcoumaranone; the acid is supposed to have the formula :



When hydroxythionaphthen, itself prepared by heating the carb-oxylic acid, is condensed with 6-hydroxy-*m*-toluoylformic acid, 1-*ketothionaphthenyl*-(2)-4-*methylcoumaranone*, formula I, is produced; it forms red needles, m. p. 257°, is very stable towards aqueous alkalis, and does not give a sparingly soluble salt with alcoholic potassium hydroxide. It sublimes in a vacuum, and may also be obtained by heating dibromohydroxythionaphthen and 4-methylcoumaranone in acetic acid in 60% yield.



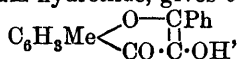
The condensation of isatin and 4-methylcoumaranone leads to the formation of (1)-4-*methylcoumaranonyl*-3-*indole*, formula II, which crystallises from glacial acetic acid in dark red needles, m. p. 286°, and contains acetic acid, which is only driven off at 200°. W. R.

Conversion of Benzylidenecoumaranones into Flavonols.

KARL AUWERS and KARL MÜLLER (*Ber.*, 1908, 41, 4233—4241).—The authors find that when dibromobenzylidene-4-methylcoumaranone is treated with 2 mols. of potassium hydroxide in hot alcoholic solution, 6-methylflavonol is obtained.

4-Methylcoumaran-2-one is best prepared by warming an alcoholic solution of *o*-chloroacetyl-*p*-cresol with a concentrated, aqueous solution of 1.5 equivs. of sodium hydroxide. It forms long, glistening, colourless needles, m. p. 51—52° (the substance is described by Stoermer and Bartsch as an oil: *Abstr.*, 1901, i, 94). The semicarbazone has m. p. 230—232°: Stoermer (private comm.), 230°, Stoermer and Bartsch, 181°; the oxime, m. p. 144—145°: Stoermer, 144—145°, Stoermer and Bartsch, 144°; the *o*-hydroxybenzylidene compound softens at 222°, m. p. 225—226°: Stoermer, 221—222°, Stoermer and Bartsch, 210°; the *p*-hydroxybenzylidene compound, m. p. 254—255°: Stoermer, 200°, Stoermer and Bartsch, 163°. The *benzylidene* derivative forms pale yellow prisms, m. p. 119°, and, on bromination, yields

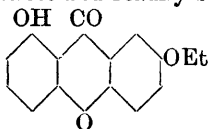
the *dibromo*-derivative, $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \diagup \text{O} \diagdown \\ \text{CO} \end{smallmatrix} \text{CBr} \cdot \text{CHBrPh}$, which crystallises in compact, broad pointed prisms, m. p. 158° (decomp.). This, on treatment with potassium hydroxide, gives 6-methylflavanol,



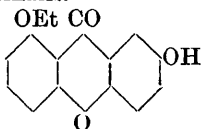
in compact, broad, pale yellow prisms, m. p. $196-197^\circ$; the *benzoate* forms glistening, colourless needles, m. p. $167-168^\circ$. 6-Methyl-

flavanone, $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \diagup \text{O} \diagdown \\ \text{CO} \cdot \text{CHPh} \\ \text{CH}_2 \end{smallmatrix}$, prepared by the action of sodium hydroxide on a mixture of *o*-acetyl-*p*-cresol and benzaldehyde, forms colourless leaflets, m. p. $106-107^\circ$: the *oxime* crystallises in small, yellow needles, m. p. $148-149^\circ$. By boiling with 10% sulphuric acid, the flavanone is converted into 6-methylflavanol. J. C. C.

The Two Isomeric Monoalkyl Ethers of Euxanthone. JOSEF HERZIG and K. KLIMOSCH (*Ber.*, 1908, 41, 3894-3897).—Of the two isomeric monoethyl ethers of euxanthone described by Herzig (*Abstr.*, 1891, 1349), one (I) is yellow and insoluble in alkalis, whilst the other (II) is colourless and readily soluble in alkalis.



(I.)

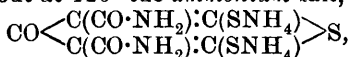


(II.)

It is now found that the colourless ether dissolves in dilute alkalis with an intense yellow colour, and a *potassium* salt has been isolated. With alkyl iodides or methyl sulphate, this gives a white dialkyl ether, and with carbon dioxide the white monoethyl ether is regenerated. The latter also gives intensely yellow solutions with acids, and the *hydrochloride* forms orange-yellow needles which readily lose hydrogen chloride. The *stannichloride* also forms yellow needles. The yellow ether (I) does not combine with acids. J. C. C.

Action of Carbon Disulphide and Potassium Hydroxide on Ketones. III. HERMANN APITZSCH [with R. BLEZINGER] (*Ber.*, 1908, 41, 4028-4039. Compare *Abstr.*, 1904, i, 510; 1905, i, 810).—Ethyl acetonedicarboxylate reacts with carbon disulphide and potassium hydroxide, yielding the dipotassium salt of *ethyl 2:6-dithiol-thiopyrone-3:5-dicarboxylate* [*2:6-dithiol-4-ketopenthiophen-3:5-dicarboxylate*], $\text{CO} \begin{smallmatrix} \diagup \text{C}(\text{CO}_2\text{Et}) \cdot \text{C}(\text{SH}) \\ \diagdown \text{C}(\text{CO}_2\text{Et}) \cdot \text{C}(\text{SH}) \end{smallmatrix} \text{S}$; the free ester, obtained by treating the potassium salt with dilute sulphuric acid, crystallises from ethyl acetate or from a mixture of chloroform and light petroleum in golden-yellow plates, m. p. 130° , after sintering at about 118° . The *potassium* salt, $\text{C}_{11}\text{H}_{10}\text{O}_5\text{S}_3\text{K}_2 \cdot \text{EtOH}$, crystallises from a mixture of alcohol and ether in small, pale yellow, nodular masses, and the *silver* salt forms a yellow, curdy precipitate. The *diethyl ether*, $\text{C}_5\text{OS}(\text{CO}_2\text{Et})_2(\text{SEt})_2$,

crystallises from dilute alcohol in colourless needles, m. p. 47—49°; the *dimethyl ether*, $C_{13}H_{16}O_5S_3$, in similar needles, m. p. 82—83°. The *dibenzoyl* derivative, $C_5OS(CO_2Et)(S\cdot CPh)_2$, forms prismatic crystals, m. p. 128—129°. The *ammonium* salt, $C_5OS(CO_2Et)_2(SNH_4)_2$, forms yellow crystals, is readily soluble in water or alcohol, and readily loses ammonia when exposed to the air. When the ethyl ester of the dithiol is heated with aqueous ammonia for four hours at 100°, the *ammonium* salt, $CO<\begin{smallmatrix} C(CO_2Et)=C(SNH_4) \\ C(CONH_2):C(SNH_4) \end{smallmatrix}>S$, is obtained as pale yellow tetrahedra, but at 120° the *ammonium* salt,



is obtained as yellow, rhombohedral crystals. The corresponding *acid*, $C_7H_6O_3N_2S_3$, crystallises from glacial acetic acid in yellow crystals. When reduced, the dithiol yields *ethyl 4-ketotetrahydropenthiophen-3:5-dicarboxylate*, $CO<\begin{smallmatrix} CH(CO_2Et)\cdot CH_2 \\ CH(CO_2Et)\cdot CH_2 \end{smallmatrix}>S$; this crystallises from dilute methyl alcohol in colourless needles, m. p. 102—103°, which are insoluble in alkalis. When oxidised with nitric acid in acetic acid solution, the dithiol yields a termolecular *sulphide*, $C_{33}H_{32}O_{15}S_9$, which separates from ethyl acetate in colourless, rhombic crystals, m. p. 185° (compare Fromm and Baumhauer, Abstr., 1908, i, 703).

A *tetrapotassium* salt, $CO<\begin{smallmatrix} C(CO_2K):C(SK) \\ C(CO_2K):C(SK) \end{smallmatrix}>S$, is formed when the dithiol is hydrolysed with aqueous alcoholic potash under pressure. It forms a greenish-yellow, crystalline mass, and contains $6H_2O$. It has not been found possible to isolate the corresponding tetrabasic acid, but the *dimethyl ether*, $C_5OS(CO_2H)_2(SMe)_2$, obtained by the action of methyl iodide or methyl sulphate on the potassium salt, crystallises from nitrobenzene in yellow needles, m. p. 230° (decomp.). The corresponding *silver* salt, $C_5H_6O_5S_3Ag_2$, crystallises in colourless needles. The *diethyl ether*, $C_5OS(CO_2H)_2(SET)_2$, forms colourless crystals, m. p. 178—180°, and is much more readily soluble than the methyl ester.

When an aqueous solution of the tetrapotassium salt is mixed with acetic and hydrochloric acids, a precipitate of 2:6-dithiol-4-ketopenthiophen-3-carboxylic acid, $CO<\begin{smallmatrix} CH=C(SH) \\ C(CO_2H):C(SH) \end{smallmatrix}>S$, is obtained; it crystallises from benzene in yellow needles, m. p. 143° (decomp.). The *tripotassium* salt is extremely readily soluble in water or alcohol; the *diethyl ether*, $C_5HOS(CO_2H)(SET)_2$, forms colourless needles, m. p. 129—131°, and the *dimethyl ether*, $C_5H_5O_3S_3$, has m. p. 215—216°.

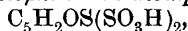
J. J. S.

Thio- γ -pyronedithiols [4-Ketopenthiophendithiols]. HERMANN APITZSCH and G. A. BAUER (*Ber.*, 1908, 41, 4039—4047).—The compound obtained by exposing 3:5-diphenylthiopyrone-2:6-dithiol (4-keto-3:5-diphenylpenthiophen-2:6-dithiol, Abstr., 1905, i, 810) to sunlight is shown to be a termolecular sulphide, formed by the oxidising action of the atmosphere on the dithiol. The same compound is formed when an acetic acid solution of the dithiol is treated with ferric chloride,

halogens, nitric acid, nitrous acid, or hydrogen peroxide. Similar sulphides are formed from ketomethyldimethylpenthiophendithiols (Abstr., 1904, i, 310), but have not been obtained pure. The alkali or alkali-earth salts of the dithiols are oxidised by hydrogen peroxide in neutral or alkaline aqueous solution to disulphonic or disulphinic acids. Fusion with potash transforms the sulphonic acid from ketodiphenylpenthiophendithiols into phenylacetic acid.

The *sulphide* from ketodiphenylpenthiophendithiol, $C_{51}H_{32}O_2S_9$, is deposited from a mixture of benzene and light petroleum in crystals, m. p. 284° , but when crystallised from chloroform or acetic acid has m. p. 278° . It is converted by alkalis, sodium thiosulphate, or hydriodic acid to the original dithiol.

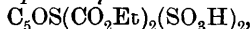
4-Keto-3 : 5-diphenylpenthiophen-2 : 6-disulphonic acid,



crystallises from its concentrated aqueous solution in colourless, hygroscopic needles, m. p. 261° . The *sodium* salt crystallises from a mixture of alcohol and ether with 2EtOH. The *barium* salt crystallises in needles with 2EtOH, or with 12H₂O in large, glistening prisms. The *silver* salt, $C_{17}H_{10}O_7S_3Ag_2$, crystallises from hot water in glistening rods. The *dimethyl* ester, $C_{19}H_{16}O_7S_3$, crystallises from warm acetone in colourless plates, m. p. $190-191^\circ$, and the *ethyl* ester has m. p. $173-174^\circ$.

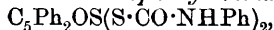
Sodium 4-keto-3-methylpenthiophen-2 : 6-disulphonate crystallises with 1EtOH, and the corresponding salt of the 3 : 5-dimethyl acid with 3H₂O.

3 : 5-Dicarbethoxy-4-ketopenthiophen-2 : 6-disulphonic acid,



obtained from ethyl 4-keto-2 : 6-dithiolpenthiophen-3 : 5-dicarboxylate (see preceding abstract), forms a *sodium* salt, $C_{11}H_{10}O_{11}S_3Na_2 \cdot H_2O$, which crystallises in colourless needles. When the barium salt of the dithiol is oxidised, *barium 3 : 5-dicarbethoxy-4-ketopenthiophen-2 : 6-disulphinate*, $C_{11}H_{10}O_9S_3Ba$, is obtained, unless an excess of barium carbonate and hydrogen peroxide is present, when the corresponding *sulphonate*, $C_{11}H_{10}O_{11}S_3Ba \cdot 2H_2O$, is formed.

When boiled with aniline, the diphenyl dithiol is decomposed, and yields diphenylcarbamide and malonanilide; when mixed with a benzene solution of phenylcarbimide, it yields the urethane, 4-keto-3 : 5-diphenylpenthiophen-2 : 6-dithiophenylurethane,

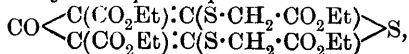


m. p. 135° (decomp.).

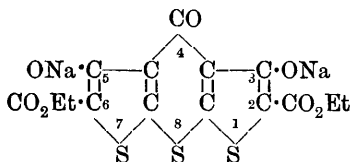
3 : 5-Dicarbethoxy-4-ketopenthiophen-2 : 6-dithiophenylurethane has m. p. 140° .

J. J. S.

Condensation of Esters of 4-Keto-2 : 6-dithiolpenthiophen-3 : 5-dicarboxylic Acid with Ethyl Chloroacetates. HERMANN APITZSCH (*Ber.*, 1908, 41, 4047—4052).—Ethyl chloroacetate readily reacts with a hot alcoholic solution of the sodium salt of ethyl 2 : 6-dithiol-4-ketopenthiophen-3 : 5-dicarboxylate (this vol., i, 46), yielding *ethyl 3 : 5-dicarbethoxy-4-ketopenthiophen-2 : 6-dithiolacetate*,



as a viscid, heavy oil, which reacts with aqueous or alcoholic sodium hydroxide, yielding the sodium derivative of *ethyl 3:5-dihydroxy-4-ketopenthiophendithiophen-2:6-dicarboxylate* (annexed constitution) as an amorphous, reddish-yellow powder. The free *dihydroxy*-compound, $C_{15}H_{12}O_7S_3$, crystallises from hot alcohol in pale yellow, strongly re-



fractive, rhombic plates, m. p. 242° , after sintering at 232° . The corresponding *diethyl ether*, $C_{19}H_{20}O_7S_3$, forms colourless needles, m. p. $217-218^\circ$; the *dibenzoate*, $C_{29}H_{20}O_9S_3$, sinters at 263° and melts at 267° .

When methyl chloroacetate is condensed with the dithiol, a certain amount of *methyl 3:5-dicarbethoxy-4-ketopenthiophen-2:6-dithiolacetate*, $C_{14}H_{10}O_7S_3$, is obtained. It forms slender, pale yellow needles, m. p. 245° , after sintering at 220° , and yields a *dibenzoate*, $C_{28}H_{18}O_9S_3$, m. p. 270.5° , after sintering at 267° . *Methyl 3:5-dihydroxy-4-ketopenthiophendithiophen-2:6-dicarboxylate*, $C_{13}H_8O_7S_3$, crystallises from ethylene dibromide or from much chloroform in straw-yellow needles, m. p. 294° . Its *dibenzoate*, $C_{27}H_{16}O_9S_3$, has m. p. $297-298^\circ$.

The corresponding *diamyl ester*, $C_9OS_3(OH)_2(CO_2C_5H_{11})_2$, has m. p. 182° , and yields a *dibenzoate*, $C_{35}H_{32}O_9S_3$, m. p. $202-203^\circ$. J. J. S.

Double Fluorides of Titanium. JOHN A. SCHAEFFER (*J. Amer. Chem. Soc.*, 1908, 30, 1862—1865).—The following double fluorides of titanium with alkaloids have been prepared in the hope of discovering an improved method for separating titanium from columbium and tantalum. *Quinine titanium fluoride*, $C_{20}H_{24}O_2N_2 \cdot 2H_2TiF_6 \cdot H_2O$; the *strychnine salt*, $2C_{21}H_{22}O_2N_2 \cdot H_2TiF_6 \cdot 3H_2O$; the *quinidine salt*, $2C_{20}H_{24}O_2N_2 \cdot H_2TiF_6 \cdot 4H_2O$; the *brucine salt*,

$4C_{23}H_{26}O_4N_2 \cdot 2H_2TiF_6 \cdot 13H_2O$; the *cinchonidine salt*, $C_{19}H_{22}ON_2 \cdot H_2TiF_6 \cdot 2H_2O$; the *narcotine salt*, $2C_{22}H_{23}O_7N \cdot H_2TiF_6 \cdot 3H_2O$; the *cinchonine salt*, $C_{19}H_{22}ON_2 \cdot H_2TiF_6$; the *narceine salt*, $3C_{23}H_{27}O_8N \cdot H_2TiF_6 \cdot 5H_2O$; the *morphine salt*, $4C_{17}H_{19}O_3N \cdot 2H_2TiF_6 \cdot 5H_2O$; the *codeine salt*,

$8C_{18}H_{21}O_3N \cdot 4H_2TiF_6 \cdot 3H_2O$; the *papaverine salt*, $8C_{20}H_{21}O_4N \cdot 4H_2TiF_6 \cdot 3H_2O$; and the *apomorphine salt*, $2C_{17}H_{17}O_2N \cdot H_2TiF_6 \cdot 4H_2O$.

Aniline titanium fluoride, $2C_6H_5 \cdot NH_2 \cdot H_2TiF_6 \cdot H_2O$, forms pink needles. E. G.

Isomerism of Ephedrine and ψ -Ephedrine. JOHANNES GADAMER (*Arch. Pharm.*, 1908, 246, 566—574).—Emde's representa-

tion of ephedrine and ψ -ephedrine by the formulæ: $Me \cdot \overset{OH}{\underset{H}{C}} - \overset{HNMe}{\underset{H}{C}} \cdot Ph$

and $Me \cdot \overset{OH}{\underset{H}{C}} - \overset{H}{\underset{HNMe}{C}} \cdot Ph$ respectively is accepted, but his explanation of

the reversible conversion of the one isomeride into the other by the

action of hot hydrochloric acid, as due to racemisation in the right-hand half of the molecule as represented by the above formulæ, is inadmissible (Abstr., 1908, i, 203). The chief grounds for this opinion are: (1) that taking account of the relative weights of the atoms and atomic complexes concerned, and assuming racemisation to occur in the right-hand portion of the molecule only, ephedrine would be dextrorotatory instead of levorotatory, as it actually is; (2) Emde's explanation would imply that by adding a further complex to the right-hand portion of the molecule, the dextrorotation of ψ -ephedrine should be increased, but ψ -ephedrylphenylthiocarbamide, although still dextrorotatory, has a lower rotation than either ψ -ephedrine or its hydrochloride. These difficulties disappear if racemisation is assumed to occur in the left-hand portion of the molecule, as represented above.

Ephedrylphenylthiocarbamide, m. p. 115° (decomp.), $[\alpha]_D^{20} - 105.1^{\circ}$ in alcohol, crystallises from alcohol in rosettes of prisms. *ψ -Ephedrylphenylthiocarbamide*, m. p. 122° , $[\alpha]_D^{20} + 22.8^{\circ}$ in alcohol, crystallises from alcohol in transparent, rectangular tablets. T. A. H.

apoMorphine Hydrochloride. ERNST SCHMIDT and R. GAZE (*Chem. Zentr.*, 1908, ii, 1187; from *Apoth. Zeit.*, 1908, 23, 657—658).—The authors find that this substance when dried in a desiccator or at 100° contains 3.61—3.95% of water, and is not anhydrous, as stated by Matthiesen and Wright (*Annalen, Sup.* 7, 172). The amount of water found present is in close agreement with both of the following formulæ: $2(C_{17}H_{17}O_2N, HCl), H_2O$ or $C_{17}H_{17}O_2N, HCl, H_2O$.

Anhydrous *apomorphine* hydrochloride darkens in colour when heated above 200° , and does not melt below 250° . As characteristic of this substance, it is stated that one drop of ferric chloride solution (1:10) gives a blue coloration to 10 c.c. of an aqueous solution of the hydrochloride (1:10,000). Further, that 10 c.c. of this *apomorphine* hydrochloride solution with 1 c.c. chloroform, rendered alkaline by sodium hydroxide, and shaken with air, gives a reddish-violet colour to the aqueous portion, and a blue colour to the chloroform portion, of the mixture. J. V. E.

Morpholones. ERNEST FOURNEAU (*Bull. Soc. chim.*, 1908, [iv], 3, 1141—1145).—The publication by Wolfenstein with Mamlock (Abstr., 1908, i, 281), and with Rolle (*ibid.*, 282) of the results obtained in condensing haloid acid chlorides with tropine has led the author to give an account of the different results he has obtained in condensing α -halogenated acid chlorides with $\alpha\beta$ -amino-alcohols.

Dimethylaminodimethylethylcarbinol (Süsskind, Abstr., 1906, i, 133) condenses, when warmed during two hours at 100° , with ethyl phenylbromoacetate to form *phenylmethylethylmorpholonedimethylammonium bromide*,

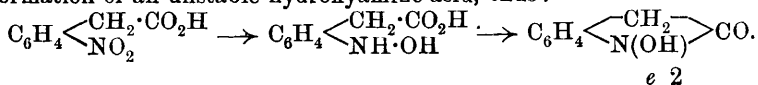
$$\begin{array}{c} \text{CH}_2 \cdot \text{NMe}_2 \text{Br} \cdot \text{CHPh} \\ | \qquad \qquad \qquad | \\ \text{CMeEt} \text{---} \text{O} \text{---} \text{CO} \end{array}$$
 , m. p. 195° , which crystallises from alcohol, is soluble in water, but nearly insoluble in acetone, and has a very bitter taste. With moist silver hydroxide, it furnishes the corresponding substituted *ammonium hydroxide*, m. p. 163° , which

is crystalline and very bitter, readily soluble in water or chloroform, and is neutral to litmus. On heating, both the bromide and the hydroxide, the former with the loss of methyl bromide, and the latter with the loss of methyl alcohol, form the corresponding *tertiary* base, $\text{CH}_2 \cdot \text{NMe} \cdot \text{CHPh}$
 $\text{CMeEt} \cdot \text{O} \cdot \text{CO}$, m. p. about 650° (?), b. p. $187^\circ/12$ mm. or $210^\circ/33$ mm., which crystallises from light petroleum and furnishes a *picrate*, m. p. 138° , and an *aurichloride*, m. p. about 98° . With boiling baryta water, the base yields the corresponding *hydroxyamino-acid*, $\text{OH} \cdot \text{CEtMe} \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{CHPh} \cdot \text{CO}_2\text{H}$. T. A. H.

Surinamine. H. BLAU (*Zeitsch. physiol. Chem.*, 1908, 58, 153—155. Compare Hiller-Bombien, *Abstr.*, 1893, i, 182).—The base forms colourless, glistening needles, begins to decompose at 233° , and is completely molten at 246° . When subjected to dry distillation, it yields a sublimate, from which a *platinichloride*, (Pt, 27.5%), m. p. 205° , was obtained. When fused with potash, the base yields *p*-hydroxybenzoic acid. J. J. S.

Synthesis of Tertiary Pyridylalkines [Pyridyldialkylcarbinols] and their Derivatives. WLADISLAW SOBECKI (*Ber.*, 1908, 41, 4103—4110).—The interaction of magnesium methyl iodide ($3\frac{1}{2}$ mols.) and ethyl picolinate in dry ether leads to the formation of *dimethyl- α -pyridylalkine* [2-pyridyldimethylcarbinol], $\text{C}_5\text{NH}_4 \cdot \text{CMe}_2 \cdot \text{OH}$, m. p. $50-51^\circ$, b. p. $204-205^\circ$ (corr.) or $83.5-84^\circ/10$ mm.; the *platinichloride*, *aurichloride*, and *picrate* have m. p. 178° , $117-118^\circ$, and $100-101^\circ$ respectively. Similarly, magnesium ethyl bromide and ethyl nicotinate yield 3-pyridyldiethylcarbinol, $\text{C}_5\text{NH}_4 \cdot \text{CEt}_2 \cdot \text{OH}$, b. p. $152-155^\circ/24$ mm., which forms a *platinichloride*, which decomposes at 199° , an *aurichloride*, m. p. 108° , and a *picrate*, m. p. $112-113^\circ$. The reduction of 2-pyridyldimethylcarbinol by sodium and alcohol yields *isopropylpiperidine* and 2-pyridyldimethylcarbinol, $\text{C}_5\text{NH}_{10} \cdot \text{CMe}_2 \cdot \text{OH}$, b. p. $209-210^\circ$ (corr.) or $92.5-93^\circ/12$ mm., D_4^{20} 0.9787, which forms a *picrate*, m. p. 139° , *aurichloride*, m. p. $128-129^\circ$, and a *platinichloride*, which decomposes at 185° . When heated with phosphoric oxide, 2-piperidyldimethylcarbinol loses water in two ways, yielding *isopropyl- Δ^2 -piperidine*, identical with Ladenburg's compound (*Abstr.*, 1887, 740), and *α -methovinylpiperidine*, $\text{C}_5\text{NH}_{10} \cdot \text{CMe} \cdot \text{CH}_2$, which are separated by means of their picrates. Methovinylpiperidine forms a *hydrochloride*, $\text{C}_8\text{H}_{15}\text{N} \cdot \text{HCl}$, m. p. 193° , a *platinichloride*, decomposing at $175-176^\circ$, and is resolved by *d*-tartaric acid, the regenerated bases, slightly diluted with ether, showing a 1.4° in a 3 cm. tube and -0.9° in a 5 cm. tube respectively. C. S.

***N*-Hydroxyindole Derivatives from *o*-Nitrophenylacetic Acid.** ARNOLD REISSERT (*Ber.*, 1908, 41, 3921—3931).—When *o*-nitrophenylacetic acid is reduced with zinc dust and dilute sulphuric acid at $28-34^\circ$, 1:2-dioxindole is obtained with the probable intermediate formation of an unstable hydroxyamino-acid, thus:

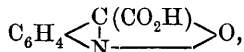


When the reduction is effected in neutral solution with the addition of ammonium chloride, there is also formed *o*-azoxyphenylacetic acid, $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, in yellow needles, m. p. 250—251° (decomp.). The reduction in acid solution may be carried out with a solution of *o*-nitrophenylacetic acid, prepared by oxidising *o*-nitrophenylpyruvic acid with hydrogen peroxide; a small amount of oxindole (m. p. 126°, not 120° as given in the literature) is also formed.

1:2-Dioxindole crystallises from water in small, hard, colourless rhombs; when a drop of ferric chloride is added to its cold aqueous solution, a characteristic blue coloration is produced.

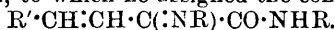
1-Methoxyoxindole, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2 \\ \text{N(OMe)} \end{smallmatrix}\rangle\text{CO}$, prepared by treating dioxindole with methyl sulphate, forms slender, colourless rods or feathery crystals, m. p. 88·5°. 1-Acetoxoxindole crystallises in colourless needles, m. p. 101°.

1-Benzoyloxyoxindole forms small, pale red crystals, m. p. 124—125°. 1-Hydroxyisatoxime, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{C(N}\cdot\text{OH)} \\ \text{N(OH)} \end{smallmatrix}\rangle\text{CO}$, prepared by boiling dioxindole with aqueous sodium nitrite, forms small, yellow needles, m. p. 223° (decomp.) with previous sintering; the sodium salt is described. 1-Methoxyisatoxime, prepared by treating methoxyoxindole with nitrous acid and subsequently adding sodium hydroxide, crystallises in small, yellow needles, m. p. 172°. 1-Hydroxyisatin, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{N(OH)} \end{smallmatrix}\rangle\text{CO}$, is formed in small amount (recognised by the preparation of the phenylhydrazone) when hydroxyisatoxime is reduced with zinc and ammonia and subsequently oxidised with ferric chloride; the chief product of the reaction is anthroxanic acid,

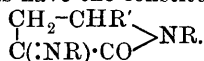


m. p. 196° (decomp.), which is also formed by boiling the oxime with dilute hydrochloric acid. J. C. C.

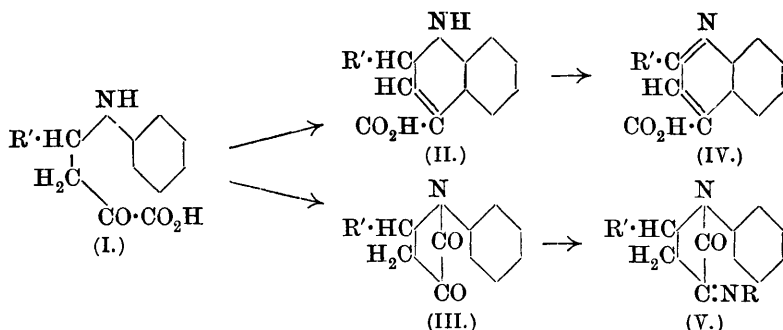
Synthesis of α -Substituted Cinchonic Acids by Doebner's Method. WALTHER BORSCHKE (*Ber.*, 1908, 41, 3884—3894).—By the interaction of a primary, aromatic amine containing a free ortho-position, pyruvic acid, and an aldehyde, Doebner (*Abstr.*, 1888, 299) found that, in addition to an α -substituted dihydrocinchonic acid, compounds were formed, to which he assigned the constitution



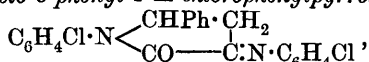
From experiments on phenylpyruvic acid, however, the author finds that these compounds have the constitution



The first stage of the interaction consists in the formation of a γ -anilino- α -ketonic acid (I), which loses water in two ways, giving the compounds (II) and (III). The former then loses hydrogen, yielding the cinchonic acid (IV), and the latter condenses with a second mol. of the base to form the anil (V).

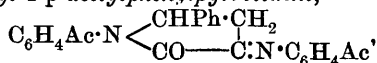


2-Phenyl-7-methylcinchononic acid, $C_9NH_4MePh \cdot CO_2H$, prepared by condensing benzaldehyde, *m*-toluidine, and pyruvic acid in alcoholic solution, forms a white, crystalline powder, m. p. 212—214°. *7-Hydroxy-2-phenylcinchononic acid*, $C_9NH_4Ph(OH) \cdot CO_2H$, similarly prepared from *m*-aminophenol, crystallises from hot dilute hydrochloric acid as a yellow, crystalline powder, m. p. 333—334°; carbon dioxide is lost at the m. p., with the formation of *7-hydroxy-2-phenylquinoline*, which crystallises in pale yellow needles, m. p. 229—230°. *7-Chloro-2-phenylcinchononic acid*, $C_9NH_4ClPh \cdot CO_2H$, prepared from *m*-chloroaniline, best in glacial acetic acid solution, forms colourless needles, m. p. 244—246° (decomp.); in the same reaction there is also formed *3-m-chloroanilo-2-keto-5-phenyl-1-m-chlorophenylpyrrolidine*,



crystallising in small, colourless needles, m. p. 199—200°. Similarly, by the use of *p*-chloroaniline, there is obtained a mixture of *6-chloro-2-phenylcinchononic acid*, white, crystalline grains, darkening at 225°, m. p. 243°, and *3-p-chloroanilo-2-keto-5-phenyl-1-p-chlorophenylpyrrolidine*, colourless needles, m. p. 203—204°.

When *p*-aminoacetophenone is condensed with benzaldehyde and pyruvic acid in alcoholic solution, there is formed *3-p-acetylanilo-2:3-diketo-5-phenyl-1-p-acetylphenylpyrrolidine*,



small, colourless needles, m. p. 238—239°. By carrying out the reaction in glacial acetic acid solution, *7-acetyl-2-phenylcinchononic acid* is formed in small, colourless needles, m. p. 200°.

o-Nitroaniline does not condense with pyruvic acid and either benzaldehyde or *m*-nitrobenzaldehyde.

The interaction of benzaldehyde, pyruvic acid, and *m*-nitroaniline leads to the formation of *3-m-nitroanilo-2-keto-5-phenyl-1-m-nitrophenylpyrrolidine*, $NO_2 \cdot C_6H_4 \cdot N \begin{cases} CHPh \cdot CH_2 \\ CO - C : N \cdot C_6H_4 \cdot NO_2 \end{cases}$, yellow needles,

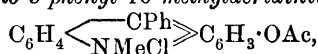
m. p. 212° (decomp.), and when *p*-nitroaniline is used in alcoholic solution, *2:3-diketo-5-phenyl-1-p-nitrophenylpyrrolidine*, yellow needles, m. p. 188—189°, is obtained. The *3-p-nitroanilo*-derivative is formed

in glacial acetic or formic acid solution; it crystallises in small, yellow, glistening needles, m. p. 220—221° (decomp.). J. C. C.

Derivatives of 5-Phenylacridine. FRIEDRICH KEHRMANN and A. STÉPANOFF (*Ber.*, 1908, 41, 4133—4141).—The object of the present investigation is to obtain in the acridine series the analogues of the rosindones, prasindones, etc.

Hess and Bernthsen's method for the preparation of 3-amino-5-phenylacridine (Abstr., 1885, 800) has been improved by the use of the benzoyl derivative of *p*-aminodiphenylamine instead of the base itself. The interaction of *p*-benzoylamino-diphenylamine, benzoic acid, and anhydrous zinc chloride for twelve hours at 215—220° leads to the production of 3-amino-5-phenylacridine, m. p. 204°, its benzoyl derivative (compare Ullmann and Ernst, Abstr., 1906, i, 205), 3-hydroxy-5-phenylacridine (Hess and Bernthsen, *loc. cit.*), and a substance, $C_{38}H_{26}N_4$, m. p. 308°, which is possibly diaminodiphenyl-diacyridine.

3-Acetyl-amino-5-phenylacridine, dissolved in nitrobenzene, is treated with methyl sulphate at 150°, and the precipitate, obtained by the addition of ether to the cooled solution, is dissolved in luke-warm water; by the addition of concentrated hydrochloric acid or sodium chloride, 3-acetyl-amino-5-phenyl-10-methylacridinium chloride,



is obtained, which forms orange-yellow crystals, and gives a yellow, fluorescent aqueous solution. The *platinichloride*, $(C_{22}H_{19}ON_2)_2PtCl_6$, forms golden-yellow, slender crystals. When a solution of the chloride is partly evaporated with hydrochloric acid, neutralised with ammonium carbonate, and treated with solid sodium nitrate, 3-amino-5-phenyl-10-methylacridinium nitrate, $C_{20}H_{17}N_2 \cdot NO_3$, is obtained, which crystallises in reddish-black needles, and forms a blood-red, non-fluorescent solution in water and alcohol; the *platinichloride*, $(C_{20}H_{17}N_2)_2PtCl_6$, is a dark red, crystalline powder. 3-Acetyloxy-5-phenyl-10-methylacridinium *platinichloride*, $(C_{22}H_{18}O_2N)_2PtCl_6$, is a citron-yellow, crystalline powder, obtained in a similar manner to the acetyl-amino-salt. 3-Hydroxy-5-phenyl-10-methylacridinium chloride crystallises in long, golden-yellow needles, and, in not too dilute aqueous solution, yields with sodium carbonate or ammonium hydroxide the *base*, $C_6H_4 \begin{array}{c} \text{CPh} \\ \diagup \quad \diagdown \\ \text{NMe(OH)} \end{array} > C_6H_3 \cdot OH$, which crystallises in reddish-black needles, and loses $1H_2O$ at 120°. It is doubtful whether the resulting anhydride is analogous to the prasindones, since the prasindone hydrates of the azonium series do not anhydride by heating (Abstr., 1908, i, 297). C. S.

Dianthraquinonylphenylenediamine. IV. EDUARD LAUBÉ and C. KÖNIG (*Ber.*, 1908, 41, 3874—3879).—Further derivatives of *p*-phenylenebis-1-aminoanthraquinone have been prepared, and the investigation extended to the corresponding *o*-phenylene compounds (compare Laubé, Abstr., 1907, i, 941).

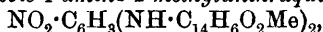
1-*p*-Nitroanilino-2-hydroxyanthraquinone, $C_{20}H_{12}O_5N_2$, prepared by boiling together 1-chloro-2-hydroxyanthraquinone, *p*-nitroaniline, potass-

ium carbonate, and copper acetate in nitrobenzene, is a dark brown powder, m. p. 342° (corr.). It is reduced by an aqueous solution of sodium sulphide to 1-*p*-aminoanilino-2-hydroxyanthraquinone, $C_{20}H_{14}O_8N_2$, a black powder with a high m. p. The latter compound condenses with 1-chloro-2-hydroxyanthraquinone when the two substances are boiled with copper powder in nitrobenzene, forming *p*-phenylenebis-1-amino-2-hydroxyanthraquinone, $C_6H_4(NH \cdot C_{14}H_6O_2 \cdot OH)_2$, a brownish-black powder, m. p. above 360° .

The following compounds are obtained by similar methods: 1-*p*-Bromoanilino-2-methylantraquinone, $C_{21}H_{15}O_2NBr$, crystallises in small, scarlet needles, m. p. 190° (corr.). *p*-Phenylenebis-1-amino-2-methylantraquinone, $C_{36}H_{24}O_4N_2$, is a black powder, giving a violet mark on porcelain, and has a high m. p.

1-*o*-Chloro-*p*-nitroanilino-2-methylantraquinone, $C_{21}H_{13}O_4N_2Cl$, crystallises in glistening, coppery leaflets, m. p. $272-273^{\circ}$ (corr.).

p-Nitro-*o*-phenylenebis-1-amino-2-methylantraquinone,



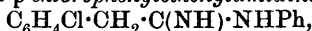
is a brownish-black powder with a high m. p.

1-*o*-Acetylaminonaphthylaminoanthraquinone, $C_{26}H_{18}O_8N_2$, prepared from 1-aminoanthraquinone and 2-chloro-1-acetylaminonaphthalene, is a brown powder with a high m. p. It yields, on hydrolysis, 1-*o*-aminonaphthylaminoanthraquinone (1-anthraquinonyl-*o*-naphthylenediamine), a black powder which condenses with 1-chloroanthraquinone, forming *o*-naphthylenebis-1-aminoanthraquinone, $C_{10}H_6(NH \cdot C_{14}H_7O_2)_2$, a brownish-black powder, m. p. 350° .
W. H. G.

Amidines. LXXXVIII. REINHOLD VON WALTHER and A. GROSSMANN (*J. pr. Chem.*, 1908, [ii], 78, 478—496).—A further contribution to the chemistry of the amidines.

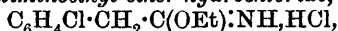
Phenylacetoneitrile readily interacts with aniline, but not with the chloroanilines, although the latter readily form amidines with benzonitrile. Similarly, *p*-chlorophenylacetoneitrile does not combine readily with aniline.

p-Chlorophenylacetoneitrile, when heated with aniline hydrochloride at 180° , yields *phenyl-p*-chlorophenylethenylamidine,



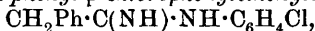
which crystallises in glistening leaflets, m. p. $153-154^{\circ}$; it may also be prepared (1) by the action of aniline on the imino-chloride obtained by treating *p*-chlorophenylacetamide with phosphorus pentachloride; (2) by treating a solution of *p*-chlorophenylacetoneitrile (2 mols.) and aniline (1 mol.) in benzene with sodium (2 mols.); the hydrochloride has m. p. $213-214^{\circ}$; the sulphate forms small needles, m. p. 185° ; the platinichloride, $C_{28}H_{26}N_4Cl_2 \cdot H_2PtCl_6$, crystallises in small, orange prisms, m. p. 185° (decomp.).

p-Chlorophenylacetiminoethyl ether hydrochloride,



obtained by the action of hydrogen chloride on an alcoholic solution of *p*-chlorophenylacetoneitrile, crystallises in small, slender needles, m. p. $170-173^{\circ}$; it is converted by aniline at 35° into *diphenyl-p*-chlorophenylethenylamidine, $C_6H_4Cl \cdot CH_2 \cdot C(NPh) \cdot NHPh$, small, slender needles, m. p. $97-98^{\circ}$.

Phenylacetonitrile and *p*-chloroaniline, when heated together, yield *ω*-phenyl-*p*-chloroacetanilide, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$, glistening needles, m. p. 163—164°, and phenyl-*p*-chlorophenylethenylamidine,



white needles, m. p. 112—113°; the hydrochloride of the latter crystallises in prisms, m. p. 106—108°. The following amidines were prepared by similar methods.

Phenyl-*m*-chlorophenylethenylamidine, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$, crystallises in needles, m. p. 91—93°; the hydrochloride forms glistening needles, decomposing at 205—220°; the sulphate forms rectangular plates, m. p. 179—181°; the nitrate forms needles, m. p. 108—109°.

m-Chlorophenylbenzenylamidine, $\text{NH}\cdot\text{CPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$, crystallises in prisms and needles, m. p. 115—116°; the hydrochloride crystallises with H_2O , and has m. p. 95°; the anhydrous salt has m. p. 186—189°; the picrate has m. p. 134—135°; the platinichloride has m. p. about 195° (decomp.). The hydrochloride is converted by water under pressure at 170° into benzoyl *m*-chloroaniline. The dibenzoyl derivative, $\text{NBz}\cdot\text{CPh}\cdot\text{NBz}\cdot\text{C}_6\text{H}_4\text{Cl}$, has m. p. 139°; the phenylcarbamide derivative, $\text{NHPh}\cdot\text{CO}\cdot\text{N}\cdot\text{CPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$, is obtained by acting on the amidine with phenylcarbimide, and crystallises in small prisms, m. p. 172—173°; the phenylthiocarbamide derivative, $\text{NHPh}\cdot\text{CS}\cdot\text{N}\cdot\text{CPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$, obtained in a similar manner, crystallises in rhombohedra, m. p. 131—132°. The amidine is converted by hydroxylamine hydrochloride into *m*-chlorophenylbenzenylamino-oxime, $\text{CPh}\cdot\text{C}(\text{NOH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$, which crystallises in rectangular plates, m. p. 85—87°. Phenylhydrazine converts the amidine hydrochloride into the hydrazidine, $\text{NHPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$, pale yellow needles, m. p. 127—128°, the picrate of which has m. p. 155—156° (decomp.). The amidine reacts with picryl chloride, yielding *m*-chlorophenyltrinitrophenylbenzenylamidine, $\text{NH}\cdot\text{CPh}\cdot\text{N}(\text{C}_6\text{H}_4\text{Cl})\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, which crystallises in yellow octahedra, m. p. 148° (decomp.).

The following compounds were prepared by the same methods as the corresponding meta-derivatives.

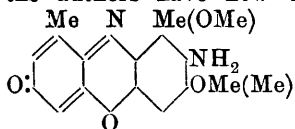
o-Chlorophenylbenzenylamidine, $\text{C}_{13}\text{H}_{11}\text{N}_2\text{Cl}$, crystallises in needles, m. p. 114—115°; the hydrochloride forms white crystals, m. p. 205—206°; the platinichloride crystallises in dark yellow needles, m. p. 200—202° (decomp.); the picrate has m. p. 193—194°; the dibenzoyl derivative, $\text{C}_{27}\text{H}_{19}\text{O}_2\text{N}_2\text{Cl}$, forms needles, m. p. 146—147°; the phenylcarbamide derivative, $\text{C}_{20}\text{H}_{16}\text{ON}_2\text{Cl}$, crystallises in glistening leaflets, m. p. 177—178°; the phenylthiocarbamide derivative, $\text{C}_{20}\text{H}_{16}\text{N}_2\text{SCl}$, forms yellow needles, m. p. 123—125°. *o*-Chlorophenylbenzenylamino-oxime, $\text{C}_{13}\text{H}_{11}\text{ON}_2\text{Cl}$, crystallises with $\text{Et}\cdot\text{OH}$ in slender needles or prisms, m. p. 163—164°. *o*-Chlorophenylbenzenylphenylhydrazidine, $\text{C}_{19}\text{H}_{16}\text{N}_3\text{Cl}$, crystallises in groups of yellow needles, m. p. 93—95°. *o*-Chlorophenyltrinitrophenylbenzenylamidine, $\text{C}_{19}\text{H}_{12}\text{O}_6\text{N}_5\text{Cl}$, forms yellow crystals, m. p. 146—148°.

W. H. G.

[Action of Amyl Nitrite on Phenyl-*m*-nitrobenzylidenehydrazine.] EUGEN BAMBERGER and WILHELM PEMSEL (*Ber.*, 1908, 41, 4246—4249. Compare *Abstr.*, 1903, i, 285).—Polemical. A reply to Minunni (*Abstr.*, 1904, i, 91).

J. J. S.

Orcinol Monomethyl Ether and an Oxidation Product of Amino-orcinol Monomethyl Ether (2-Amino-5-hydroxy-3-methoxytoluene). FERDINAND HENRICH and PAUL ROTERS (*Ber.*, 1908, 41, 4210—4214).—Henrich and Schierenberg have shown (*Abstr.*, 1905, i, 93) that 2-amino-3-hydroxy-5-methoxytoluene is oxidised in alkaline solution by air to a phenoxazine derivative, and the authors have now found that 2-amino-5-hydroxy-3-methoxytoluene, when oxidised under the same conditions, yields a phenoxazine derivative having the annexed formula.

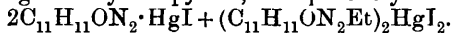


Orcinol monomethyl ether, previously obtained as an oil (Henrich and Nachtigall, *Abstr.*, 1903, i, 414), has now been prepared in the crystalline form, m. p. 63°, from the fraction b. p. 256—260°; on adding bromine to its solution in carbon disulphide, a *dibromo*-derivative is formed in white needles, m. p. 113°. 4-Amino-3(5)-methoxy-5(3):7-dimethylphenoxazone, $C_{15}H_{14}O_3N_2$, crystallises in red, slender, felted needles or right-angled or six-cornered tablets, m. p. 258—260°; the *dihydrochloride* forms golden leaflets, changing in the air to steel-blue crystals, and the *monoacetyl* derivative is a deep red powder, m. p. 256°.

J. C. C.

Compounds of Pyrazolones with Mercury Oxide. J. EURY (*Chem. Zentr.*, 1908, ii, 1037—1038; from *Bul. Sci. Pharmacol.*, 1908, 15, 384—394).—When a boiling alkaline solution of antipyrine is treated with a mercury salt, or with freshly-precipitated mercuric oxide, *mercury antipyrine*, $(C_{11}H_{11}ON_2)_2Hg \cdot H_2O$, crystallises from the liquid on cooling. This substance forms colourless, prismatic crystals, m. p. 180° (corr.), having neither taste nor smell, is optically active, and soluble in water at 15° to 0.42%, at 100° to 4.37%, in 10% salt solution at 15° to 1.26%, in cold 90% alcohol to 2.02%, and in boiling 90% alcohol to 43.48%. The aqueous solution of mercury antipyrine reacts weakly alkaline, and shows the characteristic reaction of antipyrine, but, with the exception of hydrogen sulphide, no usual test indicates the presence of mercury.

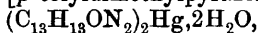
It is completely soluble in most acids, although hydrochloric and nitric acids produce a white precipitate which is soluble in excess of the acid. With the object of obtaining evidence as to the position of mercury in the molecule, it was treated with ethyl iodide in presence of chloroform, when there was produced a compound of the formula $C_{48}H_{54}O_4NI_4Hg_3$, which formed yellow crystals, m. p. 202°. Inasmuch as this substance when treated with hydrogen sulphide or potassium cyanide did not give ethylantipyrine, it is probably



Methyl and propyl iodides behave in a similar manner, giving respectively a pale yellow, crystalline compound, m. p. 186°, and yellow, needle-shaped crystals, m. p. 186°.

Methylphenylpyrazolone, dimethylaminoantipyrine, and diantipyrinemethane reduce freshly-precipitated mercuric oxide in boiling water, whereas tolylpyrine with mercuric oxide yields mercury

p-tolylldimethylpyrazole [*p*-tolylldimethylpyrazolone],



white crystals, m. p. 187°.

From this it appears that a free hydrogen atom in position 4 conditions the interaction of pyrazolones with mercuric oxide.

J. V. E.

1-Phenyl-4-alkyl-3:5-pyrazolidones and Antipyrines of the Malonic Acid Series. AUGUST MICHAELIS and KONRAD SCHENK (*Ber.*, 1908, 41, 3865—3873).—Several derivatives of 1-phenyl-3:5-pyrazolidone (3-hydroxy-1-phenyl-5-pyrazolone) containing an alkyl group in position 4 have been prepared by the method described previously (Abstr., 1907, i, 966). 1-Phenyl-4:4-dimethyl-3:5-pyrazolidone is converted by phosphoryl chloride under pressure at 150° into 3-chloro-1-phenyl-4:4-dimethyl-5-pyrazolone; that is, it reacts in a similar manner to 3-pyrazolone derivatives (compare Michaelis, Abstr., 1905, i, 377), and, like these, yields with methyl iodide an antipyrine-like compound, namely, 1-phenyl-2:4:4-trimethyl-

3:5-pyrazolidone (dimethylmalonylantipyrine), $\begin{array}{c} \text{NMe}\cdot\text{NPh} \\ \diagup \quad \diagdown \\ || > \text{O} \\ \text{C} - \text{CMe}_2 \end{array} \begin{array}{c} \diagdown \\ \diagup \\ \text{CO} \end{array}$ or

$\begin{array}{c} \text{NMe}\cdot\text{NPh} \\ | \\ \text{CO} - \text{CMe}_2 \end{array} \begin{array}{c} \diagdown \\ \diagup \\ \text{CO} \end{array}$. This substance was previously described by Michaelis

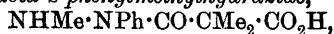
and Röhmer (Abstr., 1899, i, 233) as 3-methoxy-1-phenyl-4:4-dimethyl-5-pyrazolone, but, since it may also be prepared by the condensation of acetylphenylmethylhydrazine with dimethylmalonic acid in the presence of phosphorus trichloride, it follows that one of the methyl groups must be attached to nitrogen and not to oxygen; consequently, the chief argument in support of the view that 3:5-pyrazolidones are 3-hydroxypyrazolones becomes invalid, although 3:5-pyrazolidones undoubtedly behave in most cases as hydroxy-compounds. 1-Phenyl-2:4:4-trimethyl-3:5-pyrazolidone, unlike other antipyrines, is readily decomposed by aqueous sodium hydroxide, yielding a substance, m. p. 178°, which, originally described by Michaelis and Röhmer (*loc. cit.*), is now shown to be a *s*-phenylmethylhydrazide of dimethylmalonic acid. It also follows from this investigation that the substance, m. p. 70°, obtained by Michaelis and Röhmer by the action of phosphorus pentachloride on the pyrazolidone

is a 5-chloro-3-antipyrine, $\begin{array}{c} \text{NMe}\cdot\text{NPh} \\ \diagup \quad \diagdown \\ || > \text{O} \\ \text{C} - \text{CMe} \end{array} \begin{array}{c} \diagdown \\ \diagup \\ \text{CCl} \end{array}$, and the acid, m. p. 173°,

derived from the latter is the *s*-phenylmethylhydrazide of methylmalonic acid, $\text{NHMe}\cdot\text{NPh}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$.

3-Benzoyl-1-phenyl-4:4-dimethyl-3:5-pyrazolidone, $\text{C}_{18}\text{H}_{16}\text{O}_3\text{N}_2$, prepared by acting on the pyrazolidone in alkaline solution with benzoyl chloride, forms white crystals, m. p. 80°; the corresponding 3-benzene-sulphonyl derivative, $\text{C}_{17}\text{H}_{16}\text{O}_4\text{N}_2\text{S}$, prepared in a similar manner, crystallises in long needles, m. p. 99°.

Dimethylmalonic acid s-phenylmethylhydrazide,



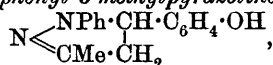
has m. p. 178° ; the *sodium* salt, $(2\text{H}_2\text{O})$, white leaflets, and *lead* salt, white precipitate, were prepared and analysed.

1-Phenyl-4-ethyl-3 : 5-pyrazolidone, $\begin{array}{c} \text{CHEt}\cdot\text{CO} \\ | \\ \text{CO}-\text{NH} \end{array} > \text{NPh}$, prepared by condensing ethyl malonate with acetylphenylhydrazine in the presence of phosphorus trichloride, forms white needles, m. p. 105° ; the *dibenzoyl* derivative, $\text{C}_{25}\text{H}_{20}\text{O}_4\text{N}_2$, crystallises in white prisms, m. p. 120° ; the *dibenzenesulphonyl* derivative, $\text{C}_{23}\text{H}_{20}\text{O}_6\text{N}_2\text{S}_2$, has m. p. 189° . 1-Phenyl-4-ethyl-3 : 5-pyrazolidone is converted by phosphoryl chloride into 3-chloro-1-phenyl-4-ethyl-5-pyrazolone, $\begin{array}{c} \text{CHEt}\cdot\text{CO} \\ | \\ \text{CCl}=\text{N} \end{array} > \text{NPh}$, large, colourless crystals, m. p. 130° , and 3 : 5-dichloro-1-phenyl-4-ethyl-pyrazole, $\begin{array}{c} \text{CEt}\cdot\text{CCl} \\ | \\ \text{CCl}=\text{N} \end{array} > \text{NPh}$, large, white crystals, m. p. 81° . 4-Benzene-azo-1-phenyl-4-ethyl-3 : 5-pyrazolidone, $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_4$, prepared by adding a solution of diazobenzene chloride to the pyrazolidone, crystallises in pale yellow leaflets, m. p. 188° .

1-Phenyl-2 : 4-dimethyl-4-ethyl-3 : 5-pyrazolidone (*methylethylmalonyl-antipyrine*), $\text{C}_{13}\text{H}_{16}\text{O}_2\text{N}_2$, formed by the action of methyl iodide on a solution of the phenylethylpyrazolidone in alcoholic potassium hydroxide, crystallises in colourless leaflets, m. p. 62° , and is converted by aqueous sodium hydroxide into *methylethylmalonic acid s-phenylmethylethylhydrazide*, $\text{C}_{13}\text{H}_{18}\text{O}_3\text{N}_2$, which forms white needles, m. p. 149° , and is reconverted by dehydrating agents into the antipyrine. W. H. G.

Transformation of Phenylhydrazones of Unsaturated Aldehydes and Ketones into Pyrazolines. KARL AUWERS and KARL MÜLLER (*Ber.*, 1908, 41, 4230—4233).—The transformation of hydrazones of unsaturated aldehydes and ketones, containing a double linking in the α -position, is readily effected by means of hot glacial acetic acid.

1-Phenyl-5-o-hydroxyphenyl-3-methylpyrazoline,

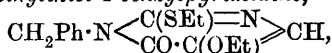


prepared by warming *o*-hydroxybenzylideneacetonephenylhydrazone (m. p. 154° : Harries, *Abstr.*, 1892, 169, gives $159-160^{\circ}$) with glacial acetic acid for half an hour, crystallises in small, compact cubes, m. p. $147-148^{\circ}$. The *O*-benzoate of the above hydrazone forms glistening, yellow needles, m. p. $118-119^{\circ}$, and when warmed with glacial acetic acid for some hours yields the *benzoate* of the corresponding pyrazoline derivative. This forms stellate clusters of yellow needles, m. p. 125° . 1 : 5-Diphenylpyrazoline (Laubmann, *Abstr.*, 1888, 726) is similarly obtained from cinnamaldehydephenylhydrazone; when the latter is heated with acetic anhydride, no transformation occurs, but the *acetate*, $\text{C}_{17}\text{H}_{16}\text{ON}_2$, is formed in white, silky needles or compact prisms, m. p. $149-150^{\circ}$. J. C. C.

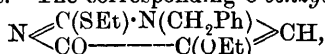
Pyrimidines. XXXIX. Syntheses of New Derivatives of 5-Hydroxyuracil (isoBarbituric Acid). TREAT B. JOHNSON and D. BREESE JONES (*Amer. Chem. J.*, 1908, 40, 538—547).—Johnson

and Clapp (Abstr., 1908, i, 931) have found that 1- and 3-alkyl derivatives of 2:6-dioxytetrahydropyrimidines can be distinguished by their behaviour towards diazobenzenesulphonic acid. This reagent has now been found of use for determining the structure of some 1- and 3-alkyl derivatives of isobarbituric acid.

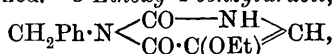
6-Oxy-5-ethoxy-2-ethylthiol-1-benzylpyrimidine,



m. p. 140—141°, obtained by the action of benzyl chloride on 6-oxy-5-ethoxy-2-ethylthiolpyrimidine in presence of potassium hydroxide, forms slender prisms. The corresponding 3-benzyl derivative,



m. p. 85—86°, produced in the same reaction, crystallises in prisms. When the 1-benzyl compound is hydrolysed with concentrated hydrochloric acid, a mixture of 5-ethoxy-1-benzyluracil and 5-hydroxy-1-benzyluracil is obtained. 5-Ethoxy-1-benzyluracil,



m. p. 150°, forms hexagonal prisms, and gives a brilliant red coloration with diazobenzenesulphonic acid in presence of sodium hydroxide. 5-Hydroxy-1-benzyluracil (1-benzylisobarbituric acid), m. p. 230° (decomp.), crystallises in clusters of radiating prisms, and gives the diazobenzenesulphonic acid reaction. When 6-oxy-5-ethoxy-2-ethylthiol-1-benzylpyrimidine is heated with concentrated hydrochloric acid in a sealed tube at 150—160° for three hours, 5-hydroxyuracil (isobarbituric acid), $\text{NH} \begin{array}{c} \text{CO} \text{-----} \text{NH} \\ \text{CO}\cdot\text{C}(\text{OH}) \end{array} \text{CH}$, is produced. 5-Ethoxy-3-

benzyluracil, $\text{NH} \begin{array}{c} \text{CO}\cdot\text{N}(\text{CH}_2\text{Ph}) \\ \text{CO} \text{-----} \text{C}(\text{OEt}) \end{array} \text{CH}$, m. p. 163—164°, crystallises in prisms or plates, and does not give a coloration with diazobenzenesulphonic acid. 5-Hydroxy-3-benzyluracil (3-benzylisobarbituric acid), m. p. 200—210°, forms irregular crystals.

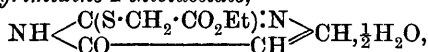
When 5-hydroxy-1-benzyluracil is treated with bromine water at 0°, 1-benzylisodialuric acid, $\text{CH}_2\text{Ph}\cdot\text{N} \begin{array}{c} \text{CO} \text{-----} \text{NH} \\ \text{CO}\cdot\text{C}(\text{OH}) \end{array} \text{C}\cdot\text{OH}$, m. p. 139° (decomp.), is produced, which forms prismatic crystals and gives a violet barium salt. E. G.

Pyrimidines. XL. Thio-derivatives of Uracil and the Preparation of Uracil in Quantity. HENRY L. WHEELER and LEONARD M. LIDDLE (*Amer. Chem. J.*, 1908, 40, 547—558).—In an earlier paper (Wheeler and Merriam, Abstr., 1903, i, 525) a method has been described for the preparation of uracil, depending on the condensation of ethyl sodioformylacetate with ψ -ethylthiocarbamide and the hydrolysis of the product. It is now found that larger yields can be obtained by using thiocarbamide instead of ψ -ethylthiocarbamide.

2-Thiouracil, $\text{NH} \begin{array}{c} \text{CS}\cdot\text{NH} \\ \text{CO}\cdot\text{CH} \end{array} \text{CH}$, m. p. 340° (decomp.), which is formed in this reaction, crystallises in prismatic plates, and is soluble

to the extent of 0.0598 gram in 100 parts of water at 17°. 6-Oxy-2-methylthiolpyrimidine and 6-oxy-2-ethylthiolpyrimidine dissolve to the extent of 0.6620 gram and 0.7930 gram respectively in 100 parts of water at 17°. 2-Thiouracil is a much stronger acid than uracil, and forms crystalline *sodium* and *potassium* salts; the *ammonium*, *mercuric*, and *copper* salts have also been prepared. When 2-thiouracil is boiled with an aqueous solution of chloroacetic acid, a nearly quantitative yield of uracil is obtained. A yield amounting to 66% of the calculated quantity was obtained in a similar manner from 6-thiouracil.

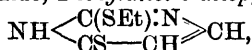
Ethyl 6-oxypyrimidine-2-thiolacetate,



m. p. 154—155°, prepared by the action of ethyl chloroacetate on 2-thiouracil, forms long, lustrous plates. The corresponding *acid*, m. p. 178°, crystallises in prisms with 1H₂O. By the action of sodium ethoxide and ethyl iodide on 2-thiouracil, 6-oxy-2-ethylthiolpyrimidine (Wheeler and Merriam, *loc cit.*) is produced. 6-Oxy-2-

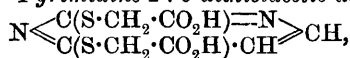
benzylthiolpyrimidine, $\text{NH} \begin{array}{c} \text{C}(\text{S} \cdot \text{CH}_2\text{Ph}) : \text{N} \\ \text{CO} \text{---} \text{CH} \end{array} \text{CH}$, m. p. 192—193°,

obtained by the action of benzyl chloride on 2-thiouracil in presence of potassium hydroxide, forms slender prisms, and is soluble in about 16 parts of hot alcohol and in 50 parts of cold; the *sodium* salt crystallises in plates. When 6-chloro-2-ethylthiolpyrimidine (Wheeler and Johnson, *Abstr.*, 1903, i, 526) is boiled with an alcoholic solution of potassium hydrosulphide, 2-ethylthiol-6-thiopyrimidine,



m. p. 149°, is obtained, which crystallises in prisms, and, when heated with concentrated hydrochloric acid, is converted into 6-thiouracil, $\text{NH} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \text{CS} \text{---} \text{CH} \end{array} \text{CH}$, m. p. 328° (decomp.), which forms light yellow needles.

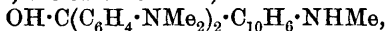
2 : 6-Dithiouracil, $\text{NH} \begin{array}{c} \text{CS} \cdot \text{NH} \\ \text{CS} \text{---} \text{CH} \end{array} \text{CH}$, obtained by heating 2 : 6-dichloropyrimidine with potassium hydrosulphide, forms bright yellow needles, and decomposes above 230°. This compound is also produced when 2-ethylthiol-6-thiopyrimidine is treated at 170° with dry hydrogen chloride. *Pyrimidine-2 : 6-dithiolacetic acid*,



obtained by the action of chloroacetic acid on 2 : 6-dithiouracil, forms a white, crystalline powder, and decomposes above 200°. E. G.

Colour Bases of Triphenylmethane Dyes. II. EMILIO NOELTING and K. PHILIPP (*Ber.*, 1908, 41, 3908—3911. Compare *Abstr.*, 1908, i, 295).—A continuation of former work. Pentamethyl-triaminodiphenylnaphthylcarbinol hydrochloride, when dissolved in hot water and acetic acid and treated with sodium hydroxide, yields the *imino*-base, $\text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 : \text{C}_{10}\text{H}_6 : \text{NMe}$, crystallising in reddish-brown

leaflets, m. p. 195—196°; when the dye is boiled with excess of ammonia, however, the *carbinol* base,



is obtained as colourless crystals, m. p. 171—172°. When heated in glycerol with the addition of a few drops of aqueous potassium hydroxide, the imino-base is formed, and this is again converted into the *carbinol* when its solution in 40—50% alcohol, to which a little ammonia or potassium hydroxide is added, is boiled for an hour.

When a cold solution of crystal-violet is mixed with a large excess of potassium hydroxide and immediately extracted with ether, reddish-brown crystals, m. p. 191—194°, of the imino-base are obtained. This is soon converted in a vacuum desiccator into the *carbinol* form, m. p. 182°, which is also formed when a solution of crystal-violet is treated with ammonia. In the case of malachite-green, ammonia decolorises the solution much more quickly than do potassium or sodium hydroxides, but the coloured base could not be obtained pure, owing to its rapid change into the *carbinol* form.

When *o*-chloromalachite-green (setoglaucin) is treated in aqueous solution with ammonia, the *carbinol* base, $\text{C}_{23}\text{H}_{25}\text{ON}_2\text{Cl}$, is obtained; this forms pale yellow crystals, m. p. 155°. By the addition of potassium hydroxide to setoglaucin, a red precipitate is obtained. Further experiments in the preparation of this coloured base are in progress. With sodium methoxide, setoglaucin furnishes the *methyl ether*, $\text{OMe}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{C}_6\text{H}_4\text{Cl}$, pale yellow crystals, m. p. 138°.

J. C. C.

Chromoisomerism and Transformation of 4-Oximino-1-phenyl-5-triazolone. OTTO DIMROTH and OSKAR DIENSTBACH (*Ber.*, 1908, 41, 4055—4068).—In connexion with 4-*isonitroso*-1-phenyl-5-triazolone (Dimroth and Taub, *Abstr.*, 1907, i, 96), two points of interest are discussed, the colour phenomena of the metallic salts and the hydrolysis of its acylated derivatives.

Three series, yellow, green, and red, of metallic salts have been obtained. The only member of the yellow series is the *potassium hydrogen* salt, $\text{KH}(\text{C}_8\text{H}_5\text{O}_2\text{N}_4)_2\cdot 3\text{H}_2\text{O}$, which forms yellow, micro-crystalline needles, decomposes at 80—100°, and is obtained by treating the dipotassium salt of 5-hydroxy-1-phenyl-1:2:3-triazole-4-carboxylic acid with potassium nitrite and acetic acid in the cold. It dissolves unchanged in alcohol or acetone, but after some time the solution contains oximinophenyltriazolone, and a precipitate is obtained of the bluish-green *potassium* salt, $\text{C}_8\text{H}_5\text{O}_2\text{N}_4\text{K}$, which is also formed from alcoholic potassium acetate and dilute alcoholic oximinophenyltriazolone. Other metallic salts have been obtained in a similar manner. The *sodium*, *ammonium*, *calcium*, *barium*, and *mercurous* salts belong to the red series. The *silver* salt, prepared from the sodium salt and silver nitrate, or from the oximinophenyltriazolone and silver nitrate in alcoholic solution, separates at the ordinary temperature as a canary-green powder (stable form), and at 50° as a brownish-red labile form, changing to the stable form by cooling.

Acyl derivatives of oximinophenyltriazolone, prepared from the silver salt and acyl chlorides in dry ether, have, in a few cases, been

obtained in yellow and red forms, but not in the green. 4-Benzoyl-oximino-1-phenyl-5-triazolone, $\text{NPh} \begin{array}{c} \text{N}=\text{N} \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{OBz} \end{array}$, separates from

alcohol in long, red needles by slow cooling, or in yellow, micro-crystalline needles by rapid cooling. Both forms behave alike, have m. p. 132—133° (decomp.), and give the same yellow solution in organic solvents at the ordinary temperature, but that they are isomeric and not polymorphic is proved by the fact that the red modification in chloroform at 0° gives a blood-red solution, the colour of which changes, however, almost instantly to yellow. When the red modification under alcohol is inoculated with a trace of the yellow isomeride, the whole mass becomes yellow in a few days. The *m*-nitrobenzoyl derivative, m. p. 153°, only occurs in yellow needles. The acetyl derivative is obtained in yellow and red modifications, the separation of the two being difficult; the former has m. p. 97—98°. Phenylcarbimide and oximinophenyltriazolone in ether yield, as the

main product, a phenylurethane, $\text{NPh} \begin{array}{c} \text{N}=\text{N} \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh} \end{array}$, m. p. 110° (decomp.), which separates in orange-yellow needles. This compound and the preceding acetyl derivative are hydrolysed by alcoholic potassium acetate, the bluish-green potassium salt of oximinophenyltriazolone being obtained. The benzoyl and the *m*-nitrobenzoyl derivatives are stable to potassium acetate, but their interaction with 5*N*-sodium hydroxide at -10°, the reaction being completed at the ordinary temperature, leads to the formation of benzoic (or *m*-nitrobenzoic) acid and Bladin's 1-phenyl-1:2:3:5-tetrazole-4-carboxylic acid (Abstr., 1886, 146), the identity being confirmed by heating the acid at 140—155°, whereby 1-phenyl-1:2:3:5-tetrazole is obtained. Several explanations are discussed to account for the formation of the tetrazole from the triazole. It appears that, in addition to the two types of the Beckmann transformation already recognised (Werner and Piguet, Abstr., 1905, i, 66; Diels and Stern, Abstr., 1907, i, 480), a third type is possible, in which the acylated hydroxyl group attached to the nitrogen atom exchanges places with a group

attached to the β -carbon atom, thus $\begin{array}{ccc} \text{R} \cdot \ddot{\text{C}} \cdot \text{C} \cdot & & \text{OAc} \cdot \ddot{\text{C}} \cdot \text{C} \cdot \\ | & & | \\ \text{OAc} \cdot \text{N} & \rightarrow & \text{R} \cdot \text{N} \end{array}$

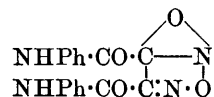
In the case in question : $\begin{array}{ccc} \text{N} \cdot \text{N} \cdot \text{NPh} \cdot \text{CO} & & \text{OBz} \cdot \text{CO} \\ | & \searrow & \nearrow \\ \text{OBz} \cdot \text{N} & \text{C} & \\ | & & \\ \text{N} \cdot \text{N} \cdot \text{NPh} \cdot \text{N} & \text{C} & \end{array} \rightarrow \begin{array}{ccc} \text{N} \cdot \text{N} \cdot \text{NPh} \cdot \text{N} & & \text{OBz} \cdot \text{CO} \\ | & \searrow & \nearrow \\ \text{OBz} \cdot \text{N} & \text{C} & \\ | & & \\ \text{N} \cdot \text{N} \cdot \text{NPh} \cdot \text{N} & \text{C} & \end{array}$

from which benzoic acid and the tetrazole derivative are obtained.

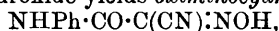
The benzoyl derivative, m. p. 169—170°, and the *m*-nitrobenzoyl derivative, m. p. 194°, of 4-oximino-1-phenyl-3-methylpyrazolone do not suffer the preceding change, being stable to cold aqueous sodium hydroxide, and hydrolysed normally by sodium ethoxide. C. S.

Decomposition Products of 4-Oximino-1-phenyl-5-triazolone. OTTO DIMROTH and OSKAR DIENSTBACH (*Ber.*, 1908, 41, 4068—4083. Compare Dimroth and Taub, Abstr., 1907, i, 96; preceding abstract).—It has already been shown that the decomposition of 4-oximino-1-phenyl-5-triazolone by warm water, or, better, by warm dilute

sulphuric acid, yields nitrogen, oxanilhydroxamic acid, and in addition, two isomeric substances, $C_{16}H_{12}O_4N_4$, m. p. 187° and 195° respectively, the constitutions of which were undetermined. The suggestion that the substance, m. p. 187° , is glyoximeperoxidedicarboxyanilide has been substantiated, but, since in the meantime the authors have accepted Wieland and Semper's bridged-ring formula for glyoximeperoxide and its derivatives (Abstr., 1908, i, 108), the name of the substance has been altered to 2:3-endoxy-2:3-dihydrofurazan-3:4-dicarboxyanilide (furoxandicarboxyanilide), and its formula to the annexed constitution. It is reduced by stannous chloride and hydrogen chloride in glacial acetic acid to

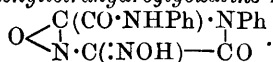


furazan-3:4-dicarboxyanilide, $\text{NHPH}\cdot\text{CO}\cdot\text{C}\cdot\text{N} > \text{O}$, m. p. 119° , the decomposition of which by aqueous sodium hydroxide or methyl alcoholic potassium hydroxide yields *oximinocyanoacetanilide*,

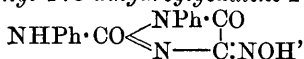


m. p. 220° (decomp.), which forms yellow and colourless crystals, and can be synthesised by heating oxanilhydroxamyl chloride dissolved in ether with silver cyanide at 100° for sixteen hours.

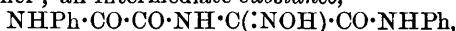
The substance, m. p. 195° , previously regarded as 3:6-dioximino-2:5-diketo-1:4-diphenylpiperazine (*loc. cit.*), is proved to be 4-oximino-2:3-endoxy-5-keto-1-phenyltetrahydroglyoxaline-2-carboxyanilide,



This constitution readily accounts for the formation of oxanilhydroxamic anilide and oxalohydroxamic acid by the action of cold 10% sodium hydroxide [Lossen, Behrend, and Schäfer's sodium oxalohydroxamate (Abstr., 1894, i, 358) is really sodium oxalodihydroxamate], and is in harmony with the behaviour of the substance by reduction by stannous chloride and hydrogen chloride in glacial acetic acid, by phenylhydrazine, or by alcoholic hydrogen chloride, whereby 4-oximino-5-keto-1-phenyl-4:5-dihydroglyoxaline-2-carboxyanilide,



m. p. 237° , is obtained. This compound, which is also prepared from 4-oximino-1-phenyl-5-triazolone, methyl alcohol, and concentrated hydrochloric acid, from the potassium hydrogen salt of the triazolone derivative and alcohol, or from the sodium salt and alcoholic sodium acetate, is decomposed by methyl alcoholic potassium hydroxide, yielding oxanilic acid and *oxanilhydroxamamide*, $\text{NHPH}\cdot\text{CO}\cdot\text{C}(\text{:NOH})\cdot\text{NH}_2$, m. p. 142° , which forms a compound, m. p. 175° , with phenylcarbimide, and is synthesised from ammonia and oxanilhydroxamic chloride in moist ether. The constitution of the dihydroglyoxaline derivative is also proved by synthesis from oxanilyl chloride and oxanilhydroxamamide in ether; an intermediate substance,



m. p. $181-183^\circ$, is formed, which crystallises in colourless needles or rhombic leaflets, and loses 1 mol. H_2O above its m. p., yielding 4-oximino-5-keto-1-phenyl-4:5-dihydroglyoxaline-2-carboxyanilide.

The conversion of the endoxyglyoxaline derivative, m. p. 195°, into the endoxydihydrofurazan, m. p. 187°, is accomplished (a) by dilute sodium hydroxide, (b) by the action of benzoyl chloride in pyridine, (c) by the prolonged shaking of its solution in ether or acetone half saturated with hydrogen chloride. When ether, saturated with hydrogen chloride at 5°, is used, the endoxyglyoxaline derivative is decomposed, ammonia, aniline, oxalic acid, phenyloxamide, and oxanilhydroxamamide being formed. C. S.

Azinpurines. FRANZ SACHS and GEORG MEYERHEIM (*Ber.*, 1908, 41, 3957—3965).—Whereas the purine compounds have been extensively examined, compounds analogous, but containing one more carbon atom in the nucleus, are almost unknown. The azinpurines may be obtained by the condensation of 4:5-diaminopyrimidines with o-diketones.

2:6-Dioxy-3:8:9-trimethylazinpurine,
$$\begin{array}{c} \text{NH} \cdot \text{CO} - \text{C} \cdot \text{N} : \text{CMe} \\ | \quad \quad | \\ \text{CO} \cdot \text{NMe} \cdot \text{C} \cdot \text{N} : \text{CMe} \end{array}$$
 obtained from 4:5-diamino-2:6-dioxy-3-methylpyrimidine and diacetyl in 93% yield, crystallises from water in small needles, m. p. 328—330°; its aqueous solution is yellow with a green fluorescence. 2:6-Dioxy-1:3:8:9-tetramethylazinpurine, $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_4$, from 4:5-diamino-2:6-dioxy-1:3-dimethylpyrimidine, is obtained in 84% yield, and crystallises in needles, m. p. 159.5°.

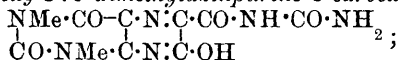
2:6-Dioxy-8-acetyl-3:9-dimethylazinpurine,
$$\begin{array}{c} \text{NH} \cdot \text{CO} - \text{C} \cdot \text{N} : \text{CAc} \\ | \quad \quad | \\ \text{CO} \cdot \text{NMe} \cdot \text{C} \cdot \text{N} : \text{CMe} \end{array}$$
 obtained by the condensation of the monomethyl base with triketopentane in aqueous acetic acid solution, crystallises from water in prisms, m. p. 267°; the solution is colourless. Condensation with the dimethyl base and triketopentane leads to the formation of 2:6-dioxy-8-acetyl-1:3:9-trimethylazinpurine, $\text{C}_{11}\text{H}_{12}\text{O}_3\text{N}_4$, which crystallises from alcohol in long needles, m. p. 164—165°.

9-Hydroxy-2:6-dioxy-3:8-dimethylazinpurine,
$$\begin{array}{c} \text{NH} \cdot \text{CO} - \text{C} \cdot \text{N} : \text{CMe} \\ | \quad \quad | \\ \text{CO} \cdot \text{NMe} \cdot \text{C} \cdot \text{N} : \text{C} \cdot \text{OH} \end{array}$$
 from monomethyl base and pyruvic acid, is purified by dissolution in aqueous ammonia and precipitation with dilute hydrochloric acid; m. p. 323—324°. The 9-hydroxy-2:6-dioxy-1:3:8-trimethylazinpurine, $\text{C}_9\text{H}_{10}\text{O}_3\text{N}_4$, from the dimethyl base, crystallises from formic acid, has m. p. 309°, and gives a yellowish-red lead, an orange silver, a yellow barium, and a yellowish-red copper salt.

9-Hydroxy-2:6-dioxy-1:3-dimethylazinpurine, $\text{C}_8\text{H}_8\text{O}_3\text{N}_4$, from the dimethyl base and ethyl dichloroacetate, separates from alcohol as a white compound, m. p. 282°. 9-Hydroxy-2:6-dioxy-1:3-dimethylazinpurine-8-carboxylic acid,
$$\begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{N} : \text{C} \cdot \text{CO}_2\text{H} \\ | \quad \quad | \\ \text{CO} \cdot \text{NMe} \cdot \text{C} \cdot \text{N} : \text{C} \cdot \text{OH} \end{array}$$
 obtained from mesoxalic acid and dimethyl base in 67% yield, crystallises in slender needles from water, m. p. 239—240° (decomp.).

Condensation of alloxan and dimethyl base leads to the formation of

9-hydroxy 2 : 6-dioxy-1 : 3-dimethylazainpurine-8-carboxycarbamide,



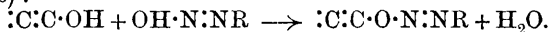
it crystallises in prisms, m. p. above 360° .

2 : 6-Dioxy-1 : 3-dimethylpiaselenolpurine, $\begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{N} \\ | \qquad \qquad | \\ \text{CO} \cdot \text{NMe} \cdot \text{C} \cdot \text{N} \end{array} \gg \text{Se}$, is

formed when an acetic acid solution of the dimethyl base is treated with selenious acid; it is brick-red in colour, m. p. $225-230^\circ$. The colour is destroyed on solution in water, from which it crystallises in long, colourless, prismatic needles, m. p. $227-228^\circ$.

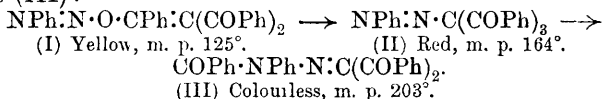
[With W. BRUNETTI.]—2-Amino-6-hydroxy-8 : 9-dimethylazainpurine, $\begin{array}{c} \text{N} : \text{C}(\text{OH}) - \text{C} \cdot \text{N} : \text{CMe} \\ | \qquad \qquad | \\ \text{C}(\text{NH}_2) \cdot \text{N} \cdot \text{C} \cdot \text{N} : \text{CMe} \end{array}$, formed by the condensation of 2 : 4 : 5-triamino-6-hydroxypyrimidine sulphate with diacetyl in aqueous solution, crystallises in small, yellow needles, which sublime without melting. It forms a yellow *picrate* and a *silver salt*, $\text{C}_8\text{H}_8\text{ON}_5\text{Ag}$. W. R.

The Mechanism of Coupling. OTTO DIMROTH and MAX HARTMANN (*Ber.*, 1908, 41, 4012—4028)—It has been shown previously (*Abstr.*, 1907, i, 662, 1090) that only the enolic forms of keto-enolic tautomerides react with diazo-compounds. It is now shown that the first stage in this reaction consists in the formation of an azo-compound in which the azo-group is attached to oxygen (*O*-azo-compounds):



The constitution of these compounds follows from their behaviour. When boiled with alcohol they react as diazo-ethers; thus benzene-*O*-azotribenzoylmethane, obtained from diazobenzene and tribenzoylmethane, decomposes into tribenzoylmethane and benzene, whilst the alcohol is oxidised to aldehydes. They also react with phenols and amines in the same manner as diazo-ethers, for example, benzene-*O*-azotribenzoylmethane reacts with an alcoholic solution of β -naphthol, yielding tribenzoylmethane and benzeneazo- β -naphthol. Similarly, the *O*-azo-compound is decomposed by an ethereal solution of hydrogen chloride, yielding diazobenzene chloride and tribenzoylmethane.

When the yellow *O*-azo-compound is kept at a temperature just above its melting point, it is transformed into a red isomeric compound (II), and when this is further heated it sets to a mass of colourless crystals (III):



The red compound has been identified as a *C*-azo-compound, owing to its stability; it does not react with amines or phenols, and is not hydrolysed by ethereal hydrogen chloride, but merely transformed more quickly into the colourless compound (III). When reduced, it yields a leuco-compound, namely, a hydrazo-compound, which is readily oxidised back to the red azo-compound. The colourless hydrazone (III) is also stable; it does not couple with phenols or

amines, and on reduction yields benzanilide. All three compounds react with sodium ethoxide, yielding ethyl benzoate and diphenyltriketone phenylhydrazone, $C(COPh)_2 \cdot N \cdot NPh$, m. p. 153—154°. The "coupling" of a phenol with a diazo-compound is also regarded as primarily consisting in the formation of an *O*-azo-derivative, $PhO \cdot N \cdot N \cdot Ph$, which undergoes molecular rearrangement to the more stable hydroxyazo-derivative (compare Kekulé, *Ber.*, 1870, 3, 233). An *O*-azo-compound of this type has been isolated by coupling *p*-bromodiazobenzene chloride with *p*-nitrophenol. It is practically colourless, and when heated at 80° yields the more stable *C*-azo-compound, $NO_2 \cdot C_6H_4(OH) \cdot N \cdot N \cdot C_6H_4Br$.

Benzene-O-azotribenzoylmethane (I) separates from its ethereal or chloroform solution on the addition of light petroleum as long, canary-yellow prisms, m. p. 125°.

Benzene-C-azotribenzoylmethane (II) is best obtained by heating the *O*-compound under reduced pressure at 100° for about two hours; it can be separated from the colourless hydrazone (III), which is also formed by extraction with ether and fractional crystallisation from acetone. It forms glistening, hard prisms of a ruby-red colour, melts at 164°, and at the same time is rapidly transformed into the colourless *benzoylphenylhydrazone* of *diphenyltriketone* (III), which crystallises from benzene in colourless needles, m. p. 203°.

The compound previously described as *p*-bromobenzeneazotribenzoylmethane (Abstr., 1907, i, 1090) is now shown to be the isomeric *O*-azo-derivative. It is rapidly transformed into the isomeric *C*-azo-compound, but this cannot be isolated, as it is immediately converted into the hydrazone (*loc. cit.*). *Diphenyl triketone bromophenylhydrazone* (*p*-bromobenzeneazodibenzoylmethane), $C_{21}H_{15}O_2N_2Br$, is formed by the action of sodium ethoxide on either the *O*-azo-compound or its isomeride. It crystallises from alcohol in golden-yellow plates, m. p. 147—149°.

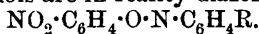
The properties of the compound previously described as benzene-azoacetyldibenzoylmethane prove that it is an *O*-azo-compound; similarly, Bülow and Hailer's ethyl phenylazodibenzoylacetate (Abstr., 1902, i, 327) is an *O*-azo-compound, although it cannot be transformed into a more stable isomeride.

Ethyl benzoylmalonate reacts with diazobenzene chloride, yielding *ethyl benzene-O-azobenzoylmalonate*, $N_2Ph \cdot O \cdot CPh \cdot C(CO_2Et)_2$, which crystallises from alcohol in glistening, yellow plates, m. p. 69°; when heated slightly above its m. p., it is completely decomposed.

Benzene-O-azo-p-nitrophenol, $N_2Ph \cdot O \cdot C_6H_4 \cdot NO_2$, has been obtained in the form of pale yellow needles, which rapidly decompose. *p*-Bromobenzene-O-azo-p-nitrophenol, $C_6H_4Br \cdot N_2 \cdot O \cdot C_6H_4 \cdot NO_2$, melts at 75—80°, and is also unstable; at 80° it is transformed into the isomeric *p*-bromobenzeneazo-p-nitrophenol, $C_6H_4Br \cdot N_2 \cdot C_6H_3(OH) \cdot NO_2$, m. p. 197°.

J. J. S.

***O*-Azo-compounds.** KARL AUWERS (*Ber.*, 1908, 41, 4304—4308. Compare Dimroth and Hartmann, preceding abstract).—It is suggested that the relatively unstable *O*-azo-compounds prepared from diazotised *p*-nitroaniline and phenols are in reality diazonium salts,

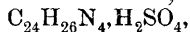


Similar compounds are obtained when diazonium salts react with phenols, the ortho-para-positions of which are occupied. The radicles need not be negative in character, as mesitol gives the reaction, although with difficulty. The compounds so obtained are more stable than those of Dimroth and Hartmann, which may be due to the fact that they cannot be transformed into hydroxyazo-compounds.

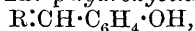
W. R.

Condensation of 2:3'-Dimethylazobenzene-4-hydrazine-sulphonic Acid, formed by the Action of Sulphurous Acid on Diazo-*m*-toluene Sulphate, with Aldehydes and Ketones. JULIUS TRÖGER and GEORG PUTTKAMMER (*J. pr. Chem.*, 1908, [ii], 78, 437—449. Compare Abstr., 1907, i, 263).—A continuation of the investigations of Tröger, Warnecke, and Schaub (Abstr., 1906, i, 993). 2:3'-Dimethylazobenzene-4-hydrazinesulphonic acid condenses with aldehydes and ketones in alcoholic solution containing hydrogen chloride or sulphuric acid, with elimination of the sulphonic group, yielding derivatives of 2:3'-dimethylazobenzene-4-hydrazone hydrochloride or sulphate. The free hydrazones are obtained by treating the salts with ammonium hydroxide. The following hydrazones were prepared in this way. In the formulæ $R = C_6H_4Me \cdot N:N \cdot C_6H_3Me \cdot NH \cdot N$. All the salts described were analysed (see following abstract).

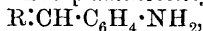
p-Tolylidene-2:3'-dimethylazobenzene-4-hydrazone, $R:CH \cdot C_6H_4Me$, crystallises in yellow leaflets, m. p. 180—181°; the *hydrochloride*, $C_{22}H_{22}N_4 \cdot HCl$, is a sandy, crystalline, violet powder. The corresponding *p*-isopropylbenzylidene derivative, $R:CH \cdot C_6H_4Pr^i$, forms stellate groups of brown crystals, m. p. 137°; the *hydrochloride* is a dark reddish violet, crystalline powder; the *hydrobromide*, $C_{24}H_{26}N_4 \cdot HBr$, is a black, crystalline powder with a violet shimmer; the *sulphate*,



is amorphous. The *m*-chlorobenzylidene derivative, $R:CH \cdot C_6H_4Cl$, forms pale orange, silky crystals, m. p. 140°; the *hydrochloride* crystallises in slender, violet needles. The *m*-bromobenzylidene derivative, $R:CH \cdot C_6H_4Br$, crystallises in pale orange leaflets, m. p. 137°; the *hydrobromide* forms dark violet needles; the *sulphate* crystallises in bronze-green needles. The *p*-hydroxybenzylidene derivative,



crystallises in brown leaflets, m. p. 202—203°; the *hydrochloride* forms bluish-green needles; the *hydrobromide* forms green needles; the *sulphate* crystallises in dark blue needles. The *p*-dimethylamino-benzylidene derivative, $R:CH \cdot C_6H_4 \cdot NMe_2$, is an orange powder, m. p. 154—155° (decomp.); the *hydrobromide*, $C_{23}H_{25}N_5 \cdot 2HBr$, is a brownish-black, crystalline powder. The *p*-aminobenzylidene derivative,



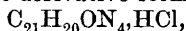
is an amorphous, orange powder, m. p. 188—190° (decomp.); the *hydrochloride*, a bronze-green powder, appears to contain 2 mols. of hydrogen chloride. The *benzophenone* condensation product, $R:CPH_2$, crystallises in reddish-orange, microscopical prisms, m. p. 137°; the corresponding *isopropylidene* derivative, $R:CM_e^i$, forms small, brown, flat, oval crystals, m. p. 125°; the *hydrochloride* is a brownish-red,

crystalline powder; the *benzil* derivative, $R:CPh \cdot CPh:R$, crystallises in orange, rectangular plates, m. p. 141—142°. W. H. G.

Additive Products of 2:3'-Dimethylazobenzene-4-hydrazones with Acids. JULIUS TRÖGER and GEORG PUTTKAMMER (*J. pr. Chem.*, 1908, [ii], 78, 450—477. Compare preceding abstract).—It is definitely shown in this communication that when 2:3'-dimethylazobenzene-4-hydrazinesulphonic acid condenses with aldehydes or ketones in the presence of strong mineral acids, only hydrazone salts are formed. The statement of Tröger, Hille, and Vasterling (*Abstr.*, 1906, i, 120), that the sulphonic acid condenses with salicylaldehyde, thus: $OH \cdot C_6H_4 \cdot CHO + 2C_7H_7 \cdot N_2 \cdot C_7H_6 \cdot N_3H_2 \cdot SO_3H + H_2O = 2H_2SO_4 + OH \cdot C_6H_4 \cdot CH(C_7H_6 \cdot N_2 \cdot C_7H_6 \cdot NH \cdot NH_2)_2$, is incorrect. The salts described in this paper, descriptions of many of which have been given in the preceding abstract in order to economise space, are obtained in a pure state only by using exceedingly pure materials, and by the following methods: (1) heating the sulphonic acid in alcohol, or, better, glacial acetic acid, with an aldehyde or ketone in the presence of a mineral acid; (2) treating the pure hydrazone with a solution of the mineral acid in glacial acetic acid. Unless otherwise stated, all the salts are composed of 1 mol. of the hydrazone with 1 mol. of acid.

Benzylidene-2:3'-dimethylazobenzene-4-hydrazone hydrochloride, $C_{21}H_{20}N_4 \cdot HCl$, forms dark violet needles; the *hydrobromide* forms black needles with violet reflex; the *sulphate* forms blue crystals.

The *o*-hydroxybenzylidene derivative forms a *hydrochloride*,



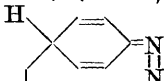
small, dark green needles; *hydrobromide*, brownish-black, crystalline powder, and *sulphate*, small, green needles. The *m*-nitrobenzylidene derivative forms a *sulphate*, $C_{21}H_{19}O_2N_5 \cdot H_2SO_4$, green crystals; *hydrochloride*, slender, dark green needles, and *hydrobromide*, slender, microscopical, reddish-violet needles. The analogous *p*-nitro-compound yields a *hydrochloride*, bluish-violet needles, and *sulphate*, deep green needles. The *hydrochloride*, *hydrobromide*, and *sulphate* of the *p*-methoxybenzylidene derivative are blue, crystalline substances. *Cinnamylidene-2:3'-dimethylazobenzene-4-hydrazone hydrochloride*, $C_{23}H_{22}N_4 \cdot HCl$, crystallises in greyish-blue needles; the *hydrobromide* forms brownish-black needles; the *sulphate* forms slender, bronze-green needles; the *hydriodide* is a bluish-black, crystalline powder. W. H. G.

Preparation of *o*-Azocarboxylic Acids. PAUL FREUNDLER and SEVESTRE (*Compt. rend.*, 1908, 147, 981—983).—The *o*-azo-carboxylic acids required for the preparation of 3-hydroxyindazol derivatives (*Abstr.*, 1906, i, 544; 1907, i, 158), and prepared by the condensation of nitrosobenzene with the meta-substituted anthranilic acid, can be obtained in a far better yield by the condensation of the primary aromatic amine with the *o*-nitroso-acid; thus *p*-chloroaniline and *o*-nitrosobenzoic acid yield *p*-chlorobenzene-*o*-azobenzoic acid to the extent of 60% of that required by theory, whilst the yield by the older method is only 15%, and the following compounds were similarly prepared: *p*-toluene-*m*-azotoluic acid forms large, red prisms, m. p. 122.5°; *p*-toluene-2-azo-5-chlorobenzoic acid crystallises in orange plates, m. p. 159—160°.

The *o*-nitroso-acids required in these preparations were obtained by oxidising the corresponding amino-acid with Caro's acid (compare Baeyer, Abstr., 1900, i, 206); *o*-nitroso-*m*-toluic acid forms small, yellow prisms, m. p. 172—173°; 5-chloro-2-nitrosobenzoic acid crystallises in plates, m. p. 193°. M. A. W.

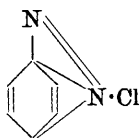
Decomposition of Diazo-solutions. JOHN C. CAIN (*Ber.*, 1908, 41, 4186—4189).—It is pointed out by the author that the value given by Hantzsch and Thompson (Abstr., 1908, i, 1021) for the rate of decomposition of a solution of pure *p*-nitrodiazobenzene chloride at 50° ($K=0.00020$) is in close agreement with that calculated for 50° ($K=0.00018$) from the result obtained by him (*Trans.*, 1902, 81, 1436) for the rate of decomposition of a solution of the same compound containing a trace of free nitrous acid (about 0.0003 gram in 70 c.c.) at 80° ($K=0.00736$). The statement made by the author previously, that the very small quantity of nitrous acid present in a diazo-solution prepared by the usual method does not appear to exert any influence on the rate of decomposition of the solution, is thus shown to be correct. W. H. G.

Theory of Diazo-compounds and Ammonium Salts. JOHN C. CAIN (*Ber.*, 1908, 41, 4189—4193).—Polemical. A reply to the criticisms of Hantzsch (Abstr., 1908, i, 1021). The objection

that a compound having the formula  would yield

p-phenylenediamine on reduction has already been answered (*Proc.*, 1907, 23, 160). The equation representing the dissociation of tetraethylammonium chloride in aqueous solution should be $\text{NEt}_3 \cdot \text{Cl} \cdot \text{Et} \rightarrow \text{NEt}_3 + \text{Cl}^- + \text{Et}^+ \rightarrow \text{NEt}_4^+ + \text{Cl}^-$; that is, the formation of the ion NEt_4^+ can take place momentarily without the separate formation of ethyl chloride. W. H. G.

Constitution of Diazonium Salts. HANS EULER (*Ber.*, 1908, 41, 3979—3981).—In connexion with Hantzsch's criticisms (Abstr., 1908, i, 1021) of Cain's formula (*Trans.*, 1907, 91, 1049), the author points out that, in 1906, he suggested the annexed formula, which has an advantage over other formulæ in that it pictorially represents the ability of aromatic, as against the inability of aliphatic and alicyclic, amines to yield diazonium salts, and the transformation of diazonium salts into *syn*-diazo-oxides, whilst it is not in discord with the chemical and electrochemical behaviour of these substances. C. S.



Dimethylaminoazoantipyrene. FRIEDRICH STOLZ (*Ber.*, 1908, 41, 3849—3854).—The method for preparing 4-dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone recently patented by the "Société chimique de l'Avanchet" (D.R.-P. 203753) must be wrong, since nitrosodimethylamine and 4-aminoantipyrene do not interact under the conditions mentioned in the patent. Dimethylaminoazoantipyrene may,

however, be readily prepared by coupling dimethylamine with diazoantipyrine, but when heated, it does not yield 4-dimethylaminoantipyrine, but passes into 1-phenyl-2-methyl-3 : 4-pyrazopyrazol-5-one with elimination of dimethylamine.

Diethylaminoazoantipyrine, $C_{15}H_{21}ON_5$, crystallises in light brown prisms, m. p. 111—112°.

Dimethylaminoazoantipyrine, $C_{13}H_{17}ON_5$, crystallises in brownish-yellow leaflets, m. p. 107° (heated rapidly), 110—112° (heated slowly). It is converted when heated at 130—140°, or more readily when its solution in xylene is boiled, into 1-phenyl-2-methyl-3 : 4-pyrazopyrazol-5-one, $NPh \begin{array}{c} \text{NMe} \cdot \text{C} : \text{CH} \\ \text{CO} - \text{C} = \text{N} \end{array} \text{NH}$, which forms small, orange crystals, m. p. 173°, and yields an *acetyl* derivative, $C_{13}H_{12}O_2N_4$, almost colourless crystals, m. p. 202—203°. W. H. G.

Decomposition Products of Albumin which Combine with Iodine. HERMANN PAULY and KARL GUNDERMANN (*Ber.*, 1908, 41, 3999—4012. Compare Wheeler and Jamieson, *Abstr.*, 1905, i, 350).

—Indole yields 3-iodoindole, $C_6H_4 \begin{array}{c} \text{Cl} \\ \text{NH} \end{array} \text{CH}$, when a dilute aqueous solution (0.5 gram per litre) is mixed with 10 c.c. of a 10% potassium hydroxide solution and *N*/10 or *N*/100 iodine is run in until a precipitate is no longer formed. The iodo-derivative is deposited as pure crystals, m. p. 72°; with mineral acids, it yields hydrogen iodide. The *picrate*, $C_8H_6NI, C_6H_3N_3O_7$, crystallises from alcohol in slender needles, which decompose at 90°. Indole, free from scatole, can be titrated in dilute alkaline solution by means of standard iodine solution. Indole is oxidised to indigo when an *N*/10 iodine solution is added gradually to an indole solution in the presence of a large excess of sodium hydrogen carbonate, but an appreciable amount of 3-iodoindole is always formed as a by-product.

α -Methylindole yields 3-iodo-2-methylindole, C_9H_8NI , which crystallises in colourless plates, m. p. 82°. It has a strong odour of scatole, and is unstable. The *picrate* crystallises in reddish-brown needles, m. p. 107° (decomp.). Indole derivatives in which the 3-position is already substituted, for example, scatole and dimethylindole, do not yield 3-iodo-compounds. When an aqueous solution of scatole is treated with iodine solution, a small amount of a compound, $C_9H_9O_2N$ or $C_9H_{11}O_2N$, is obtained as a yellow powder, m. p. 140—145°, when slowly heated.

Glyoxaline readily reacts with iodine in the presence of alkali hydroxide, yielding *tri-iodoglyoxaline*, $CI \begin{array}{c} \text{N} - \text{CI} \\ \text{NH} \cdot \text{CI} \end{array}$, in the form of its alkali salt. The free acid crystallises from 20% alcohol in large, flat, glistening prisms, m. p. 191—192° (corr.). The *hydrochloride*, $C_3H_3N_2I_3 \cdot HCl$, is deposited as glistening needles on the addition of concentrated hydrochloric acid to an alcoholic solution of the glyoxaline. It evolves iodine at 200°, and melts at 220°. When insufficient iodine is used, a *di-iodo*-derivative, m. p. 180°, is obtained.

Methylglyoxaline (Windaus and Knoop, *Abstr.*, 1905, i, 381) yields

iodo-2-methylglyoxaline, $C_4H_5N_2I$, in the absence of sodium hydroxide, but the yield is increased by the addition of alkali. The iodo-derivative crystallises from 50% alcohol in colourless needles, m. p. 157° . It is odourless, and forms soluble salts with mineral acids. The *aurochloride*, $C_4H_5N_2I \cdot HAuCl_4$, crystallises from hot water in long, orange-yellow needles, m. p. 197° .

Benziminazole is most readily obtained by heating anhydrous formic acid with *o*-phenylenediamine, and reacts with iodine in the presence of sodium hydroxide, yielding 2-iodobenziminazole, $C_6H_4 \begin{smallmatrix} \text{---} \text{N} \text{---} \\ \text{NH} \end{smallmatrix} \text{---} \text{I}$, which forms colourless plates, m. p. 187° . It is readily decomposed by acids, but is more stable in the presence of alkalis.

Iminazoles do not yield iodo-derivatives when the hydrogen of the NH-group has been substituted, as in *N*- α -dimethylglyoxaline.

Compounds which are readily iodated in the cold by iodine and alkali are regarded as containing an "iodophore" group. J. J. S.

Acid and Neutral Copper Albumins. GIUSEPPE BONAMARTINI and M. LOMBARDI (*Zeitsch. physiol. Chem.*, 1908, 58, 165—174).—When solutions of egg-albumin are mixed with copper sulphate solutions, precipitates of an acid copper albumin are obtained. The mean composition is: albumin, 86.7%; Cu, 5.2%; and SO_4 , 8.0%. The copper and SO_4 -group are practically in the same ratio as in copper sulphate. When a solution of normal potassium hydroxide is added to the precipitate until the liquid is just alkaline, a neutral copper albumin is obtained. This is deeper in colour, and contains no sulphate radicle. If a smaller amount of alkali is used, a mixture of the acid and neutral albumins is obtained. J. J. S.

Products Formed by the Decomposition of Casein. I. W. BISSEGGGER and L. STEGMANN (*Zeitsch. physiol. Chem.*, 1908, 58, 147—152. Compare Winterstein and Thöni, *Abstr.*, 1902, ii, 687).—When casein is digested for some time with pancreatin and pepsin in the presence of toluene and sodium fluoride, tetra- and penta-methylenediamines cannot be isolated, but a new basic substance can be obtained from the lysine fraction. Full details for the isolation of the base are given. The *chloride* crystallises from water in large, glistening, hard prisms, containing 12.5% N and 20.5% Cl. It has $[\alpha]_D + 11.12^\circ$, and yields a flocculent precipitate with phosphotungstic acid, and a sparingly soluble *platinichloride* (Pt = 33.51%). J. J. S.

Different Forms of Nitrogen in Proteins. THOMAS B. OSBORNE, C. S. LEAVENWORTH, and C. A. BRANTLECHT (*Amer. J. Physiol.*, 1908, 23, 180—200).—It does not appear possible to determine accurately the monoamino-acids in the cleavage products of proteins. Ammonia and the hexone bases can be determined with accuracy, and their estimation by different methods in the same protein gives constant results. It therefore appears that the determination of such substances is a trustworthy criterion in the differentiation of proteins. Hydrolysis must, however, be continued for at least twenty-four hours when dealing with vegetable proteins. Determinations are given in twenty-

six different proteins. The amount of arginine varies from 1% to 14%. Histidine is more constant, 2.5% being present in most proteins. Lysine is absent from the gliadins, and present in leguminous seed-proteins (4—5%), and in con-albumin from hen's egg (over 6%). The oil-seeds contain least arginine, then come the leguminous seed-proteins, and those of cereal grains contain most. W. D. H.

So-called "Protagon." OTTO ROSENHEIM and M. CHRISTINE TEBB (*Quart. J. exp. Physiol.*, 1908, 1, 297—304).—Further proofs are advanced that protagon, even when prepared with all the precautions recommended by Wilson and Cramer, is a mixture of different substances. Its composition is completely changed by recrystallisation from alcohol, but the readiest way of separating its constituents is by means of pyridine. Protagon is soluble in this reagent at 30—45°, and a precipitation occurs on cooling; the precipitate consists of the phosphorus-rich constituent (Thudichum's sphingomyelin); the filtrate contains the constituent phrenosin, which is phosphorus-free, and which is precipitable by adding acetone. Their optical activity is different, and the results given fully explain Wilson and Cramer's statements on this subject. Both yield fluid sphæro-crystals, but the appearances, which are figured, of these are very different in the two cases. W. D. H.

Kinetics of Enzymes. SVEN G. HEDIN (*Zeitsch. physiol. Chem.*, 1908, 57, 468—475).—The velocity of the action of trypsin on caseinogen (the quantity of substrate being constant) is inversely proportional to the amount of the ferment. If white of egg is mixed with the caseinogen, the partition of the ferment between the two proteins is unequal. W. D. H.

Fermentative Cleavage of Polypeptides. VI. EMIL ABDERHALDEN and CARL BRAHM (*Zeitsch. physiol. Chem.*, 1908, 57, 342—347. Compare Abstr., 1908, i, 488).—A comparison is made of the action of intestinal juice and yeast juice on *D*-alanyl-glycine and glycyl-*L*-leucine. Both juices act at about the same rate. The same is true for their action on tripeptides, *D*-alanyl-glycyl-glycine being split into *D*-alanine and glycyl-glycine, and glycyl-*D*-alanyl-glycine being split into glycine and *D*-alanyl-glycine. W. D. H.

Accelerating Influence of Magnesium on Sugar Inversion. J. TRIBOT (*Compt. rend.*, 1908, 147, 706—707).—Yeast invertase was purified by successive precipitations from aqueous solution by alcohol, and its sacroclastic activity compared with the percentage and composition of the ash. Crude invertase gave 45.76% of ash, of which 1.8% consisted of MgO. In purified invertase, the ash was almost entirely MgO, which gradually diminished from 10.9% to 0.69% on further purification. The activity of the invertase also diminished. It is therefore supposed that magnesium oxide exercises a positive accelerating effect on sugar inversion. R. J. C.

Action of Colloidal Ferric Hydroxide on Expressed Yeast-juice. FRIEDRICH RESENSCHECK (*Biochem. Zeitsch.*, 1908, 15, 1—11).—By precipitating yeast-juice with colloidal ferric hydroxide, the former underwent a preliminary loss of fermentative power. The precipitate, when added to fresh yeast-juice, increased its power, and was also capable of reactivating old juice. The iron precipitate contained phosphorus, and other experiments indicated that it contained the co-enzyme. S. B. S.

Hydrolysis of Amygdalin by Emulsin. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1908, 246, 710. Compare Abstr., 1908, i, 817).—A reply to Feist (Abstr., 1908, i, 903), re-stating the author's contention. T. A. H.

Asymmetric Syntheses by means of Enzyme Action. LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1908, 14, 238—253).—*d*-Benzaldehydecyanohydrin can be synthesised by the action of emulsin on a mixture of benzaldehyde and 5% hydrocyanic acid.

In the experiments, the mixtures were placed in a shaking machine and kept at a constant temperature. The largest amounts of active cyanohydrin are formed at about 25°, and the optimum is reached after two to three hours. Comparative experiments with and without emulsin show that the emulsin acts as a catalyst, since a much larger percentage of the hydrogen cyanide is fixed during a given time when emulsin is present. The synthetical enzyme is apparently not identical with the hydrolysing enzyme, which is capable of hydrolysing emulsin, since a 2% emulsin solution when heated at 45° during eight days can no longer act on amygdalin, although it is capable of synthesising benzaldehydecyanohydrin to a certain extent. The amount of active cyanohydrin formed tends to increase with the amount of emulsin present, but an excess of hydrogen cyanide has but little effect; the greatest optical effect is produced when a considerable excess of benzaldehyde (more than 1 equivalent) is added slowly to a mixture of emulsin and hydrocyanic acid (less than 1 equivalent).

The mandelic acid obtained by hydrolysing the active nitrile is the pure *l*-acid, with $[\alpha]_D - 153.78^\circ$.

Reductases in yeast and milk appear to be able to reduce benzoyl-formic acid to *l*-mandelic acid. J. J. S.

The Rennet from Decapod Crustaceans. C. GERBER (*Compt. rend.*, 147, 708—710).—The preparations were made both from gastric juice and by maceration of the hepatic glands. The rennet thus obtained differs from other rennets of animal origin in its resistance to the action of heat and of acids. In this respect it is similar to the rennets of vegetable origin. Neutral salts of alkalis and alkaline earths accelerate the action when in small quantities, but retard it when in larger quantities. S. B. S.

The Effect of Dialysis on Juices of Vegetable Origin containing Rennet. C. GERBER (*Compt. rend.*, 1908, 147, 601—603).—The juices from *Ficus Carica* and *Broussonetia papyrifera*

were the subjects of experiment. On submitting them to dialysis, they lost their rennet-like action, and a precipitate formed at the same time. The latter, however, on solution in 5% sodium chloride, exerted a much stronger action than the solution from which it had separated, salt being added to the latter. The rennet-like enzyme appears therefore to be either a globulin or to be carried down with the globulins.

S. B. S.

Destruction of Rennet by Light. SIGNE SCHMIDT-NIELSEN and SIGVAL SCHMIDT-NIELSEN (*Zeitsch. physiol. Chem.*, 1908, 58, 233—254).—The weakening of rennet by light is a unimolecular reaction. The reaction velocity, as in other photochemical reactions, is but little influenced by temperature. The most active rays are those between 220 and 250 $\mu\mu$; about 4% of the action is due to rays between 250 and 313 $\mu\mu$, and about 0.3% to visible rays.

W. D. H.

Peroxydase Accelerators and their Possible Significance for Biological Oxidations. JOSEPH H. KASTLE (*Amer. Chem. J.*, 1908, 40, 251—266).—It is well known that, owing to the liability of cows' milk to vary considerably in peroxydase activity, the application of the peroxydase reaction for discriminating between raw and boiled milk is not admissible. Recently, however, Kastle and Porch (Abstr., 1908, ii, 409) have shown that this power of milk to induce the reaction may be greatly intensified by the addition of certain phenols. The author now shows that with some specimens of fresh cows' milk, over thirty times as much phenolphthalein is oxidised in the presence of the three cresols as is oxidised by the milk and hydrogen peroxide alone; and on an average three times as much. With β -naphthol the average is about eight times. In general, the activity of the peroxydase, from whatever source, is found to be greatly increased by phenol, the cresols, and β -naphthol. Tables are given showing the effect of various substances on the peroxydase activity of extracts of horse-radish root, malt, and human saliva. It is suggested that peroxydase accelerators act as auxiliary oxygen carriers, and are themselves oxidised more or less completely by such processes, and are of considerable significance in biological oxidations.

J. V. E.

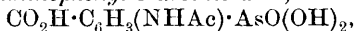
Hydrogenase or Reductase? J. GRÜSS (*Ber. Deut. bot. Ges.*, 1908, 26a, 627—630).—The author discusses the reductions effected by the yeast cell, and concludes that they are effected by nascent hydrogen, and are not due to any direct action of a yeast constituent on the substance reduced. This being the case, the enzyme producing the reduction should be called "hydrogenase" and not "reductase."

E. J. R.

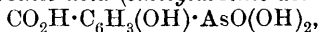
Some Homologues and Derivatives of Arsanilic Acid. II. Oxidation of Aminotolylarsinic Acids. ROBERT KAHN and LUDWIG BENDA (*Ber.*, 1908, 41, 3859—3865).—An investigation on the carboxylic acids obtained by oxidising the acetyl derivatives

of the methyl homologues of arsanilic acid (compare Abstr., 1908, i, 591).

1-Carboxy-6-acetaminophenyl-3-arsinic acid,



is prepared by oxidising 6-acetaminotolyl-3-arsinic acid in aqueous solution with potassium permanganate; it crystallises in very long, slender, white needles, with $1\text{H}_2\text{O}$, m. p. about 230° (decomp.), and when hydrolysed with alkali or acid yields *1-carboxy-6-aminophenyl-3-arsinic acid* (*anthranilarsinic acid*), $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{AsO}(\text{OH})_2$, crystallising in slender needles, m. p. 245° (decomp.). The latter substance may be diazotised and coupled with amines and phenol. An aqueous solution of the diazo-sulphate when heated yields *1-carboxy-6-hydroxyphenyl-3-arsinic acid* (*salicylarsinic acid*),

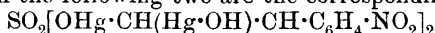


which crystallises in small, transparent, rhombic plates and commences to decompose at 325° .

1-Carboxy-5-acetaminophenyl-2-arsinic acid, $\text{C}_9\text{H}_{10}\text{O}_6\text{NAs}$, crystallises in brittle needles, m. p. about 260° (decomp.). It is decomposed by acids, but is hydrolysed by alkalis, yielding *1-carboxy-5-aminophenyl-2-arsinic acid*, $\text{C}_7\text{H}_8\text{O}_5\text{NAs}$, which forms thin, transparent, colourless leaflets.

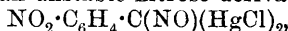
W. H. G.

Preparation of *o*-Nitrobenzaldehyde and *o*-Nitrobenzaloxime. KALLE & Co. (D.R.-P. 199147. Compare Abstr., 1907, i, 1046).—The dimercury compound of *o*-nitrotoluene has the formula $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\begin{smallmatrix} \text{Hg} \\ \text{Hg} \end{smallmatrix}\text{O}$, and yields two series of (basic and normal) salts, of which the following two are the corresponding *sulphates*:

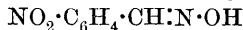


and $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\begin{smallmatrix} \text{Hg}\cdot\text{O} \\ \text{Hg}\cdot\text{O} \end{smallmatrix}\text{SO}_2$.

The sparingly soluble *dinitrite*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{Hg}\cdot\text{NO}_2)_2$, is best prepared by shaking together a paste of the mercury base, sodium nitrite, and 10% sulphuric acid. When treated with 25% hydrochloric acid, this dinitrite decomposes, giving rise to *o*-nitrobenzaldehyde and *o*-nitrobenzaloxime in approximately equal amounts. It is assumed that nitrous acid and an unstable nitroso-derivative,



are first formed, and that the latter is further decomposed into



and mercuric chloride; the nitrous acid reacts with some of the oxime, giving rise to the corresponding aldehyde. G. T. M.

Organic Chemistry.

Density of Methane; Atomic Weight of Carbon. GEORGES BAUME and F. LOUIS PERROT (*Compt. rend.*, 1909, 148, 39—42).—The methane was prepared by the action of water on magnesium methyl iodide, and, after being passed through different reagents and then dried, was purified by liquefaction and fractional distillation. The density determinations were carried out in three bulbs of different size in the usual way. As a mean of nine moderately concordant experiments, the weight of a litre of the gas at 0°/760 mm. is 0.7168 gram. From the results, the atomic weight of carbon is calculated by the physico-chemical methods of Leduc, D. Berthelot, and Guye respectively; the mean value is $C=12.004$ ($H=1.0077$), in good agreement with the accepted value. G. S.

Hydrocarbons, C_5H_{12} ; New Synthesis of Tetramethylmethane [Dimethylpropane]. ENOS FERRARIO and F. FAGETTI (*Gazzetta*, 1908, 38, ii, 630—634).—Dimethylpropane may be prepared by the action of (1) methyl magnesium iodide on *tert.*-butyl iodide (15—20% yield); (2) *tert.*-butyl magnesium iodide on methyl iodide (15—20% yield); (3) methyl sulphate on *tert.*-butyl magnesium iodide (75% yield). The *tert.*-butyl alcohol required in the last of these syntheses may be obtained in 75% yield by the action of carbon dioxide on methyl magnesium iodide (compare Grignard, *Abstr.*, 1904, i, 213). T. H. P.

Synthesis of Ethylene from Carbon Monoxide and Hydrogen by Contact with Nickel and Palladium. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1588—1590).—When a mixture of approximately equal volumes of carbon monoxide and hydrogen is passed over pieces of coke impregnated with reduced nickel and palladium and heated at 95—100°, no formaldehyde is produced, the gaseous mixture obtained consisting of carbon monoxide, hydrogen, and ethylene, with a small proportion of air. In one experiment, the gases contained 6.6% of ethylene, and in another, 8.3%. The first part of the reaction probably consists in the reduction of the carbon monoxide to water and the methylene group: $CO + 2H_2 = H_2O + CH_2$, two methylene groups then combining to form ethylene.

Attempts to absorb the ethylene in the mixture of gases formed by means of bromine or bromine water met with failure, which the author accounts for by the great dilution of the ethylene with other gases. A concentrated solution of potassium mercuric iodide, $HgI_2, 2KI$, in sodium hydroxide constitutes a far more certain absorbent of ethylene than either bromine or bromine water.

The formation of ethylene instead of methane, which would be expected from the results of Sabatier and Senderens and of Ipatieff, is not in accord with the thermal changes occurring during these

reactions, which would indicate the formation of methane rather than ethylene.

When a mixture of carbon dioxide and hydrogen is passed over coke impregnated with nickel and palladium and heated at 95—100°, the resultant gases do not contain either formaldehyde, ethylene, or methane.

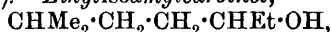
At higher temperatures, also, no formation of formaldehyde is observable, carbon dioxide and hydrogen yielding ethylene and methane; this observation is not in accord with those of other investigators, who state that only methane is formed by the reduction of carbon dioxide. The carbon dioxide first undergoes reduction in the presence of heated coke to carbon monoxide, which is then reduced to ethylene and methane.

T. H. P.

Preparation of Nitromethane. WILHELM STEINKOPF (*Ber.*, 1908, 41, 4457—4458).—A modification of the original Preibisch method (this Journ., 1874, 462), which not only gives a much better yield of nitromethane, but also avoids the evolution of hydrogen cyanide. A solution, containing potassium chloroacetate (=200 grams of acid) and 300 grams of potassium nitrite in one litre of water, is heated in a flask fitted to a condenser until carbon dioxide begins to be evolved. The reaction then proceeds, and the nitromethane distils in the steam. The yield is 49% of the theoretical.

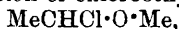
W. R.

Ethylisoamylcarbinol and Methylisohexylcarbinol. ARMAND BUELENS (*Bull. Acad. roy. Belg.*, 1908, 921—929. Compare Henry, *Abstr.*, 1906, i, 723).—*Ethylisoamylcarbinol*,



m. p. 61°, b. p. 165—166°, $D_{20} 0.8084$, $n_D 1.42011$, obtained by the action of magnesium *isoamyl* bromide on propaldehyde, is a liquid of pleasant odour and burning taste. The *acetyl* derivative, b. p. 184—185°, $D_{20} 0.8554$, $n_D 1.41602$, is a colourless, mobile, pleasant-smelling liquid.

Methylisohexylcarbinol, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OH}$, b. p. 171—172°/760 mm., $D_{20} 0.8128$, $n_D 1.42381$, obtained by the interaction of magnesium *isohexyl* bromide with acetaldehyde, is a liquid of agreeable odour and sharp taste. The *acetate*, b. p. 187—188°/768 mm., $D_{20} 0.8494$, $n_D 1.4137$, is a colourless, mobile, pleasant-smelling liquid. *Methyl isohexyl ketone*, b. p. 166°/770 mm., $D_{20} 0.8151$, obtained by oxidising the alcohol with chromic acid, is a colourless liquid, and forms a sodium bisulphite compound. The *methyl ether*, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OMe}$, b. p. 149—150°/760 mm., $D_{20} 0.7945$, obtained by the action of chloroethyl methyl ether,



on magnesium *isohexyl* bromide, is a liquid of agreeable odour.

β-Methylheptane, $\text{CHMe}_2 \cdot [\text{CH}_2]_4 \cdot \text{CH}_3$, b. p. 118°/760 mm., $D_{20} 0.7134$, $n_D^{20} 1.39807$, was obtained by the action of metallic sodium on a mixture of propyl iodide and *isoamyl* iodide, the normal hexane and the decane simultaneously formed being eliminated by fractional distillation. It is a colourless, very mobile, pleasant-smelling liquid.

The *isohexyl* alcohol, b. p. 147—148°, used in the research was prepared by the action of trioxymethylene on magnesium *isoamyl* bromide in presence of zinc chloride. *isoHexyl bromide*, b. p. 146—147°/760 mm., D^{20} 1.1683, n_D 1.44897, obtained by saturating the alcohol with hydrogen bromide and warming in a closed vessel, is a colourless, mobile liquid of slight, not unpleasant odour.

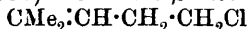
T. A. H.

Direct Dehydration of Certain Tertiary Alcohols. LOUIS HENRY (*Compt. rend.*, 1908, 147, 1260—1262).—In the production of $\beta\gamma$ -dimethyl- Δ^{α} -butylene and $\beta\gamma$ -dimethyl- Δ^{β} -butylene by heating dimethylisopropylcarbinol with acetic anhydride containing a small amount of sulphuric acid (Abstr., 1907, i, 374), it was originally considered that, since only a very small proportion of sulphuric acid was present, the acetic anhydride acted as the dehydrating agent. Delacre, however, has shown (Abstr., 1907, i, 459) that dimethylisopropylcarbinol is transformed into its acetate by the action of acetic anhydride. Thus the sulphuric acid must be the active agent in the reaction, which seems to be a curious instance of catalysis. That the acetic anhydride takes part in the reaction, however, is shown by the fact that it is only in the presence of a few drops of sulphuric acid that the decomposition of the acetate already formed takes place more easily and more rapidly than that of the alcohol as such.

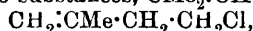
Contrary to the behaviour of dimethylisopropylcarbinol, cyclopropylmethylcarbinol (Abstr., 1908, i, 881), when heated with acetic anhydride containing a little sulphuric acid, does not undergo dehydration, but is completely transformed into its acetate. The conclusion is drawn that the existence of a closed chain in the molecule confers stability on the alcohol.

E. H.

$\gamma\gamma$ -Dimethylallylcarbinol. MAURICE VAN AERDE (*Bull. Acad. roy. Belg.*, 1908, 929—939).— ϵ -Chloro- β -methyl- Δ^{β} -amylene,



(Henry, Abstr., 1907, i, 106), yields a liquid *dibromide*, D^{20} 1.71, and is converted into the corresponding acetate (the *dibromide* of this has D^{20} 1.551) by heating in closed tubes with potassium acetate and acetic acid, and this, on treatment with potassium carbonate, yields $\gamma\gamma$ -dimethylallylcarbinol, $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, b. p. 157—158°/771 mm., D^{20} 0.8615, n_D 1.44416, a colourless liquid with a slight terebinthinous odour and sharp, acrid taste. On re-conversion into the *acetate*, D^{20} 0.9183, n_D 1.4303, by the action of acetic anhydride, the product obtained boiled at 165—175°, which would seem to indicate that the alcohol and chloride referred to above are mixtures, in spite of their constant boiling points. Having regard to its method of formation, the supposed chloride might consist of the two substances, $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ and



but it does not yield acetone on oxidation with chromic acid, as the second suggested constituent should do.

On adding acetic anhydride to the mixture resulting from the

action of magnesium methyl bromide on ethyl γ -chlorobutyrate (Abstr., 1907, i, 106), adding water, and extracting with ether, a mixture of ϵ -chloro- β -methylpentane- β -ol, $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Cl}$ (*loc. cit.*), and dimethyltetramethylene oxide, $\text{O} \begin{array}{c} \text{CMe}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 - \text{CH}_2 \end{array}$, was obtained in place of the expected chloroacetin, $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{OAc}$.

T. A. H.

Physico-chemical Properties of Ethylene Glycol and of its Solutions in Water. F. SCHWERS (*Bull. Acad. roy. Belg.*, 1908, 814—854).—The author has determined the densities of ethylene glycol and of its mixtures with water at temperatures from 0—100°, the specific heats of ethylene glycol and its mixtures with water, and the heats developed when it is mixed with water in various proportions. From the results obtained, which are given both in tabular and in graphic form, the following conclusions are drawn: (1) Ethylene glycol has D_4^{20} 1.12570, and its expansion by heat can be represented by the expression:

$$V_t = V_0(1 + 0.0005657t + 0.0000017074t^2 + 0.00000000293t^3).$$

(2) A contraction in volume, accompanied by a development of heat, occurs when ethylene glycol is mixed with water in any proportion. At 0° the maximum contraction (1.545% of the initial volume) is observed with a concentration of 58% of glycol and 42% of water, corresponding with the hydrate, $2\text{C}_2\text{H}_4(\text{OH})_2, 5\text{H}_2\text{O}$. The contraction decreases generally with increase in temperature, but between 50° and 70° a slackening in the rate of this decrease is observed for all concentrations, and is indicated by a flattening of the curves between these temperatures. This phenomenon, which seems to be connected with the boiling points of the components of the mixture, is also exhibited by mixtures of glycerol and water between 70° and 90°. Mixtures of the monohydric alcohols with water of certain concentrations undergo the same contraction at all temperatures, but a similar behaviour is not observed with aqueous solutions of the diols and triols. (3) The specific heat of ethylene glycol is 0.563 at 20° and 0.591 at 35°, whilst that of its aqueous solutions is always greater than that calculated additively from the specific heats of the glycol and of water (= 1). (4) The heat developed by mixing glycol with water reaches a maximum for the concentration of 37% of glycol and 63% of water, which corresponds with the hydrate, $\text{C}_2\text{H}_4(\text{OH})_2, 6\text{H}_2\text{O}$. It decreases with rise in temperature, but the diminution is relatively small, so that it is still positive at the boiling point. The system ethylene glycol–water follows the thermodynamic rule that the difference between the calculated and observed specific heats is equal to the coefficient of the heat of admixture.

In all the above respects, the properties of the diols are intermediate between those of the mono- and tri-hydric alcohols. E. H.

Expansion of Ethyl Ether and of Some Mixtures of the Ether and Ethyl Alcohol. WILLY BEIN (*Abhand. K. Normaleichungskom.*, 1908, 7, reprint from author).—The density, at 5°, 10°, 15°, 20°, 25°, 30°, 35°, 40°, 45°, 50°, 55°, 60°, 65°, 70°, 75°, 80°, 85°, 90°, 95°, 100°, is given for pure ethyl ether and for mixtures with ethyl alcohol in the following proportions: 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 parts of ether to 100 parts of alcohol.

15°, 20°, and 25°, of the purest commercial ethyl ether (Kahlbaum), $D_4^{15} = 0.7200$, of a specimen of ordinary commercial ether, $D_4^{15} = 0.7274$, and of two mixtures obtained by mixing Kahlbaum's ether with 5% and 10% of a commercial spirit containing 90% of alcohol by volume, have been determined. The two latter specimens had $D_4^{15} = 0.7280$ and 0.7354 respectively. As the investigations were carried out mainly for revenue purposes, no measurements were made with absolutely pure ethyl ether. The density determinations were made in a U-shaped dilatometer, the upper parts of the two branches being long, graduated capillary tubes; at the extreme ends the capillaries were so narrow that no appreciable error was caused by leaving them open.

The density results are probably accurate to some units in the fifth decimal place, and for convenience of reference they are also tabulated to 1 in 10,000. The mean expansion for 1°, $\epsilon_t = [(V_t/V_0) - 1]t$, between 0° and t° is as follows, allowance being made for the expansion of the glass:

Purest ether.....	0.001522 + 0.0000040 <i>t</i> .
Ether of $D = 0.7280$...	0.001480 + 0.0000042 <i>t</i> .
„ $D = 0.7354$...	0.001438 + 0.0000040 <i>t</i> .

The results are compared in detail with those obtained by previous observers.

In an appendix, the impurities which may be present in commercial ethyl ether, and the methods of detecting and removing them, are given. G. S.

Alkylated Halohydrin and Vinyl Ethers. PAUL HÖRING (*Ber.*, 1908, 41, 4459—4460. Compare *Abstr.*, 1908, i, 497).—Polemical. A reply to Houben (*Abstr.*, 1908, i, 935). W. H. G.

Action of Alkalis on Sodium Alkyl Thiosulphates. T. SLATER PRICE and DOUGLAS F. TWISS (*Ber.*, 1908, 41, 4375—4378. Compare *Trans.*, 1908, 93, 1395).—The formation of disulphides by the action of alkalis on complex organic thiosulphates was observed originally by Bernthsen (*Abstr.*, 1889, 775). The existence of Gutmann's thioethyl hydroperoxide (*Abstr.*, 1908, i, 497) is questioned. Fromm's experiments (*ibid.*, 1908, 969) are also regarded as pointing to the non-existence of this compound. The authors' previous view of the reaction between alkalis and alkyl thiosulphates is adhered to.

J. J. S.

Indirect Analysis by means of the Dilatometer. Lower Hydrate of Sodium Acetate. W. LASH MILLER (*J. Physical Chem.*, 1908, 12, 649—654).—When sodium acetate trihydrate is heated, it partly melts at 58°, with formation of a solution and separation of a new salt occurring in leaflets. The leaflets consist of a normal acetate of sodium, but they cannot readily be separated from the solution for purposes of analysis.

It is shown, however, on the basis of the phase rule, that the composition of the leaflets can be deduced by adding to a definite quantity

of the trihydrate a known amount of the anhydrous acetate, and determining the proportion of trihydrate present in equilibrium at 58°. The amount of trihydrate present has been determined by dilatometer measurements. In this way it is shown that the leaflets consist of the anhydrous salt, a conclusion confirmed by the direct experiments of Green (next abstract). G. S.

The Melting Point of Hydrated Sodium Acetate. Solubility Curves. W. F. GREEN (*J. Physical Chem.*, 1908, 12, 655—660).—The leaflets separating when sodium acetate is heated to its apparent melting point at 58° have been drained at 95°, and shown by analysis and m. p. determination to be the anhydrous salt.

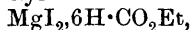
The solubility of the anhydrous salt has been determined from 0° to 123°, the boiling point of the saturated solution, and that of the trihydrate from its cryohydric point to 58°. The latter temperature is a transition point, at which the reaction $\text{CH}_3\cdot\text{CO}_2\text{Na}\cdot 3\text{H}_2\text{O} = 0\cdot092\text{CH}_3\cdot\text{CO}_2\text{Na} + \text{solution } (0\cdot098\text{CH}_3\cdot\text{CO}_2\text{Na} + 3\text{H}_2\text{O})$ is in equilibrium.

The lowest temperature at which a clear solution can be obtained is 79°, when the solution saturated with the anhydride has the same composition as the crystals of the trihydrate. G. S.

Molecular Compounds of Magnesium Bromide and Iodide with Derivatives of Acetic and other Organic Acids. BORIS N. MENSCHUTKIN (*Zeitsch. anorg. Chem.*, 1909, 61, 100—118. Compare Abstr., 1907, i, 19, 395).—Magnesium iodide combines with methyl acetate, forming the compound $\text{MgI}_2\cdot 6\text{CH}_3\cdot\text{CO}_2\text{Me}$. Mixtures containing from 2·5% to 74·5% of the compound separate into two layers on melting. On the other hand, the ethyl, propyl, and *iso*-butyl acetate compounds, $\text{MgI}_2\cdot 6\text{CH}_3\cdot\text{CO}_2\text{Et}$, $\text{MgI}_2\cdot 6\text{CH}_3\cdot\text{CO}_2\text{Pr}^a$, and $\text{MgI}_2\cdot 6\text{CH}_3\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9^{\beta}$, give regular freezing-point curves, and do not separate into two liquid layers. Separation into two layers is brought about in the case of the ethyl acetate compound by the addition of a little water.

Magnesium bromide forms compounds containing 3 mols. of ester, which, however, crystallise badly.

Magnesium iodide and ethyl formate form a compound,



which is less hygroscopic than the acetate compounds.

The following compounds have been prepared, but not further described:

$\text{MgBr}_2\cdot 2\text{C}_6\text{H}_5\cdot\text{CO}_2\text{Et}$, m. p. about 110°; $\text{MgBr}_2\cdot 2\text{C}_6\text{H}_5\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9^{\beta}$, m. p. about 130°; $\text{MgI}_2\cdot 3\text{C}_6\text{H}_5\cdot\text{CO}_2\text{Me}$, m. p. 115—117°; $\text{MgI}_2\cdot 3\text{C}_6\text{H}_5\cdot\text{CO}_2\text{Et}$, m. p. 105°.

Ethyl malonate gives $\text{MgBr}_2\cdot 2\text{CH}_2(\text{CO}_2\text{Et})_2$, m. p. 135°, and $\text{MgI}_2\cdot 4\text{CH}_2(\text{CO}_2\text{Et})_2$, m. p. about 115°. C. H. D.

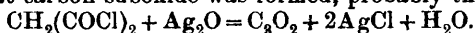
The Waxes of the Coniferæ. A New Group of Natural Principles. J. BOUGAULT and LÉON BOURDIER (*Compt. rend.*, 1908, 147, 1311—1314).—By employing the method described by Bourquelot (*J. Pharm. Chim.*, 1901, [vi], 14, 481), the authors have isolated white,

crystalline powders, resembling certain known vegetable waxes in appearance, from many of the Coniferae, for example, from *Juniperus Sabina*, *J. communis*, *Picea excelsa*, *Pinus sylvestris*, and *Thuja occidentalis*. Kawalier, the only previous worker on these substances (*J. pr. Chem.*, 1853, 60, 321; 1855, 64, 16), owing to the defective method used, obtained erroneous results. The purified wax is not a simple substance, that from *J. Sabina* having m. p. 73—78° and yielding, on repeated recrystallisation, a series of substances having m. p.'s 65° to 84°. All the substances isolated, however, have the following properties: they are acids with an acidity value varying from 25 to 54 (indicating a molecular weight of 2000—1000 if they are monobasic acids), contain an alcohol group, and are esters with saponification values of about 230. All their saponification products are acids, that is, the waxes do not give any substances analogous to glycerol, or cetyl or melissyl alcohol. Thus the products of saponification are alcohol-acids, and from the results obtained on acetylation, seem to contain only a single alcohol and carboxyl group. So far only two of these acids have been isolated. The first has the composition, $C_{16}H_{32}O_3$, of a hydroxypalmitic acid, it has m. p. 95°, and is designated *juniperic acid*. The second, *sabinic acid*, m. p. 84°, seems to be a hydroxylauric acid, $C_{12}H_{24}O_3$. By connoting the results obtained, the authors deduce the scheme

$R:CH(OH) \cdot [CH_2]_n \cdot CO \cdot O \cdot CHR' \cdot [CH_2]_m \cdot CO \cdot O \cdot CHR'' \cdot [CH_2]_p \cdot \dots CO_2H$
for the constitution of the waxes, R, R', R'', etc., and n, m, p being either identical or different. The frequent appearance of juniperic acid suggests that they are generally identical. The name *etholides* is proposed for this group of natural substances, which probably differ by the number of acid-alcohol molecules associated in them rather than by differences in the acid-alcohol molecules themselves. They thus resemble the polypeptides more nearly than the polysaccharides.

E. H.

Ketens. XI. New Method of Formation of Carbon Suboxide. HERMANN STAUDINGER and ST. BEBEZA (*Ber.*, 1908, 41, 4461—4465. Compare Staudinger and Ott, *Abstr.*, 1908, i, 602).—In attempting to prepare malonic anhydride by acting on malonyl chloride in ether or ethyl acetate with silver, lead, or zinc oxide, it was found that carbon suboxide was formed, probably thus:



Carbon suboxide is also obtained when malonyl chloride is treated with either silver oxalate or malonate; however, in none of these cases does the yield of carbon suboxide exceed 10%.

Silver malonate interacts with acid chlorides, such as cinnamoyl chloride, yielding small quantities of carbon suboxide; the latter must result from the decomposition of malonic anhydride or a mixed anhydride; consequently, malonic anhydride differs from its alkyl derivatives in that it yields carbon suboxide and not keten when it decomposes. Acetyl chloride forms with silver malonate a substance which is probably identical with that obtained by Diels and Lalin (*Abstr.*, 1908, i, 939) by acting on carbon suboxide with acetic acid. It is also probable that the analogous compound derived from carbon

suboxide and formic acid (*loc. cit.*) is a mixed anhydride of formic and malonic acid having the formula $\text{CH}_2(\text{CO}\cdot\text{O}\cdot\text{CHO})_2$. A compound having this constitution, when heated, would decompose, yielding carbon monoxide, carbon suboxide, carbon dioxide, acetic acid, and formic acid.

A 50—80% yield of carbon suboxide may be readily obtained by treating a solution of dibromomalonyl chloride in ether or ethyl acetate with zinc shavings.

Dibromomalonyl chloride, $\text{CBr}_2(\text{COCl})_2$, prepared by the action of phosphorus pentachloride on an ethereal solution of dibromomalonic acid, is a colourless oil, b. p. $75-77^\circ/15\text{ mm.}$, which solidifies to a colourless, crystalline mass at the ordinary temperature. It reacts with aniline, forming *dibromomalonanilide*, $\text{CBr}_2(\text{CO}\cdot\text{NHPh})_2$, compact crystals, m. p. $143-144^\circ$. W. H. G.

Action of Zinc Dust at High Temperatures on Various Types of Aliphatic and Aromatic Acids. ALEXANDRE HÉBERT (*Bull. Soc. chim.*, 1909, [iv], 5, 11—19).—A continuation of previous work (Abstr., 1901, i, 251; 1903, i, 396) on the products of the distillation of acids with zinc dust. The acids were mixed with from three to four times their weight of zinc dust, and heated at $350-400^\circ$.

Succinic acid yielded carbon dioxide and inflammable gases, composed principally of hydrogen, water, and liquid olefines. The residue in the flask contained some carbon and zinc carbonate. Oxalic acid gave hydrogen, carbon dioxide, carbon monoxide, and water. Benzoic acid furnished hydrogen, carbon dioxide, water, benzene, benzaldehyde, some unchanged benzoic acid, and a little naphthalene. The decomposition which ensued with cinnamic acid was very complicated. The gases evolved consisted of carbon dioxide, hydrogen, and some hydrocarbons. The liquid distillate included water, benzene, toluene, xylene, styrene, diphenyl, naphthalene and its homologues, stilbene, fluorene, fluoranthrene, homologues of anthracene and phenanthrene, toluene, and phenylmethanes (?) with some tarry matters. The residue in the flask contained carbon and some zinc carbonate. Distillation of cinnamic acid with lime showed that styrene is not, as is generally supposed, practically the sole product of the reaction. The distillate resembled in composition that described above, but contained more benzene and a little benzaldehyde.

Phthalic acid gave carbon dioxide, hydrogen, gaseous hydrocarbons, water, benzene, phthalic anhydride, and tar. T. A. H.

Action of Sulphuric Acid on Acetaldehyde and Paracetaldehyde. Preparation of Crotonaldehyde. MARCEL DELÉPINE (*Compt. rend.*, 1908, 147, 1316—1318*).—The method of preparing crotonaldehyde described previously (Abstr., 1902, i, 133) has been improved by using paracetaldehyde instead of acetaldehyde. Paracetaldehyde (50 grams) is added in portions of 10—15 grams to ordinary concentrated sulphuric acid (250 c.c.) contained in a flask, which is continually shaken and cooled by a stream of cold water. After fifteen minutes, the product is diluted to 2 litres with water and

* and *Ann. Chim. Phys.*, 1909, [viii], 16, 136—144.

distilled. By rectification of the product, 43% of the theoretical yield of crotonaldehyde is obtained. In the reaction there are also formed a compound, $C_8H_{12}O_2$, b. p. 92—98°/30 mm., which seems to be a bimolecular polymeride of crotonaldehyde, and a considerable amount of resin. The new polymeride differs from those described by Kekulé (*Annalen*, 1872, 162, 105), Raper (*Trans.*, 1907, 91, 1831), and Zeisel and Bitió (*Abstr.*, 1908, i, 761) in that it forms a *semicarbazone*, $C_9H_{15}O_2N_3$, m. p. 191—194°, and a stable *oxime*, m. p. 106°. The resins formed are fawn-coloured, and on oxidation with nitric acid give oxalic acid and a yellow, amorphous substance, which dissolves in ammonia to an orange solution. E. H.

Anodic Oxidation of Aldehydes. GEORGE W. HEIMROD and PHOEBUS A. LEVENE (*Ber.*, 1908, 41, 4443—4448).—It has already been shown that acetaldehyde is a good depolariser in acid solution (Dony-Hénault, *Abstr.*, 1900, ii, 644) and in alkali solution (Baur, *Abstr.*, 1902, i, 77), and further, Law (*Trans.*, 1905, 87, 198) obtained quantities of carbon dioxide and monoxide as well as the corresponding fatty acid on electrolytic oxidation.

Acetaldehyde in sodium sulphate or 0.85*N*-sulphuric acid solution at 4—5° with a current of 1 ampere, using a spiral platinum electrode, is oxidised almost quantitatively to acetic acid, only small quantities of the oxides of carbon being liberated. In 0.9*N*-sodium hydroxide solution, however, only 92% of the oxygen is absorbed by the aldehyde, a large amount of carbon monoxide, dioxide, and oxygen being liberated in the anode gas. Formic acid is found in the liquid, and it is probable that acetic acid is only formed in small amount.

Butaldehyde and isobutaldehyde in *N*-alkali solution give only small amounts of acid and a large volume of carbon dioxide; in the latter case, acetone was found, but formic acid could not be detected.

W. R.

Syntheses by means of Mixed Organo-metallic Zinc Derivatives, β -Ketone Alcohols, and $\alpha\beta$ -Acyclic Unsaturated Ketones. EDMOND E. BLAISE and M. MAIRE (*Ann. Chim. Phys.*, 1908, [viii], 15, 556—576).—Mainly a résumé of work already published (compare *Abstr.*, 1907, i, 749; 1908, i, 79, 248, 318, 596); the following compounds are described for the first time: γ -Hydroxy- γ -ethylhexan- δ -one, $OH \cdot C_2Et_2 \cdot COEt$, b. p. 68°/11 mm., prepared by the action of magnesium ethyl iodide on ethyl semi-ortho-oxalate; γ -methyl- Δ^7 -hepten- ϵ -one, $CMeEt \cdot CH \cdot COEt$, b. p. 164°, forms a *semicarbazone*, m. p. 159°; ethyl acetoxy-sec.-butyl ketone [α -acetoxy- β -ethylpentan- γ -one], $OAc \cdot CH_2 \cdot CHEt \cdot COEt$, b. p. 102°/12 mm.; γ -methylenehexan- δ -one, $CH_2 \cdot C_2Et \cdot COEt$, b. p. 137°; β -acetoxy- γ -ethylhexan- δ -one, $OAc \cdot CHMe \cdot CHEt \cdot COEt$, b. p. 102°/12 mm.; β -methyl- Δ^6 -hexen- δ -one, $CMe_2 \cdot CH \cdot COEt$, b. p. 148°, forms a *semicarbazone*, m. p. 162°. Ethyl β -hydroxy- α -ethylisovalerate, $OH \cdot CMe_2 \cdot C_2Et \cdot CO_2Et$, b. p. 84°/9 mm.; the corresponding acid has m. p. 73°; ethyl $\beta\beta$ -dimethyl- α -ethylacrylate, $CMe_2 \cdot C_2Et \cdot CO_2Et$, b. p. 167°, obtained from the above ester by the action of phosphoric acid; the corresponding acid has

b. p. $100^{\circ}/10$ mm., and the *chloride*, b. p. $49^{\circ}/13$ mm., reacts with zinc ethyl to form β -methyl- γ -ethyl- Δ^{β} -hexen- δ one, $\text{CMe}_2\text{:CEt}\cdot\text{COEt}$, b. p. 164° , of which the *semicarbazone* has m. p. 117° . M. A. W.

Formation of Hydrocelluloses by means of Sulphuric Acid.

GEORG BÜTTNER and J. NEUMAN (*Zeitsch. angew. Chem.*, 1908, 21, 2609—2611. Compare Girard, Abstr., 1879, 779; Bumke and Wolfenstein, Abstr., 1899, 852; Tauss, *Ding. Poly. J.*, 1889, 286).—Amyloid, prepared by leaving cotton wool in contact with sulphuric acid (1.53) for several days, then carefully precipitating and washing, has the composition C 41.89, 42.00, and H 6.0, 6.07%.

An ideal hydrocellulose can be obtained by Ulzer's method (Wagner's *Jahresber.*, 1905, 192). The cotton is impregnated with 4% sulphuric acid, pressed, and kept at the ordinary temperature for four days or until dry, and then carefully heated at 75° for eight hours. When touched, the mass falls to a white powder, and its suspensions in acid have a colloidal nature and do not clear when kept. Analyses of the washed material dried at 100° gave C 43.86, H 5.41%, which agree with values required for the formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n\cdot\text{H}_2\text{O}$.

When this hydrocellulose is further treated with 50% sulphuric acid, sometimes it does not undergo any further change, sometimes it yields compounds of the types $3\text{C}_6\text{H}_{10}\text{O}_5\cdot\text{H}_2\text{O}$ and $2\text{C}_6\text{H}_{10}\text{O}_5\cdot\text{H}_2\text{O}$.

The hydrocelluloses are white powders with a gritty feel, and are resistant to acids and alkalis. With sulphuric acid and acetic anhydride, they yield cellulose acetates, which can be precipitated by water. They are coloured blue by zinc chloriodide, or a solution of iodine in potassium iodide solution, and have reducing properties, but are not turned black by the oxidising action of the atmosphere (compare Girard). J. J. S.

Humin Substances in Peat Wool ("Ouate de Tourbe").

L. ROGER and E. VULQUIN (*Compt. rend.*, 1908, 147, 1404—1406).—The humic acids extracted from peat wool by sodium hydroxide are derived from cellulose-like substances, from which they differ in containing more carbon and nitrogen. They contain neither pentosans nor hexosans; alcoholic hydroxyls still seem to be present, for acetyl derivatives and thiocarbonates can be formed, as in the case of cellulose. The benzene nucleus, the grouping $\cdot\text{CH}_2\cdot\text{CO}$, and double linkings are also present. G. B.

Example of Isodimorphism. [Ethylamine Halides.] H. MARAIS (*Compt. rend.*, 1909, 148, 45—47).—Ethylamine hydrochloride and the corresponding hydrobromide are monoclinic at the ordinary temperature. At 80° , the hydrochloride changes to a uniaxial modification, which fuses at 108° . At 83° , the hydrobromide is also changed to a uniaxial form, which melts at 146° . Further, in the superfused hydrobromide, an unstable, uniaxial form appears, which fuses at 118° , but under ordinary conditions rapidly changes to the stable form.

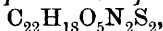
The monoclinic forms of the two compounds are miscible in all proportions, the temperature of transformation remains between 80°

and 83° . The forms obtained at higher temperatures are isomorphous, the stable form of one being isomorphous with the unstable form of the other. Further, as the composition approaches the point corresponding with 45% of the hydrobromide at 100° , the unstable forms tend to become relatively stable. G. S.

Valyl-leucine Anhydride. E. KRAUSE (*Monatsh.*, 1908, 29, 1119—1130).—The paper is mainly an account of unsuccessful experiments and of compounds already described (Fischer, *Abstr.*, 1907, i, 684). *Valyl-leucine anhydride*, m. p. 273 — 274° , is formed by heating equal molecular quantities of valine and leucine esters at 180 — 190° , or equal quantities of valine and leucine in an evacuated tube at 340° . C. S.

Some Amides of Amino-acids. ERNST KOENIGS and BRUNO MYLO (*Ber.*, 1908, 41, 4427—4443).—The amides of amino-monocarboxylic acids are not easily obtained in the pure state, but it is found that the ethyl esters are converted into the amides by liquid ammonia, and, as a rule, they are unstable in the presence of water.

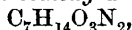
When the ester of glycine is treated with three times its volume of liquid ammonia, there is formed diketopiperazine, glycyglycinamide, and *glycinamide*, $C_2H_6ON_2$; the latter compound crystallises from chloroform in needles, m. p. 65 — 67° (corr.). It is strongly alkaline and hygroscopic. The *dinaphthalenesulphonylglycinamide*,



from naphthalenesulphonyl chloride and amide, crystallises in slender needles, m. p. 201° (corr., decomp.); β -naphthalenesulphonamide is obtained on its hydrolysis with *N*/10-sodium hydroxide, showing that the two naphthalenesulphonyl radicles are attached to the amidonitrogen and not to the amino-group. Carbethoxyglycinamide (Fischer, *Abstr.*, 1903, i, 609) may also be prepared from the amide by the action of ethyl chlorocarbonate in the presence of alkali, and a 10% yield of hydantoin is obtained from carbethoxyglycinamide by the action of *N*/2-sodium hydroxide during twenty-four hours at the ordinary temperature.

d-Alaninamide, $C_3H_5ON_2$, crystallises from chloroform in colourless, slender prisms, m. p. 72° (corr.), $[\alpha]_D + 6^{\circ}$ in 5.2% aqueous solution. The *dl*-alaninamide, prepared by liquid ammonia, agrees in all respects with that obtained by Franchimont and Friedmann in 1906. Carbethoxy-*dl*-alaninamide can be obtained in 86% yield from the amide (compare Fischer and Axhausen, *Abstr.*, 1905, i, 689), and α -methylhydantoin from the carbethoxy-compound has m. p. 146.5° (corr.). β -Naphthalenesulphonyl-*dl*-alaninamide, $C_{13}H_{14}O_5N_2S$, has m. p. 220° (corr., decomp.).

dl- α -Amino-*n*-butyramide, $C_4H_{10}ON_2$, crystallises in prisms, m. p. 74 — 75° (corr.), and yields carbethoxy-*dl*- α -amino-*n*-butyramide,



which forms colourless needles, m. p. 115 — 116° (corr.). α -Ethyl hydantoin, $C_5H_8O_2N_2$, crystallises from chloroform in slender needles, m. p. 118 — 120° (corr.), and β -naphthalenesulphonyl-*dl*-aminobutyramide, $C_{14}H_{16}O_5N_2S$, has m. p. 251° (corr., decomp.).

dl-Valinamide, $C_5H_{12}ON_2$, only results after the ester and liquid

ammonia have been in contact three months; it has m. p. 78—80° (corr.), and yields β -naphthalenesulphonyl-dl-valinamide, $C_{15}H_{18}O_3N_2S$, of m. p. 256—257° (corr.); carbethoxy-dl-valinamide, $C_8H_{16}O_3N_2$, slender needles, m. p. 143—144° (corr.).

dl-Leucinamide, $C_6H_{14}ON_2$, has m. p. 106—107° (corr.); the β -naphthalenesulphonyl derivative has m. p. 176—178° (corr.); carbethoxy-dl-leucinamide, $C_9H_{18}O_3N_2$, m. p. 108°, and β -isobutylhydantoin (compare Pinner and Lifschütz, Abstr., 1887, 1055) is readily obtained from the preceding compound by shaking with sodium hydroxide.

dl-Phenylalaninamide, $C_9H_{12}ON_2$, crystallises in prisms, m. p. 138—140° (corr.), and yields the β -naphthalenesulphonyl compound,

$C_{19}H_{18}O_3N_2S_2$, of m. p. 164—166° (corr.), and the carbethoxy-dl-phenylalaninamide, $C_{12}H_{16}O_3N_2$, m. p. 141° (corr.).

l-Tyrosinamide, $C_9H_{12}O_2N_2$, crystallises from alcohol in large, flat prisms, m. p. 153—154°, $[\alpha]_D^{20} + 19.49^\circ$ in water, and its dicarbethoxy-derivative, $C_{15}H_{20}O_6N_2$, forms needles, m. p. 185° (corr.); the mono-carbethoxy-l-tyrosinamide, $OH \cdot C_6H_4 \cdot CH_2 \cdot CH(NH \cdot CO_2Et) \cdot CO \cdot NH_2$, has m. p. 155—157° (corr.). The dinaphthalenesulphonyl compound, $C_{29}H_{24}O_6N_2S_2$, has m. p. 204° (corr.).

Carbethoxy-l-asparagine, $C_7H_{12}O_5N_2$, crystallises from water, and has m. p. 169—171° (corr.); the β -naphthalenesulphonyl-l-asparagine, $C_{14}H_{14}O_5N_2S$, has m. p. 192—193° (corr.). W. R.

Preparation of Glycocyamines or Guanino-acids. HENRIK RAMSAY (*Ber.*, 1908, 41, 4385—4393. Compare Strecker, *Compt. rend.*, 1861, 52, 1212; Duvillier, Abstr., 1880, 897; 1887, 850; Nencki and Sieber, Abstr., 1879, 70).—One of the simplest methods for the preparation of guanino-derivatives of fatty acids (glycocyamines) is warming the halogenated fatty acid with a large excess of guanidine (5—10 mols.) and a little water. With the simpler compounds up to bromoisohexoic acid, a temperature of 60° for a few hours is sufficient. With the derivatives of higher fatty acids, for example, bromopalmitic acid or α -bromophenylacetic acid, eight hours at 100° or ten hours at 80° are necessary. Guaninoacetic, α -guaninopropionic, α -guanino-*n*-butyric, α -guaninoisovaleric, α -guaninoisohexoic, α -guaninopalmitic, and α -guaninophenylacetic acids have been prepared by this method.

α -Guaninopropionic acid (alacreatine) has m. p. 226° (corr.) when quickly heated, whereas Baumann gives (Abstr., 1873, 1024) m. p. 180°; the nitrate decomposes at 150°, and the sulphate at 155—160°.

α -Guanino-*n*-butyric acid (oxybutyrocyamine) crystallises from hot water in slender needles or rectangular prisms, and has m. p. 243—245° (corr., decomp.). The nitrate decomposes at 162°, and the sulphate at 165—168°.

α -Guaninoisovaleric acid (oxyvalerocyamine) forms rectangular plates, and has m. p. 242° (corr., decomp.). The nitrate decomposes at 172—176°, and the sulphate at 178—180°.

α -Guaninoisohexoic acid (α -aminohexocyamine) crystallises in needles, and decomposes at 242—243° (corr.). The nitrate decomposes at 177—180°, and the sulphate at 182—185°.

α-Guaninopalmitic acid, $\text{CH}_3 \cdot [\text{CH}_2]_{13} \cdot \text{C}(\text{CH}_4\text{N}_3) \cdot \text{CO}_2\text{H}$, crystallises from methyl alcohol in octahedra, has m. p. 173° (corr., decomp.), and dissolves in alkalis and in concentrated acids. The *nitrate*,

$(\text{C}_{17}\text{H}_{35}\text{O}_2\text{N}_3)_2, \text{HNO}_3$, crystallises in slender, glistening needles, and has m. p. $155\text{--}156^\circ$ (corr., decomp.). The *hydrochloride* decomposes at $132\text{--}134^\circ$ (corr.).

Phenylguaninoacetic acid (glycolylphenylguanidine), $\text{CH}_4\text{N}_3 \cdot \text{CHPh} \cdot \text{CO}_2\text{H}$, appears to be identical with the product obtained by Berger (Abstr., 1880, 802) from phenylcyanamide and glycine. The *nitrate*,

$(\text{C}_9\text{H}_{11}\text{O}_2\text{N}_3)_2, \text{HNO}_3$, decomposes at $220\text{--}226^\circ$, and the *hydrochloride* at $255\text{--}258^\circ$ (corr.).
J. J. S.

Acetamide as a Solvent. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1415—1434).—The author has determined the solubility curves of various salts in acetamide, only salts being chosen for which the solubility curves in water have been worked out. The results show that acetamide closely resembles water, both in the form of the solubility curves of salts in it and in other properties, for example, the ionising power. It may, indeed, be expected that every salt which forms hydrates will give corresponding compounds with amides, those formed with formamide and acetamide approximating in their properties most closely to those formed with water.

No hydrate of potassium iodide is known, yet Walker and Johnson (Trans., 1905, 87, 1597) state that this salt forms with acetamide a stable compound, $\text{KI} \cdot 6\text{COMe} \cdot \text{NH}_2$, m. p. 54° . Besides the fact that compounds of such a type are usually formed by haloid salts of metals of the second and higher groups, the low m. p. given argues against the existence of this compound. The author's investigation of the system acetamide-potassium iodide characterises this system as one in which the components do not combine. The curve, which has a form very closely resembling that of the water-potassium iodide curve, consists of two branches: (1) the curve of lowering of the m. p. of acetamide by the addition of potassium iodide, and (2) the curve of solubility of the iodide in acetamide. These two branches meet in a eutectic point, about 53° , the composition there corresponding approximately with the formula $\text{KI} \cdot 7 \cdot 1\text{COMe} \cdot \text{NH}_2$. Crystallisation from methyl alcohol of mixtures of potassium iodide and acetamide of the compositions $\text{KI} \cdot 6\text{COMe} \cdot \text{NH}_2$ to $\text{KI} \cdot 7\text{COMe} \cdot \text{NH}_2$ yielded apparently homogeneous crystals, which, however, the microscope showed were merely mixtures of crystals of potassium iodide and acetamide. Hence the conclusion is drawn that Walker and Johnson's compound, $\text{KI} \cdot 6\text{COMe} \cdot \text{NH}_2$, does not exist.

The diagram for the system acetamide-sodium bromide indicates the existence of the compound, $\text{NaBr} \cdot 2\text{COMe} \cdot \text{NH}_2$, which decomposes at $135\text{--}136^\circ$ (compare Titherley, Trans., 1901, 79, 413). Comparison of this diagram with that for the system water-sodium bromide shows that the three branches: (1) curve of lowering of m. p. of acetamide or water by addition of sodium bromide, (2) curve of solubility of

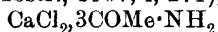
$\text{NaBr}, 2\text{H}_2\text{O}$ or $\text{NaBr}, 2\text{COMe}\cdot\text{NH}_2$, and (3) curve of solubility of pure sodium bromide, are practically identical in form in the two cases. The diacetamide compound is less stable than the dihydrate, a fact which may account for the non-existence of a compound,



corresponding with the pentahydrate.

The curve representing the lowering of the m. p. of acetamide by sodium iodide ends in a eutectic point, $41\cdot5^\circ$, corresponding with $\text{NaI}, 5\text{COMe}\cdot\text{NH}_2$, from which starts the curve of solubility in acetamide of the compound, $\text{NaI}, 2\text{COMe}\cdot\text{NH}_2$, which decomposes at 125° (compare Titherley, *Trans.*, 1901, 79, 413). In this case, also, no acetamide compound is formed corresponding with the pentahydrate.

In the system acetamide-calcium chloride, the eutectic point is very low, namely, 46° , corresponding with $\text{CaCl}_2, 3\text{COMe}\cdot\text{NH}_2$. Beyond this point comes the solubility curve of $\text{CaCl}_2, 6\text{COMe}\cdot\text{NH}_2$, continuing to the m. p., 64° ; this compound crystallises from methyl alcohol in hygroscopic plates. At 64° begins the solubility curve of the compound, $\text{CaCl}_2, 3\text{COMe}\cdot\text{NH}_2$, which crystallises in hygroscopic needles decomposing at 186° , the solid phase beyond this temperature being probably $\text{CaCl}_2, \text{COMe}\cdot\text{NH}_2$. Comparison of this diagram with that for the system water-calcium chloride shows that the solubility curves for $\text{CaCl}_2, 6\text{COMe}\cdot\text{NH}_2$ and $\text{CaCl}_2, 6\text{H}_2\text{O}$ are very similar; with acetamide, however, no compounds are formed analogous to the α - and β -tetrahydrates and the dihydrate. Like the solubility curve of $\text{CaCl}_2, 3\text{MeOH}$ (compare *Abstr.*, 1907, i, 271), that of



also closely resembles that of $\text{CaCl}_2, 2\text{H}_2\text{O}$. The triacetamide compound decomposes the trialcoholate with evolution of methyl alcohol, the compounds $\text{CaCl}_2, 3\text{MeOH}$, $\text{CaCl}_2, 3\text{COMe}\cdot\text{NH}_2$, and $\text{CaCl}_2, x\text{H}_2\text{O}$ being in order of increasing stability. T. H. P.

The Action of Chlorine on Carbamide, whereby a Dichloro-carbamide is Produced. FREDERICK D. CHATTAWAY (*Proc. Roy. Soc.*, 1908, A, 81, 381—388).—*Dichlorocarbamide*, $\text{CO}(\text{NHCl})_2$, prepared by passing a very rapid stream of chlorine into a well-cooled solution of carbamide (20 grams) in water (40 c.c.), separates in thin, colourless plates. The compound is endothermic, and detonates when heated rapidly, owing to the formation of nitrogen chloride; when heated cautiously it has m. p. about 83° (decomp.). It is readily hydrolysed by water, and when kept in aqueous solution at the ordinary temperature, carbon dioxide, nitrogen, nitrogen chloride, and ammonium chloride are formed slowly. Acids and alkalis accelerate the hydrolysis, and also alter the nature of the end products; thus in presence of dilute acids all the chlorine in the compound is liberated as nitrogen chloride, but this compound is not formed when hydrolysis takes place in alkaline solution. The addition of potassium hydroxide causes violent evolution of nitrogen, the reaction taking place quantitatively in accordance with the following equation:



When carbamide is treated with excess of an alkaline hypobromite,

it is probable that a dibromocarbamide is first formed; the manner in which this undergoes hydrolysis is supposed by the author to furnish an explanation of the variable amount of nitrogen liberated during the decomposition.

Dichlorocarbamide is an acidic substance, and its aqueous solution reddens and then bleaches litmus; it shows all the reactions of a typical nitrogen chloride. W. O. W.

Desmotropy and Merotropy. V. Constitution of Hydrogen Cyanide. ARTHUR MICHAEL and HAROLD HIBBERT (*Annalen*, 1909, 364, 64—76).—In continuation of previous work on the use of tertiary amines for distinguishing between enolic and ketonic derivatives (Michael and Smith, *Abstr.*, 1908, i, 943), the authors have applied this method towards the elucidation of the constitution of hydrogen cyanide.

When tertiary amines are brought into contact with anhydrous hydrogen cyanide at 0°, no salt is formed, but only a very slight polymerisation takes place. The rapidity of the latter decreases according to the series, triethyl-, tripropyl-, and triisooamyl-amine, that is, the capacity possessed by tertiary amines of polymerising hydrogen cyanide changes in the same relation as their capacity of enolising desmotropic ketones.

On the other hand, primary and secondary amines unite with hydrogen cyanide, forming unstable salts, and polymerisation does not take place. This can only be explained by the assumption that hydrogen cyanide exhibits keto-merotropy, and that primary and secondary amines can bring about merotropy in the substance, whilst tertiary amines can not. The authors' experiments show that the dialkyl- are less dissociable than the trialkyl-ammonium cyanides, that is, by substituting a hydrogen atom in $\text{NH}_2\text{R}_2\text{NC}$ by a third alkyl radicle, the affinity between hydrogen and nitrogen is lessened, and hence secondary amines can effect merotropy in hydrogen cyanide with the formation of salts, whilst tertiary amines can not. The existence of trialkylammonium cyanide shows that if hydrogen cyanide were in the acidic form (HNC), salt formation with tertiary bases would be possible. The conclusion is drawn, therefore, that hydrogen cyanide possesses the nitrile constitution HCN .

Dipropyl- and diisobutyl-ammonium cyanides are white, unstable salts; the latter has m. p. 25°. *Diisooamylammonium cyanide* is a white, crystalline, very unstable substance, m. p. 68—70°. *Piperidonium cyanide* is a white, crystalline salt, m. p. 47—48°; it is more stable than the other cyanides examined, being decomposed only after twenty minutes on keeping in a desiccator under diminished pressure.

isoButyl- and isoamyl-ammonium cyanides remain, on evaporation of their solutions in a vacuum, partly as oils and partly crystalline. *Allylammonium cyanide* is a viscid, yellow oil. Aniline does not react with hydrogen cyanide. From the rise of temperature (15°) observed on mixing 90% aqueous hydrocyanic acid and triethylamine at 0°, the authors conclude that salt formation takes place. By treating the trialkylammonium chlorides with silver cyanide in methyl-alcoholic solution, double salts are obtained. Thus trimethylammonium chloride

gives the *salt*, $\text{NMe}_3\text{HNC}\cdot\text{AgNC}$, a white, crystalline substance, and triethylammonium chloride yields the *salt*, $\text{NEt}_3\text{HNC}\cdot\text{AgNC}$, in white, felted needles. On adding hydrogen cyanide to an equimolecular mixture of triethylamine and water, and evaporation of the solution in a vacuum, an oil was obtained which gave the above double salt with silver cyanide, and hence contained *triethylammonium cyanide*. Tripropylamine behaves similarly.

Dry ammonia combines instantly with dry hydrogen cyanide or its ethereal solution to form ammonium cyanide. J. C. C.

Reaction between Ferric Salts and Thiocyanates. ARNALDO BRIONI (*Gazzetta*, 1908, 38, ii, 638—640).—The author criticises Bongiovanni's views (*Abstr.*, 1908, i, 770, 859) on the interaction of a ferric salt and a thiocyanate. T. H. P.

Simple Preparation of Mercuric Oxycyanide Solution from its Components. ERWIN RUPF and F. LEHMANN (*Chem. Zentr.*, 1908, ii, 1816; from *Apoth. Zeit.*, 1908, 23, 793—794. Compare *Abstr.*, 1908, i, 770).—The reaction indicated by the equation $\text{HgCl}_2 + \text{HgCy}_2 + 2\text{KOH} = \text{HgCy}_2\cdot\text{HgO} + 2\text{KCl} + \text{H}_2\text{O}$ is brought about by mixing aqueous solutions of molecular proportions of the components. For the preparation of a 1% solution, the following details are given: mercuric chloride, 5.8 grams; mercuric cyanide, 5.4 grams, dissolved in 800 grams of water, are added slowly to potassium or sodium hydroxide, 44.8 grams and water, 1000 grams. This solution contains 0.25% sodium chloride, or 0.32% potassium chloride. After keeping a solution of mercuric oxycyanide prepared in this manner for three months, the mercury, mercuric cyanide, and also the oxy-component were estimated, and the results were in good agreement with $\text{HgCy}_2\cdot\text{HgO}$. J. V. E.

Decomposition of Calcium Cyanamide. FELIX LÖHNIS and R. MOLL (*Centr. Bakt. Par.*, 1908, ii, 22, 254—281. Compare *Abstr.*, 1908, ii, 220, and Kappen, *ibid.*, 414).—It is considered probable that, in dissolving, calcium cyanamide is converted into the compound $\text{Ca}(\text{NH}\cdot\text{CN})_2$, which subsequently decomposes into calcium hydroxide and cyanamide. The latter, when heated with lime, or when subjected to the action of carbon dioxide, yields first ammonium cyanate and then carbamide, which is converted by bacteria into ammonium carbonate.

A direct action of bacteria on cyanamide seems to be impossible. The bacteria flora found in solutions of the substance consists of varieties which are able to resist the poisonous actions of cyanamide and cyanates.

Dicyanodiamide is not attacked by bacteria, and there is no evidence that it exists in soils. N. H. J. M.

Chemical Changes of Calcium Cyanamide in Manuring. HUBERT KAPPEN (*Centr. Bakt. Par.*, 1908, ii, 22, 281—298. Compare *Abstr.*, 1908, ii, 728).—A criticism of Löhnis' results and conclusions. When calcium cyanamide is digested for some time with distilled

water at 60°, the filtered solution yields crystals of dicyanodiamide. The same change takes place at the ordinary temperature when solutions are kept for a long time. In the case of concentrated solutions, the sparingly soluble compound, $\text{CN}\cdot\text{N}(\text{Ca}\cdot\text{OH})_2\cdot 6\text{H}_2\text{O}$, and cyanamide are formed, the latter changing gradually into dicyanodiamide under the influence of alkali. In dilute solutions the calcium compound is not formed; calcium hydroxide separates in crystals, whilst the cyanamide all remains in solution and gradually polymerises.

N. H. J. M.

[**Organo-mercury Compounds.**] WALTER SCHRAUTH and WALTER SCHOELLER (*Ber.*, 1908, 41, 4479—4480. Compare Abstr., 1908, i, 617).—A reply to Billmann (this vol., i, 17).

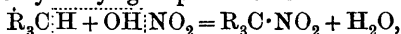
W. H. G.

Action of Nitric Acid on Saturated Hydrocarbons. II. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1570—1579. Compare Abstr., 1908, i, 329).—Experiments on the action of nitric acid (D 1·2) on *cyclohexane* show that the yield of nitro-products diminishes, and that of acid oxidation products increases, as the proportion of nitric acid used increases.

Nitrocyclohexane, $\text{C}_6\text{H}_{11}\cdot\text{NO}_2$, is a colourless liquid with a characteristic smell, b. p. 109·5°/40 mm., 202°/742 mm. (decomp.), D_4^{20} 1·0853, D_4^{19} 1·0680, n_D^{19} 1·4612.

This nitro-derivative is not an intermediate product in the oxidation of *cyclohexane* to adipic acid, as the latter is formed more readily from *cyclohexane* than from *nitrocyclohexane*. Such intermediate product is almost certainly unstable *isonitrocyclohexane*, which, immediately it is formed, is transformed partly into the stable *nitrocyclohexane* and partly into aldehyde (or ketone, according to the nature of the hydrocarbon), which undergoes further oxidation to the corresponding carboxylic acid.

The process of formation of tertiary nitro-derivatives is essentially different from that of primary or secondary nitro-compounds, the most striking difference lying in the mechanism of the formation of water in the two cases. In the first, water is formed from the tertiary hydrogen and the hydroxyl group of the nitric acid :



whilst with primary or secondary hydrocarbons, the oxygen atom only is taken from the nitric acid and the two hydrogen atoms from the hydrocarbon, $\text{R}_2\text{C}\cdot\text{H}_2 + \text{O}\cdot\text{NO}\cdot\text{OH} = \text{R}_2\text{C}\cdot\text{NO}_2\text{H} + \text{H}_2\text{O}$. T. H. P.

Preparation of 2-Chloro-3-nitrotoluene. ARNOLD F. HOLLEMAN (*Rec. trav. chim.*, 1908, 27, 455—457).—This paper contains details for the preparation of 2-chloro-3-nitrotoluene from 3-nitro-*o*-toluidine by means of the Sandmeyer reaction. An 84% yield is obtained, and the product has m. p. 21·5° (compare Wynne and Greeves, *Proc.*, 1905, 21, 151).

W. O. W.

Bromination of Toluene. II. ARNOLD F. HOLLEMAN and J. J. POLAK with VAN DER LAAN and EUWES (*Rec. trav. chim.*, 1908, 27, 435—454. Compare Abstr., 1906, i, 154).—The authors continue

the studies on the bromination of toluene, and in the present communication discuss the influence of temperature and dilution, and the action of catalysts on the ratio bromotoluenes : benzyl bromide.

Tables are given showing the percentages of benzyl bromide formed with various proportions of bromine and toluene at 25° and 50°. The authors claim that their results are more accurate than those obtained by Bruner and Dluska (Abstr., 1908, i, 146). On plotting in the form of a curve the values obtained by these authors in their experiments on the influence of temperature and comparing these with the data obtained by van der Laan, certain discrepancies appear, for which, at present, no explanation can be found.

To explain the action of catalysts, it has been supposed that these are capable of converting benzyl bromide into a mixture of bromotoluenes, no experimental evidence in support of this view could be obtained, however, since it was found that when benzyl bromide or chloride is boiled with toluene and ferric bromide, the sole product is *p*-benzyltoluene. A similar experiment, in which antimony tribromide was the catalyst, resulted in the formation of a small quantity of a liquid containing 50.9% bromine (bromotoluene requires 46.78%). Bromine itself was found to be incapable of behaving as an autocatalyst.

Cohen, Dawson, and Crosland (Trans., 1905, 87, 1034) have recorded the production of chlorotoluene by the action of nascent chlorine, generated by electrolysis, on boiling toluene. The hypothesis put forward by Bruner and Dluska (*loc. cit.*) and by Bancroft (Abstr., 1908, ii, 788), who suppose that the molecules of bromine attack the side-chain, whilst the atoms bring about substitution in the benzene nucleus, cannot, however, be sustained, inasmuch as a repetition of Cohen's experiments, using toluene and hydrogen bromide, showed that benzyl bromide and bromotoluene were both formed, but that the former underwent reduction by hydrogen produced in the electrolysis.

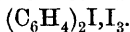
The suggestion is made that the true explanation is to be found in the existence of compounds of the type HBr_n , that these attack the benzene nucleus, whilst the molecules of bromine act only on the side-chain. This theory accounts satisfactorily for the influence of dilution, for the increase in the amount of benzyl bromide at higher temperatures, and for the increase in the proportion of bromotoluenes brought about by substances, such as acetic acid or nitrobenzene, which act as solvents for hydrogen bromide. An explanation is also afforded of the specific action of the bromides of iron, aluminium, and antimony, which also promote substitution in the ring.

W. O. W.

Properties of Diphenyleneiodonium Hydroxide and of some of its Derivatives. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 580—583; *Gazzetta*, 1908, 38, ii, 619—629. Compare Abstr., 1907, i, 1021).—On treating diphenyleneiodonium

iodide with moist silver oxide, it yields the hydroxide, $\text{C}_6\text{H}_4 > \text{C}_6\text{H}_4 \text{I} \cdot \text{OH}$, which is a strong base and could not be isolated, owing to the readiness with which it absorbs carbon dioxide from the air. In aqueous

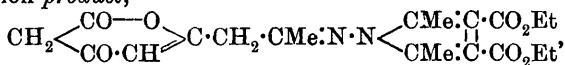
solution the hydroxide is reduced by sodium amalgam, giving an almost quantitative yield of diphenyl: $C_{12}H_8I \cdot OH + 2H_2 = C_{12}H_{10} + HI + H_2O$. This decomposition indicates the slight stability of the heterocyclic ring containing carbon and iodine, which is confirmed by the quantitative change of diphenyleneiodonium iodide into *o*:*o*-di-iododiphenyl when it is heated for a short time at its melting point. Evidence has been obtained of the formation of a periodide,



Diphenyleneiodonium bromide, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} > I \cdot Br$, separates from water as a white, crystalline powder, m. p. 245—250° (decomp.). When heated at its melting point, it is converted into 2-bromo-2'-iododiphenyl (?), m. p. 91.5°, which is under investigation. T. H. P.

Action of *N*-Amino-compounds on Dehydracetic Acid. CARL BÜLOW [with HANS FILCHNER] (*Ber.*, 1908, 41, 4161—4168).—Dehydracetic acid reacts with *p*-toluidine in alcoholic solution to form *dehydracetic-p-toluidide*, $CH_2 < \begin{matrix} CO-O \\ CO-CH \end{matrix} > C \cdot CH_2 \cdot CMe \cdot N \cdot C_7H_7$, crystallising in colourless needles, m. p. 154°. Boiling with 10% sodium hydroxide resolves it into its components again. It reacts with phenylhydrazine, *p*-toluidine being eliminated, and dehydracetic acid phenylhydrazone formed, crystallising in golden-yellow plates, m. p. 202°, and identical with the compound obtained by the direct interaction of phenylhydrazine and dehydracetic acid. It gives a characteristic blue coloration with concentrated sulphuric acid and a trace of ferric chloride, and is resolved on boiling with 10% sodium hydroxide into its components.

Ethyl-1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate condenses with dehydracetic acid in a similar manner to *p*-toluidine. The condensation product,



has m. p. 160°; it is of acid character, and dissolves in dilute alkali, whence it is precipitated by carbon dioxide.

Dehydracetic acid formylhydrazone, $C_8H_8O_3 \cdot N \cdot NH \cdot CHO$, crystallises in colourless needles, m. p. 154°, and likewise possesses a faintly acid character.

Dehydracetic acid semicarbazone, $C_8H_8O_3 \cdot N \cdot NH \cdot CO \cdot NH_2$, crystallises in colourless needles, m. p. 197—198°; it dissolves in weak alkali, and is precipitated unchanged in crystalline form by weak acids.

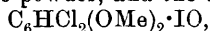
E. F. A.

Chromophores without Double Linkings. HUGO KAUFFMANN and IMMANUEL FRITZ (*Ber.*, 1908, 41, 4413—4422).—Ullmann and Loewenthal's 2-iodo-1:4-dimethoxybenzene (*Abstr.*, 1904, i, 725), m. p. 23°, b. p. 157°/10 mm., is conveniently obtained in 90% yield by treating an alcoholic solution of quinol dimethyl ether with iodine and mercuric oxide. A small quantity of *di-iodoquinol dimethyl ether*, $C_6H_2I_2(OMe)_2$, m. p. 171°, is also obtained. *Chloroiodoquinol dimethyl ether*, $C_6H_2ClI(OMe)_2$, m. p. 115°, in which the position of the chlorine

has not been ascertained, is prepared by treating a chloroform solution of 2-iodo-1:4-dimethoxybenzene at 0° with chlorine, digesting the red product with 10% sodium hydroxide, and treating the resulting iodoso-compound with an acidified solution of potassium iodide; it separates from alcohol in white needles. The *iododichloride*,



m. p. 45—50° (decomp.), is a brick-red, crystalline powder, prepared by the action of chlorine on a chloroform solution of chloriodoquinol dimethyl ether at 0°; by treatment with 10% sodium hydroxide it yields a white, amorphous *iodoso-compound*, $\text{C}_6\text{H}_2\text{Cl}(\text{OMe})_2 \cdot \text{IO}$, m. p. 106° (decomp.). *Dichloriodoquinol dimethyl ether*, $\text{C}_6\text{HCl}_2\text{I}(\text{OMe})_2$, m. p. 81°, is obtained when the preceding iododichloride is kept in a closed vessel for some days, and separates from alcohol in white, woolly crystals; the *iododichloride*, $\text{C}_6\text{HCl}_2(\text{OMe})_2 \cdot \text{ICl}_2$, m. p. 130°, is a citron-yellow, crystalline powder, and the *iodoso-compound*,



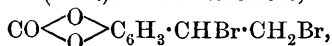
m. p. 70° (decomp.), is a white, amorphous substance.

Trichloriodoquinol dimethyl ether, $\text{C}_6\text{Cl}_3\text{I}(\text{OMe})_2$, m. p. 135°, crystallises in colourless needles, and is prepared by leading chlorine into a chloroform solution of 2-iodo-1:4-dimethoxybenzene, which is only slightly cooled, so that the final temperature is about 30°. The *iododichloride*, $\text{C}_6\text{Cl}_3(\text{OMe})_2 \cdot \text{ICl}_2$, m. p. 125—130° (decomp.), is a pale yellow, crystalline powder, and the *iodoso-compound*, $\text{C}_6\text{Cl}_3(\text{OMe})_2 \cdot \text{IO}$, m. p. 120—125°, prepared in the dark, is white and amorphous. *1:4-Dimethoxyphenyl di-iododichloride*, $\text{C}_6\text{H}_2(\text{OMe})_2(\text{ICl}_2)_2$, m. p. 50—60° (decomp.), prepared by leading chlorine into a chloroform solution of di-iodoquinol dimethyl ether at 0°, is an orange, crystalline powder, which by keeping for a few days in a closed vessel is converted into colourless *dichlorodi-iodoquinol dimethyl ether*. The *di-iodoso-compound*, $\text{C}_6\text{H}_2(\text{OMe})_2(\text{IO})_2$, is a yellow powder. C. S.

Nitroquinol Dimethyl Ether. HUGO KAUFFMANN (*Ber.*, 1908, 41, 4396—4412).—See this vol., ii, 107.

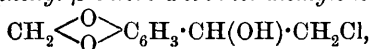
Fluorescence of Potassium Quinoldisulphonate. HUGO KAUFFMANN (*Ber.*, 1908, 41, 4422—4423).—In reply to Hantzsch (*Abstr.*, 1908, ii, 446), the author states that the fluorescence of potassium quinoldisulphonate, so far from being slight, is visible to the naked eye in an ordinary test-tube. C. S.

Derivatives of Ethyl Catechol. HERMANN PAULY and KARL NEUKAM (*Ber.*, 1908, 41, 4151—4161. Compare *Abstr.*, 1907, i, 916).—The dibromide of 3:4-dihydroxystyrene (vinylcatechol) methylene ether forms colourless, matted needles, m. p. 82° (compare Barger and Jowett, *Trans.*, 1905, 87, 967). When heated with bromine in carbon disulphide, a *tribromide*, m. p. 62°, crystallising in colourless needles, is formed. The cyclic carbonate, $\text{CO} \begin{smallmatrix} \diagup \text{O} \diagdown \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{CH} : \text{CH}_2$ (*Abstr.*, 1907, i, 916), exists in two forms: needles, m. p. 195° (corr.), and needles, m. p. 200° (corr.). The *dibromide*,



obtained by the action of bromine in carbon disulphide solution at -10° , crystallises in short, obliquely-cut prisms, m. p. $69-70^{\circ}$. Free vinylcatechol is best prepared by hydrolysis of the carbonate with aqueous pyridine. It is obtained as a deep yellow, viscid oil, which easily polymerises; it dissolves in fuming hydrochloric acid with a rose-red coloration, which disappears on dilution. The view formerly expressed that vinylcatechol exists in a quinonoid form is now held with all reserve.

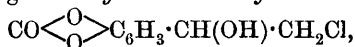
3 : 4-Dihydroxyphenyl- β -chloro- α -ethanol methylene ether,



prepared by the addition of hypochlorous acid to the styrene, was obtained as a yellow oil, which on purification by distillation in a vacuum formed a colourless, odourless oil, b. p. 157° (corr.)/9 mm., $163-164^{\circ}$ /13 mm. When kept, the chlorine content increases, and β -chloro-

*methylenedioxy*styrene, $\text{CH}_2 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{CH} : \text{CHCl}$, is formed with the elimination of water. This is also formed on slow distillation of the chlorohydrin; it is a transparent, colourless oil with an anise or piperonaldehyde-like odour, b. p. 138° /11 mm., $141-142^{\circ}$ /13 mm. It forms an oily additive *dibromide*. At the same time as the above chlorohydrin, a substance containing an additional atom of chlorine is formed by the action of hypochlorous acid; this crystallises in well-formed, glistening, colourless needles, m. p. 127.5° (corr.). It shows no catechol reaction when heated with sodium carbonate.

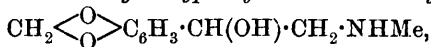
The corresponding *chlorohydrin* of the *cyclic carbonate*,



prepared in a similar manner, forms colourless crystals, m. p. $95-96^{\circ}$. The *bromohydrin*, prepared by the decomposition of the dibromide of vinylcatechol carbonate, separates in small, colourless prisms, which melt at 100° to a red liquid, and decompose to a greyish-violet dye, m. p. slowly heated 96° , or quickly heated, 107° . These carbonate derivatives give yellowish-brown colorations with ferric chloride.

The *chlorohydrin* of the *catechol* is obtained from the corresponding carbonate by heating with magnesium carbonate in acetone solution. The phenol is transferred to warm benzene, and quickly brought to crystallisation, using special precautions to prevent the formation of dyes. It crystallises in thin, colourless, pointed plates, m. p. 102° , decomposing instantly into a greyish-violet dye.

β -Methylamino-3 : 4-dihydroxyphenyl- α -ethanol methylene ether,

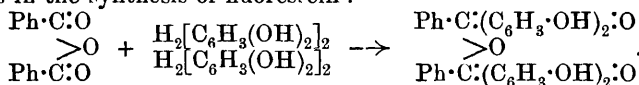


prepared by double decomposition of the chlorohydrin with methylamine, is a viscid, colourless oil with a faint violet fluorescence, b. p. 170° /12—13 mm. It turns litmus blue, and is perhaps identical with the methylalkamine described by Barger and Jowett (*loc. cit.*). The picrate forms small, yellow, sandy crystals, m. p. 188° (corr.) (Barger and Jowett give 178°). It unites with phenylcarbimide in alcoholic solution, forming in the first place an easily soluble oil, and subsequently, a crystalline compound, m. p. 155° , probably a hydrothiazole.

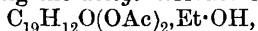
The carbonate of the chlorohydrin forms an amorphous base with methylamine very similar to epinephrine (Abel, Abstr., 1900, i, 72).

E. F. A.

Resorcinolbenzein. HANS VON LIEBIG (*J. pr. Chem.*, 1908, [ii], 78, 534—543. Compare Abstr., 1908, i, 445; Kehrman and Dengler, Abstr., 1908, i, 1002; Doebner, Abstr., 1883, 861; Cohn, Abstr., 1894, i, 120).—Resorcinolbenzein is formed by fusing resorcinol with either benzil or benzoic anhydride. It is possible that in the latter case a reaction takes place similar to that which occurs in the synthesis of fluorescein:



Resorcinolbenzein forms a *barium* salt, $\text{C}_{76}\text{H}_{52}\text{O}_{13}\text{Ba}_4$, glistening, bluish-red leaflets, and a *hydrochloride*, $\text{C}_{76}\text{H}_{50}\text{O}_{12}\cdot 4\text{HCl}$, brownish-yellow leaflets. It is converted by an alcoholic solution of ammonia into *anhydroresorcinolbenzein*, $\text{C}_{76}\text{H}_{52}\text{O}_{13}\cdot\text{EtOH}$ (?), which crystallises in brownish-red leaflets with a blue shimmer. The latter compound and resorcinolbenzein, when boiled with glacial acetic acid, yield a *substance*, $\text{C}_{76}\text{H}_{54}\text{O}_{14}\cdot\text{Ac}\cdot\text{OH}$, obtained as brownish-red leaflets with a blue reflex. An alcoholic solution of potassium hydroxide converts resorcinolbenzein into a *substance*, $\text{C}_{38}\text{H}_{30}\text{O}_9$, almost colourless needles, m. p. 147° , and 2:4:2':4'-tetrahydroxytritan-2:2'-ether, $\text{C}_{19}\text{H}_{14}\text{O}_3$, which crystallises with benzene of crystallisation in colourless leaflets or aggregates of prisms, m. p. 170 — 171° . The latter substance is identical with Doebner's tetrahydroxytritan, which, however, because it was crystallised from dilute spirit, contained an additional H_2O . It yields an *acetyl* derivative, $\text{C}_{19}\text{H}_{12}\text{O}(\text{OAc})_2$, m. p. 184° , and a *dimethyl* derivative, $\text{C}_{19}\text{H}_{12}\text{O}(\text{OMe})_2$, thin, colourless leaflets, m. p. 126° . Resorcinolbenzein reacts with methyl sulphate, forming a *methyl* derivative, $\text{C}_{19}\text{H}_{11}\text{O}(\text{OMe})_3$, colourless crystals, m. p. 105° , and with acetic anhydride, yielding the *acetyl* derivative,



colourless, pointed prisms, m. p. 147° ; when the acetylation is carried out in the presence of zinc dust, the *acetyl* derivative, $\text{C}_{38}\text{H}_{26}\text{O}_3(\text{OAc})_4$, is formed; it crystallises in colourless, glistening needles, m. p. 179° .

W. H. G.

The Structure of Guaiol. A. GANDURIN (*Ber.*, 1908, 41, 4359—4363).—Guaiol (Wallach and Tuttle, Abstr., 1894, i, 538. Compare this vol., i, 112), extracted from guaiacum-wood oil by means of ether, crystallises from 70% alcohol in large, colourless prisms, $[\alpha]_D^{25} - 26\cdot64^\circ$; it is triboluminescent. *Dihydroguaiene*, prepared by the action of zinc dust on guaiol, is a colourless, almost odourless oil, b. p. $122^\circ/11$ mm., $[\alpha]_D^{18\cdot5} - 26\cdot65^\circ$, $D_4^{25} 0\cdot9089$, $D_4^{25} 0\cdot8914$, $n_D^{20\cdot2} 1\cdot49317$. *Guaiol methyl ether* is a colourless, almost odourless oil, b. p. 141 — $143^\circ/9$ mm., $[\alpha]_D^{20} - 31\cdot81^\circ$, $D_4^{25} 0\cdot9513$, $D_4^{25} 0\cdot9332$, $n_D^{18\cdot5} 1\cdot48963$. Guaiene, prepared from guaiol through the xanthate (compare Wallach and Tuttle, *loc. cit.*), is a colourless, almost odourless oil, b. p. $124^\circ/11$ mm.,

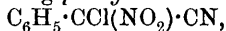
$[\alpha]_D^{25} - 66.11^\circ$, $D_4^{25} 0.9133$, $D_4^{25} 0.8954$, $n_D^{25} 1.49468$. The author draws the conclusion, particularly from the mol. refraction of the above substances, that guaicol is a tertiary dicyclic alcohol containing an ethylene linking. J. C. C.

Triphenylcarbinols. HUGO KAUFFMANN and IMMANUEL FRITZ (*Ber.*, 1908, 41, 4423—4427. Compare Abstr., 1905, i, 280, 773).—2-Iodo-1:4-dimethoxybenzene readily reacts with magnesium in dry ether, and the reaction of the oily product with ethereal 2:5-dimethoxybenzophenone leads to the formation of 2:5:2':5'-tetramethoxytriphenylcarbinol, $\text{OH}\cdot\text{CPh}[\text{C}_6\text{H}_3(\text{OMe})_2]_2$, m. p. 120° , which develops a dark green colour with concentrated sulphuric acid, and is reduced by warm alcoholic hydrogen chloride to 2:5:2':5'-tetramethoxytriphenylmethane, m. p. 74° . The ethereal solution of the preceding organomagnesium compound reacts with carbon dioxide, yielding in the usual way a small amount of dimethylgentisic acid and, as the main product, Kauffmann and Grombach's 2:5:2':5'-tetramethoxybenzophenone. The interaction of the latter and the organo-magnesium compound leads to the formation of 2:5:2':5':2'':5''-hexamethoxytriphenylcarbinol, $\text{OH}\cdot\text{C}[\text{C}_6\text{H}_3(\text{OMe})_2]_3$, m. p. 136° , which gives an indigo-blue coloration with concentrated sulphuric acid, a green coloration with concentrated hydrochloric acid, and yields by reduction with alcoholic hydrogen chloride or with zinc and glacial acetic acid, 2:5:2':5':2'':5''-hexamethoxytriphenylmethane, m. p. 151° . C. S.

Electrolytic Reduction of Benzoic and Salicylic Acids to the Corresponding Aldehydes. CARL METTLER (*Ber.*, 1908, 41, 4148—4150).—Benzoic acid in presence of mineral acids is electrolytically reduced to the corresponding alcohol (Abstr., 1905, i, 436; 1906, i, 851; 1907, i, 315), and no trace of aldehyde is formed during the reaction. In neutral or alkaline solution, hydrogenated carboxylic acids are formed. On reduction, however, in presence of boric acid, considerable quantities of aldehyde are formed (compare Weil, Abstr., 1908, i, 800). It is convenient to use an aqueous boric acid solution and sodium benzoate with a mercury cathode, which gives rise to sodium amalgam on passing the current, and this reduces the benzoic acid to aldehyde. It is necessary to ensure the continued presence of boric acid and to remove the aldehyde formed from further reducing action. To this end benzene is added, and the liquid stirred rapidly to keep it in a constant state of emulsion. Benzoic and salicylic acids and some of their derivatives can be reduced to aldehyde in this manner; the reaction takes place only with difficulty in the case of the halogen benzoic acids and of hydroxynaphthoic acid. E. F. A.

Preparation of Benzoyl Cyanide. WILHELM WISLICENUS and ROBERT SCHÄFER (*Ber.*, 1908, 41, 4169—4171).—It has previously been shown (Abstr., 1908, i, 973; this vol., i, 29) that the group $\text{:C}(\text{NO}_2)\text{Br}$ has a pronounced tendency to eliminate bromine and nitric oxide and form the keto-group. Phenylacetoneitrile is readily converted by means of ethyl nitrate and sodium ethoxide into the sodium

derivative of phenylisonitro-acetonitrile (Abstr., 1902, i, 541), which Flürscheim (Abstr., 1903, i, 79) has converted into bromocyanophenylnitromethane. Chlorine acts on the acetonitrile even more readily than bromine, forming *phenylchloronitrocyanomethane*,



a light yellow oil. This rapidly decomposes when warmed, and affords almost the theoretical quantity of benzoyl cyanide, crystallising in large plates, m. p. 32—34°. Iodine is without action on phenyliso-nitro-acetonitrile.

E. F. A.

***l*-Campholic Acid.** MARCEL GUERBET (*Compt. rend.*, 1909, 148, 98—101).—*l*-Campholic acid can be prepared by the method described previously for the dextro-acid (Abstr., 1908, i, 661). When *l*-borneol, identified with *l*-camphol by Haller's method (Abstr., 1889, 1206), is heated in sealed tubes with recently-fused potassium hydroxide, it is

oxidised thus: $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}\cdot\text{OH} \end{smallmatrix} + \text{KOH} = \text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CO}_2\text{K} \end{smallmatrix} + \text{H}_2$. The

resulting *l*-campholic acid forms colourless crystals, m. p. 106—107°, $[\alpha]_D^{25} - 49\cdot1^\circ$ (molecular solution in 95% alcohol). Its chemical properties are similar to those of the *d*-acid (compare Guerbet, Abstr., 1896, i, 56). The ammonium salt readily dissociates, evaporation of its aqueous solution leaving the acid. It cannot be esterified by the direct action of alcohols with or without the presence of hydrogen chloride. *l*-Campholic anhydride, $(\text{C}_{10}\text{H}_{17}\text{O})_2\text{O}$, prepared by dehydrating the acid with acetic anhydride, crystallises from acetone in colourless, square tablets, m. p. 57—58°, which are not attacked by cold alcohol, but give ethyl campholate on boiling with the latter. It is gradually hydrolysed by boiling aqueous potash. The *chloride*, $\text{C}_{10}\text{H}_{17}\text{OCl}$, obtained by treating the acid with a slight excess of phosphorus pentachloride, is a colourless liquid, b. p. 222° (the same as the *d*-isomeride), which, when heated with a trace of phosphoric oxide, decomposes into hydrogen chloride, carbon monoxide, and *i*-campholene, C_9H_{16} . *Ethyl l*-campholate, $\text{C}_{10}\text{H}_{17}\text{O}_2\text{Et}$, prepared by the action of alcohol on either the anhydride or the chloride, is a colourless, oily liquid, b. p. 228°/765 mm. (corr.), having a strong odour of pears. It is not saponified by alkalis under ordinary conditions, but is readily decomposed on heating with hydriodic acid.

The *sodium* salt, $\text{C}_{10}\text{H}_{17}\text{O}_2\text{Na}\cdot 8\text{H}_2\text{O}$, crystallises in efflorescent, nacreous lamellae, whilst the *copper* salt, $(\text{C}_{10}\text{H}_{17}\text{O}_2)_2\text{Cu}\cdot\text{OEt}_2$, crystallises from ether in large, green prisms containing ether of crystallisation.

l-Campholamide, obtained by the action of ammonia on an ethereal solution of the chloride, forms colourless needles, m. p. 77—78°, which are difficultly hydrolysed by alkalis, but readily by acids. E. H.

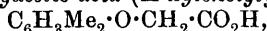
Syntheses in the Camphor Group. I. *iso*Laurolene and *iso*Lauronolic Acid (β -Campholytic Acid). GUSTAVE BLANC (*Bull. Soc. chim.*, 1909, [iv], 5, 24—31).—A résumé in greater detail of results already published (Abstr., 1906, i, 523) dealing with the syntheses of these two substances from *aa*-dimethyladipic acid as a starting point.

The product of the condensation of *isolaurelene* with acetyl chloride in presence of aluminium chloride (Abstr., 1899, i, 630; 1906, i, 524) contains a substance which is probably *tetrahydro-p-xylyl methyl ketone*, b. p. 210°. This is liquid, and yields an *oxime*, m. p. 106°, crystallising in small prisms, and sparingly soluble in light petroleum. The principal product of the condensation is the ketone, $\begin{array}{c} \text{CMe}_2 \cdot \text{CMe} \\ | \quad \quad | \\ \text{CH}_2 - \text{CH}_2 \end{array} > \text{CH} \cdot \text{COMe}$ (*loc. cit.*), which yields an *oxime*, m. p. 65°, readily soluble in light petroleum, and with care can be oxidised directly by sodium hypobromite to *isolaurenic acid*, or the ketone may be reduced by sodium in alcohol to the secondary alcohol, $\begin{array}{c} \text{CMe}_2 \cdot \text{CHMe} \\ | \quad \quad | \\ \text{CH}_2 - \text{CH}_2 \end{array} > \text{CH} \cdot \text{CHMe} \cdot \text{OH}$ (*loc. cit.*), which, on oxidation with chromic acid, is converted into 3-acetyl-1:1:2-trimethylcyclopentane, b. p. 195°, a mobile liquid with a faint odour; its *semicarbazone*, m. p. 213°, is sparingly soluble in alcohol, and the *oxime*, m. p. 47°, b. p. 137°/20 mm., forms large scales, and is readily soluble in most organic solvents. This ketone is oxidised by nitric acid, or, better, by sodium hypobromite solution, to dihydroisolaurenic acid, and this, on bromination and treatment with potassium hydroxide in alcohol, yields *isolaurenic acid*, as described already (Abstr., 1906, i, 524).

T. A. H.

Xylenolglycollic [Dimethylphenoxyacetic] Acids and their Derivatives. GIOVANNI JANDOLO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 149—155).—These acids may be obtained in good yield by melting the xylenols with chloroacetic acid, and adding a quantity of sodium hydroxide solution (1·3) three times as great as that of the xylene used.

2:4-Dimethylphenoxyacetic acid (*m-xylenolglycollic acid*),



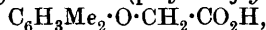
crystallises from all the ordinary solvents in flat, white needles, m. p. 141°. Its *silver*, $\text{C}_{10}\text{H}_{11}\text{O}_3\text{Ag}$, and *barium*, $(\text{C}_{10}\text{H}_{11}\text{O}_3)_2\text{Ba} \cdot 2\text{H}_2\text{O}$, salts were prepared. The corresponding *anilide*,



crystallises from alcohol in a silky mass of slender needles, m. p. 104°. The *anhydride*, $(\text{C}_{10}\text{H}_{11}\text{O}_2)_2\text{O}$, crystallises from alcohol in yellow needles, m. p. 94—95°.

a-2:4-Dimethylphenoxyacetic acid (*m-xylenolcinnamic acid*), $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{O} \cdot \text{C}(\text{CO}_2\text{H}) \cdot \text{CHPh}$, crystallises from alcohol in transparent, white prisms, m. p. 171°. The *barium* and *silver* salts were prepared.

2:5-Dimethylphenoxyacetic acid (*p-xylenolglycollic acid*),

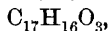


crystallises from water in transparent, white needles, m. p. 119°. The *silver* and *barium* (+2H₂O) salts were prepared. The *anilide*, $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$, crystallises from alcohol in groups of white, silky needles, m. p. 90°.

3:4-Dimethylphenoxyacetic acid (*o-xylenolglycollic acid*), $\text{C}_{10}\text{H}_{12}\text{O}_3$, crystallises in shining, white scales, m. p. 162°. The *silver* and

barium ($2\text{H}_2\text{O}$) salts were prepared. The *anilide*, $\text{C}_{16}\text{H}_{17}\text{O}_2\text{N}$, forms colourless, rectangular, monoclinic laminæ, m. p. 80° .

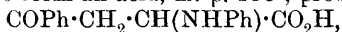
α -3 : 4-Dimethylphenoxycinnamic acid (*o*-xylenolcinnamic acid),



forms white prisms, m. p. 180° .

Attempts to prepare α -2 : 5-dimethylphenoxycinnamic acid (*p*-xylenolcinnamic acid) did not result in a pure product, owing to the difficulty of crystallising it. T. H. P.

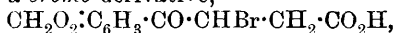
Benzoylacrylic Acid. J. BOUGAULT (*Ann. Chim. Phys.*, 1908, [viii], 15, 491—515).—A detailed account of the preparation and properties of benzoylacrylic acid and its derivatives, part of which has been already published (Abstr., 1908, i, 179, 269, 422, 537, 791). Benzoylacrylic acid, more conveniently prepared from β -bromobenzoylpropionic acid by the action of sodium acetate and acetic acid (Wolff, Abstr., 1891, 1185), combines with bromine to form the dibromo-derivative, m. p. 148° (Pechmann, Abstr., 1882, 1074, gives 135°). When treated with ammonia, benzoylacrylic acid yields the ammonium salt, m. p. 197° , of an *amino-acid*, which probably has the constitution $\text{COPh}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, whilst with aniline it combines directly to form an acid, m. p. 138° , probably



which condenses with phenylhydrazine to form the *acid*, $\text{C}_{22}\text{H}_{21}\text{O}_2\text{N}_3$, m. p. 151° .

The compound obtained by Gabriel and Colman (Abstr., 1899, i, 390) by the interaction of hydrazine and benzoylacrylic acid is probably not the hydrazone as described, but 3-phenylpyrazoline-5-carboxylic acid, $\text{CO}_2\text{H}\cdot\text{CH}\begin{smallmatrix} \text{NH}\cdot\text{N} \\ | \\ \text{CH}_2\cdot\text{CPh} \end{smallmatrix}$, which yields the crystalline bromo-

derivative, $\text{CO}_2\text{H}\cdot\text{CH}\begin{smallmatrix} \text{NH}\text{---}\text{N} \\ | \\ \text{CHBr}\cdot\text{CPh} \end{smallmatrix}$, m. p. 251° . The *oxime* and *semicarbazone* of benzoylacrylic acid have m. p. 168° and 190° respectively. *p*-Methoxy- and methylenedioxy-benzoylacrylic acids (Abstr., 1908, i, 269) can also be prepared by the action of sodium acetate and acetic acid on the bromo-derivative of *p*-methoxybenzoylpropionic acid and methylenedioxybenzoylpropionic acid respectively. *p*-Methoxybenzoylpropionic acid (anisoylpropionic acid) has m. p. 147° (Poppenberg, Abstr., 1902, i, 60, gives $140\text{—}141^\circ$); the bromo-derivative, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, has m. p. 114° ; methylenedioxybenzoylpropionic acid, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m. p. 136° , yields a bromo-derivative,



m. p. 147° .

M. A. W.

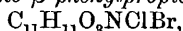
The Colours of Indoneacetic Acids and their Carbazones. HANS STOBEE and OTTO HORN (*Ber.*, 1908, 41, 4381—4384).—The colours of indoneacetic acid (this vol., i, 31), 3-methyl-1-indone-2-acetic acid (Abstr., 1904, i, 503), and 3-phenyl-1-indone-2-acetic acid (*ibid.*, 1902, i, 542), and of their semicarbazones, have been examined, and their ultra-violet absorption spectra photographed.

The substitution of methyl for hydrogen in either the acid or its semicarbazone has no effect on the colour, whereas introduction of phenyl increases the depth of the colour, the absorption limit of the phenylated acid being 34 wave-lengths nearer the red end of the spectrum. The relationships are much the same in the case of the semicarbazones (compare Abstr., 1906, i, 960).

All three semicarbazones are paler in colour than the corresponding acids.
J. J. S.

Mode of Oxidation of Phenyl Derivatives of Fatty Acids in the Animal Organism. III. Synthesis of some Derivatives of Phenylpropionic Acid. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, 5, 303—309. Compare Abstr., 1908, ii, 720, 964).—In the organism, β -hydroxy- β -phenylpropionic acid is oxidised with much greater difficulty than β -phenylpropionic acid, and is mostly excreted unchanged. In order to test the hypothesis that combination with glycine is a necessary preliminary to combustion, β -hydroxy- β -phenylpropionylglycine, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{H}$, was prepared.

Cinnamoylglycine, $\text{C}_{11}\text{H}_{11}\text{O}_3\text{N}$, obtained by the Schotten-Baumann reaction, was found to be identical with that previously obtained from urine (*loc. cit.*), and yielded successively $\alpha\beta$ -dibromo- β -phenylpropionylglycine, $\text{C}_{11}\text{H}_{11}\text{O}_3\text{NBr}_2$, prisms, m. p. 190—191°, α -bromo- β -hydroxy- β -phenylpropionylglycine, $\text{C}_{11}\text{H}_{12}\text{O}_4\text{NBr}$, needles, m. p. 87—88°, and β -hydroxy- β -phenylpropionylglycine, $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}$, needles, m. p. 146—147°. The last substance but one, yields with warm concentrated hydrochloric acid, β -chloro- α -bromo- β -phenylpropionylglycine,



m. p. 203—204°.

G. B.

isoPhthalacene Group: Structure of Phthalacene. II. GIORGIO ERRERA (*Gazzetta*, 1908, 38, ii, 588—598. Compare Abstr., 1908, i, 183).—The author has investigated the structure of the acids obtained by the action of concentrated sulphuric acid on 3 : 5-diphenyltoluene-2 : 2' : 2''-tricarboxylic acid (*loc. cit.*). It is found that this action yields the following three isomeric monobasic acids, which were separated by means of their ethyl esters : (1) the original phthalacene-carboxylic acid, which yields 3 : 5-diphenyltoluene-2 : 2' : 2''-tricarboxylic acid when fused with potassium hydroxide; (2) *isophthalacene*-carboxylic acid, which when reduced with hydriodic acid and phosphorus yields (α) an isomeride of phthalacene to which the name *iso*-phthalacene is given, and (β) *isophthalacene*-carboxylic acid; (3) *phthalaceneisocarboxylic* acid. The oxidation of *isophthalacene* yields the oxide of *isophthalacene* and *isophthalacene*, which are analogous with the corresponding oxidation products of phthalacene.

Ethyl isophthalacene-carboxylate,
$$\begin{array}{c} \text{CO}-\text{C}:\text{CMe}:\text{C}:\text{CO} \\ | \quad | \quad | \\ \text{C}_6\text{H}_4:\text{C}:\text{CH}-\text{C}:\text{C}_6\text{H}_3\cdot\text{CO}_2\text{Et} \end{array}$$
 crystallises from acetic acid in shining, golden-yellow needles, m. p. 316°, and dissolves sparingly in alcohol or benzene and readily in xylene. The corresponding acid, $\text{C}_{22}\text{H}_{12}\text{O}_4$, separates from xylene or acetic acid in minute, irregular, brownish-yellow crystals, m. p. 370° (decomp.), and dissolves sparingly in the ordinary solvents.

Ethyl phthalaceneisocarboxylate, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CH} \cdot \text{CMe} \cdot \text{C} \cdot \text{CO} \\ \text{CO} - \text{C} = \text{C} = \text{C} \cdot \text{C}_6\text{H}_3 \cdot \text{CO}_2\text{Et} \end{array}$ is deposited from xylene in shining, golden-yellow crystals, m. p. 329—330°.

isoPhthalacenecarboxylic acid, $\begin{array}{c} \text{CH}_2 - \text{C} \cdot \text{CMe} \cdot \text{C} \cdot \text{CH}_2 \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CH} - \text{C} \cdot \text{C}_6\text{H}_3 \cdot \text{CO}_2\text{H} \end{array}$ crystallises from acetic acid in faintly yellow leaflets or needles, m. p. 286—287°, and dissolves sparingly in alcohol, benzene, or xylene. The *ethyl ester*, $\text{C}_{24}\text{H}_{20}\text{O}_2$, separating from acetic acid as a dirty yellow, crystalline powder, m. p. 172—173°, and the *sodium salt*, $\text{C}_{22}\text{H}_{15}\text{O}_2\text{Na} \cdot 4\frac{1}{2}\text{H}_2\text{O}$, were prepared.

isoPhthalacene, $\begin{array}{c} \text{CH}_2 - \text{C} \cdot \text{CMe} \cdot \text{C} \cdot \text{CH}_2 \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CH} - \text{C} \cdot \text{C}_6\text{H}_4 \end{array}$, crystallises from benzene in faintly yellow laminæ, m. p. 222°.

isoPhthalacene oxide, $\begin{array}{c} \text{CO} - \text{C} \cdot \text{CMe} \cdot \text{C} \cdot \text{CH}_2 \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CH} - \text{C} \cdot \text{C}_6\text{H}_4 \end{array}$, crystallises from acetic acid in golden-yellow leaflets, m. p. 216—218°.

isoPhthalacene, $\begin{array}{c} \text{CO} - \text{C} \cdot \text{CMe} \cdot \text{C} \cdot \text{CO} \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CH} - \text{C} \cdot \text{C}_6\text{H}_4 \end{array}$, crystallises from aniline in shining, golden-yellow needles, m. p. 355—356°. T. H. P.

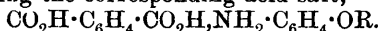
Hydrophthalic Acids ; Velocity of Addition of Bromine to the Tetrahydrophthalic Anhydrides. VI. GINO ABATI [with MAURO SOLIMENE] (*Gazzetta*, 1908, 38, ii, 577—587. Compare Abstr., 1907, i, 419, 420).—The author has investigated the rate of addition of bromine (0·01 mol. solution) to each of the five tetrahydrophthalic anhydrides dissolved in chloroform (0·01 mol. solution) at 25°.

Bauer (Abstr., 1905, i, 729 ; 1907, i, 307) finds that the accumulation of negative substituent groups at two carbon atoms connected by an ethylene linking diminishes or annuls the capacity of the compound to unite with bromine. This is in accord with the author's observation that the Δ^1 -tetrahydrophthalic anhydride requires thirty-four days to complete the addition of bromine, whilst with the *cis*- Δ^4 -anhydride less than three days is required ; with the other anhydrides examined, no such relation is observed. There appears to be a close connexion between the time occupied by the anhydride in absorbing bromine and the dissociation constant of the corresponding acid, as is seen from the following table :

	Time of absorption of bromine.	Dissociation constant of acid.
Δ^1 -Anhydride	33—34 days	0·0590
Δ^3 -Anhydride	25—26 „	0·0581
<i>trans</i> - Δ^4 -Anhydride	20—21 „	0·0118—0 0130
Δ^2 -Anhydride	14—15 „	0·0074
<i>cis</i> - Δ^4 -Anhydride	2—3 „	0·0062

The conclusion is drawn from these and other results that the unsaturated carbon atoms constituting the ethylene linking are of such a nature that the influences tending to lower the capacity of the linking to take up a negative element tend to increase the capacity of addition of a positive element, and vice versa. T. H. P.

Action of *iso*Phthalic and Terephthalic Acids on *p*-Aminophenols. DOMENICO PUGLIESE and GIAMBATTISTA SELVAGGI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 141—146).—In alcoholic solution, *isophthalic* acid (1 mol.) and *p*-aminophenol or its ethers (1 mol.) react, giving the corresponding acid salt,



With terephthalic acid, however, no reaction takes place, probably owing to the slight solubility and feeble acid properties of the acid.

When, however, *isophthalic* or terephthalic acid (1 mol.) and a *p*-aminophenol ether (1 or 2 mols.) are heated together in the absence of a solvent, they react, giving only the corresponding diamide: $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2 + 2\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OR} = \text{C}_6\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OR})_2 + 2\text{H}_2\text{O}$. In some instances, however, further changes went on to such an extent, even when the compounds were heated together in a stream of carbon dioxide, that the diamide could not be separated in quantity sufficient for analysis.

p-Anisidine hydrogen *isophthalate*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{NH}_3\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, separates in shining, white fragments, and begins to turn brown without melting at above 200°.

p-Phenetidine hydrogen *isophthalate*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{NH}_3\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$, is deposited in tufts of white needles, and decomposes at slightly above 100°.

isoPhthalodi-p-anisidide, $\text{C}_6\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$, prepared by the interaction of *isophthalic* acid (1 mol.) and *p*-anisidine (2 mols.), crystallises from alcohol in slender, neutral, white needles, m. p. 268°.

Terephthalodi-p-anisidide, $\text{C}_6\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$, crystallises from alcohol in neutral nacreous scales, m. p. 246—248°.

Terephthalodi-p-phenetidide, $\text{C}_6\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, prepared from terephthalic acid and *p*-phenetidine, was obtained mixed with terephthalic acid, which could not be removed by crystallisation.

T. H. P.

Phenylitaconic Acid. HANS STOBBE (*Ber.*, 1908, 41, 4350—4357).—The author has made a further study of the reaction between ethyl succinate and benzaldehyde (Stobbe and Klöppel, *Abstr.*, 1894, i, 594) with the object of obtaining an increased yield of phenylitaconic acid (compare Hecht, *Abstr.*, 1903, i, 700). The anhydride and the two mono-esters have also been investigated.

[With OTTO HORN.]—Phenylitaconic acid is obtained in a 35% yield by adding slowly a mixture of ethyl succinate and benzaldehyde to finely-divided sodium ethoxide suspended in boiling ether, and boiling the whole for three hours. The sodium salts of dibenzylidene-succinic, phenylitaconic, and phenylitaconic acids are separated by crystallisation and extraction with water. Phenylitaconic anhydride is readily obtained by treating the acid with cold acetyl chloride. The β -ethyl ester, $\text{CHPh}\cdot\text{C}(\text{CH}_2\cdot\text{CO}_2\text{H})\cdot\text{CO}_2\text{Et}$ (Fittig and Leoni, *Abstr.*, 1890, 894), crystallises in needles or tablets, m. p. 72°. The *barium*, *calcium*, and *silver* salts are described.

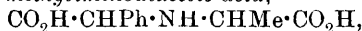
[With PHOKION NAOUM.]—The α -ethyl ester (Fittig and Leoni, *loc. cit.*) forms hairy, woolly needles, m. p. 76—79°.

J. C. C.

Iminodicarboxylic Acids. GEORGE STADNIKOFF (*Ber.*, 1908, 41, 4364—4373; *J. Russ. Phys. Chem. Soc.*, 1908, 40, 1638—1649).—The author finds that the rate of formation of derivatives of imino-acids decreases with increase of the molecular weight of the hydroxynitrile, but has no relation to the molecular weight of the amino-ester. Both in the synthesis of the imino-acids previously described (*Abstr.*, 1907, i, 393, 1015, 1016) and in the interaction of hydroxypropionitrile and ethyl aminocycloheptanecarboxylate or phenylaminoacetic acid, the reaction is at an end in five hours, whilst the interaction of mandelonitrile and ethyl aminoacetate or phenylaminoacetate requires ten days for completion; it is, however, quicker in the sunlight than in the dark.

C-Phenyliminodiacetic acid, $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared by condensing the hydrochloride of glycine ethyl ester with benzaldehyde and potassium cyanide, and hydrolysing the resulting *nitrile hydrochloride* (m. p. 82° decomp.), crystallises in starry aggregates of small needles, m. p. 220° (decomp.); the *hydrochloride* forms leaflets, m. p. 220° (decomp.); the *copper salt* ($3\text{H}_2\text{O}$) is described. The *diethyl ester* is a colourless oil with a faint odour, b. p. $195\text{--}196^\circ/17\text{ mm.}$; the *nitroso-derivative* of the latter is a yellow, viscid oil, b. p. $220\text{--}221^\circ/17\text{ mm.}$ The *dimethyl ester* is a viscid oil, b. p. $188\text{--}189^\circ/17\text{ mm.}$, and yields a *nitroso-derivative*, which is a viscid, yellow oil, b. p. $201\text{--}203^\circ/16\text{ mm.}$

sym.-*C-Phenyl-C-methyliminodiacetic acid*,



prepared by the interaction of ethyl phenylaminoacetate hydrochloride, acetaldehyde, and potassium cyanide, and hydrolysis of the resulting *nitrile hydrochloride* (m. p. $160\text{--}161^\circ$, decomp.), crystallises in starry aggregates of slender needles, decomp. $210\text{--}213^\circ$; the *hydrochloride* has m. p. $210\text{--}212^\circ$ (decomp.), and the *diethyl ester* forms a viscid oil, b. p. $182\text{--}183^\circ/13\text{ mm.}$

By the condensation of ethyl phenylaminoacetate hydrochloride, benzaldehyde, and potassium cyanide, the *hydrochloride* of the *nitrile ester*, $\text{CO}_2\text{Et}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CN}\cdot\text{HCl}$, is formed in slender needles, m. p. $156\text{--}157^\circ$; with water it gives the *nitrile ester*, a crystalline mass, m. p. $43\text{--}45^\circ$. On boiling this with 20% hydrochloric acid, it is decomposed into phenylaminoacetic acid, benzaldehyde, and hydrogen cyanide.

J. C. C.

Synthesis and Reactions of Ethyl Phloroglucinoldicarboxylate. Condensation of Esters containing Nitrogen and the Preparation of Sodium Cyanate. HERMANN LEUCHS and ARTHUR GESERICK (*Ber.*, 1908, 41, 4171—4186).—The supposed ethyl phloroglucinoltricarboxylate synthesised by Baeyer by the sodium condensation of ethyl malonate was shown by Moore (*Trans.*, 1904, 85, 165) to be in reality ethyl phloroglucinoldicarboxylate. Willstätter (*Abstr.*, 1899, i, 576) isolated ethyl acetonedicarboxylate as an intermediate product, and observed the formation of ethyl acetate, which he attributed to the action of sodium ethoxide on ethyl malonate, $\text{CH}_2(\text{CO}_2\text{Et})_2 + \text{EtOH} = \text{CH}_3\cdot\text{CO}_2\text{Et} + \text{CO}_2\text{Et}_2$. He was unable to confirm the presence of ethyl carbonate, but this the

authors have succeeded in doing. The Baeyer synthesis is explained thus: two molecules of ethyl malonate unite to form ethyl acetone-tricarboxylate, which in turn reacts with ethyl acetate.

Ethyl malonate in cold ethereal solution is half converted into the sodium salt, the ether distilled off, and the residue heated at 130—140°, any liquid which distils being collected. A yellow, semi-solid mass is obtained, which, after purification, yields colourless needles of ethyl phloroglucinoldicarboxylate, m. p. 107—108.5° (corr.). Ethyl carbonate was obtained in quantity on fractionating the distilled liquid.

Ethyl malonate dissolved in light petroleum reacts with aluminium chloride, forming colourless crystals of ethyl aluminomalonate, m. p. 97—98° (Tistshenko gives 94—95°: Abstr., 1900, i, 270). This is decomposed by neither alkalis nor acids.

By the action of nitric acid on ethyl phloroglucinoldicarboxylate, three products are obtained. A very characteristic bluish-violet coloration is at first produced. *Ethyl nitrophloroglucinoldicarboxylate*, $\text{NO}_2 \cdot \text{C}_6(\text{OH})_3(\text{CO}_2\text{Et})_2$, crystallises in colourless, six-sided plates or massive prisms, m. p. 120—121° (corr.). It is conveniently prepared by heating equal weights of carbamide and the phloroglucinol compound with concentrated nitric acid at 80°. *Ethyl 5-nitro-2:4:6-triacetoxybenzene-1:3-dicarboxylate* forms colourless, prismatic crystals, m. p. 94—95°.

Nitrophloroglucinol, $\text{C}_6\text{H}_3(\text{OH})_3 \cdot \text{NO}_2$, prepared by heating the ester at 130—135° with potassium hydroxide, crystallises in long, sealing wax-red prisms, which become yellowish-red on heating, m. p. 186—187° (corr.).

Ethyl aminophloroglucinoldicarboxylate is obtained, by reducing the nitro-compound with zinc and hydrogen chloride, in the form of the *hydrochloride*, crystallising in colourless needles, m. p. 209° (corr., decomp.). The base separates in minute needles, m. p. 96—97°. When left during several days in dilute methyl-alcoholic solution, crystals separate, and the alcohol assumes a deep red colour.

The other products of the action of nitric acid on ethyl phloroglucinoldicarboxylate are citron-yellow and dark red in colour; they are isomeric, and are formed from two molecules of ester united by an imino-group. The red substance, $\text{C}_{22}\text{H}_{21}\text{O}_{13}\text{N}$, is regarded as a quinone derived from ethyl hexahydroxydiphenylaminetetracarboxylate; it has m. p. 164—165°. By the action of acetic anhydride, a mixture of substances is produced, one of which has m. p. 138—152°, and crystallises in orange-yellow needles. The quinone is reduced on prolonged boiling with alcohol, or by means of sulphurous acid, to a brown compound, $\text{C}_{22}\text{H}_{21}\text{O}_{12}\text{N}$, which, on heating, becomes bright red at 130°, and dark brown again near the melting point, 196—197° (corr.). The *acetate* crystallises in orange-yellow needles, m. p. 175—177°.

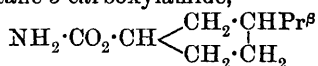
The *lactone* from ethyl hexahydroxydiphenylaminetetracarboxylate crystallises in citron-yellow needles, m. p. 220° (corr.); it forms a faintly yellow acetate, m. p. 169—171°, crystallising in needles.

The condensation of ethyl sodio-*N*-carbethoxyglycine yields an *ester*, $\text{C}_{10}\text{H}_{14}\text{O}_6\text{N}_2$, crystallising in long needles, m. p. 144—145° (corr.). This has an acid reaction in aqueous solution, and may be ethyl diketopiperazine-1-carboxylate or ethyl aminocyclobutan-2:4-dione-1:3-dicarboxylate.

Attempts to condense sodium urethane showed that reaction takes place between several molecules, but the intermolecular elimination of alcohol results in the quantitative formation of sodium cyanate. Similarly, the action of sodium on urethane in boiling benzene results in the formation of sodium cyanate alone. This is a convenient method for preparing salts of cyanic acid. E. F. A.

Sodium Benzaldehydesulphoxylate. A Correction. EMIL FROMM (*Ber.*, 1908, 41, 4385. Compare Abstr., 1908, i, 970).—When sodium benzaldehydesulphoxylate is heated with benzyl chloride and sodium hydroxide solution, the product is not the unaltered sulphoxylate as previously stated, but sodium benzylsulphonate. J. J. S.

Syntheses of Derivatives of Camphenilone. J. BOUVEAULT and GUSTAV BLANC (*Compt. rend.*, 1908, 147, 1314—1315).—From previous work, the conclusion has been drawn (Abstr., 1908, i, 134) that the amide formed by the action of sodamide on camphenilone is *isopropylcyclopentane-3-carboxylamide*,

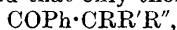


This conclusion is now verified by direct synthesis. *isoPropylcyclopentan-3-one* is obtained by the decomposition of β -*isopropyladipic anhydride*, and is shown to be identical with the ketone obtained from camphenilone, by preparation of its semicarbazone and its dibenzylidene derivative. On reduction with sodium and boiling alcohol, it gives a secondary alcohol, identical with that obtained from 3-amino-1-*isopropylcyclopentane* by the action of nitrous acid. This alcohol, when heated at 100° with hydrobromic acid, is transformed into 3-bromo-1-*isopropylcyclopentane*, $\text{CHBr} \begin{cases} \text{CH}_2 \cdot \text{CHPr}^s \\ \text{CH}_2 \cdot \text{CH}_2 \end{cases}$, a heavy, colourless liquid, b. p. 82°/16 mm.

The latter reacts with Grignard's reagents, giving magnesium derivatives, which, when saturated with dry carbon dioxide, give 3-*isopropylcyclopentanecarboxylic acid*, identical with that derived from camphenilone. The acid, on treatment with phosphorus pentachloride and then with gaseous ammonia, readily furnishes the amide.

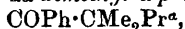
E. H.

A General Method of Preparing Mono-, Di-, and Tri-alkylacetophenones. ALBIN HALLER and ED. BAUER (*Compt. rend.*, 1909, 148, 70—74).—It has been shown previously (Abstr., 1908, i, 987) that aromatic ketones of the type of benzophenone, when heated with sodamide in benzene solution, give either additive or decomposition products. The authors, attempting to apply this reaction to mixed fatty-aromatic ketones, find that only those of the type

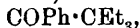


in which R, R', and R'' are alkyl groups, undergo the decomposition observed with diaryl ketones, that is, they break down into benzene and trialkylacetamides. Of the ketones employed, *aaa*-trimethylacetophenone, $\text{COPh} \cdot \text{CMe}_3$, has been described by Nef (Abstr., 1900, i, 349); the others were prepared by alkylating acetophenone in the presence

of sodamide, as in the method adopted with cyclic ketones (Haller, Abstr., 1904, i, 600; 1905, i, 214, 602), and by Claisen (Abstr., 1905, i, 286). *aa*-Dimethyl- α -ethylacetophenone, $\text{COPh}\cdot\text{CMe}_2\text{Et}$, obtained by twice methylating propiophenone or by ethylating phenyl isopropyl ketone, is a mobile, agreeably smelling liquid, b. p. $112\cdot5^\circ/10$ mm.; the *oxime* forms needles, m. p. 139° ; *aa*-dimethyl- α -propylacetophenone,



prepared by propylating phenyl isopropyl ketone, is a liquid with a penetrating odour, b. p. $121\text{--}123^\circ/10$ mm.; its *oxime*, prepared by means of Crismer's reagent, crystallises in needles, m. p. $132\text{--}133^\circ$; α -methyl-*aa*-diethylacetophenone, $\text{COPh}\cdot\text{CMeEt}_2$, an aromatic smelling liquid, b. p. $125\text{--}126^\circ/11$ mm., results on twice ethylating phenyl ethyl ketone; the *oxime* has m. p. 121° ; *aaa*-triethylacetophenone,



obtained by successively ethylating acetophenone or by ethylating phenyl propyl ketone, is an agreeably smelling liquid, b. p. $145\text{--}146^\circ/16$ mm.; the *oxime*, prepared with Crismer's reagent, forms needles, m. p. $160\text{--}161^\circ$; α -methyl- α -ethyl- α -propylacetophenone,



prepared by successively methylating and propylating propiophenone, is a liquid, b. p. $135\text{--}136^\circ/11$ mm., which forms an *oxime*, m. p. $99\text{--}100^\circ$; *aa*-dimethyl- α -allylacetophenone, $\text{COPh}\cdot\text{CMe}_2\cdot\text{C}_3\text{H}_5$, a pleasant-smelling liquid, b. p. $121^\circ/11$ mm., is formed by the action of allyl iodide on phenyl isopropyl ketone; its *oxime* could not be obtained.

By the action of propyl or allyl iodide on the additive product of sodamide and acetophenone, not substituted ketones, but condensation products of very high boiling point are formed; the higher homologues of acetophenone, however, undergo the normal reaction with these iodides.

E. H.

Quinhydrone. WILHELM SIEGMUND (*Monatsh.*, 1908, 29, 1087—1109. Compare Urban, Abstr., 1907, i, 539).—By the addition of light petroleum to a benzene solution of *p*-benzoquinone and catechol, a *quinhydrone*, $\text{C}_{18}\text{H}_{16}\text{O}_6$, m. p. 90° (decomp.), D^{20}_D 1.359, is obtained, which forms red needles, is stable in boiling benzene, and is decomposed by distillation with steam, yielding *p*-benzoquinone and catechol, the weight of the latter, estimated as the lead derivative, indicating that the quinhydrone contains 1 mol. $\text{C}_6\text{H}_4\text{O}_2$ and 2 mols. $\text{C}_6\text{H}_4(\text{OH})_2$.

Quinol and β -naphthaquinone do not react in water, alcohol, ether, or benzene. In warm benzene, *p*-benzoquinone and 1:2-dihydroxynaphthalene yield, in the molecular proportion 1:1, quinol and β -naphthaquinone; in proportion 2:1, β -naphthaquinone and ordinary quinhydrone, and in the proportion 1:2, quinol and a bluish-black substance, $\text{C}_{20}\text{H}_{12}\text{O}_4$, m. p. 120° , which seems to be identical with Stenhouse and Grove's dinaphthyldiquinhydrone (*Trans.*, 1878, 33, 417).

The addition of light petroleum to a benzene solution of *p*-benzoquinone and 2:3-dihydroxynaphthalene produces tufts of blackish-red needles of the mixed *quinhydrone*, $\text{C}_{16}\text{H}_{12}\text{O}_4$.

The formulæ of the preceding quinhydrones are expressed in accordance with Thiele's theory of partial valencies. C. S.

Complete Synthesis of Camphor. GUSTAV KOMPPA (*Ber.*, 1908, 41, 4470—4474).—The synthesis of camphor from a compound containing a smaller number of carbon atoms described by Wallach recently (*Abstr.*, 1908, i, 997), is not the first synthesis of camphor to be recorded, since the author had previously synthesised racemic camphoric acid (*Abstr.*, 1901, i, 668; 1904, i, 141), which he was subsequently able to convert into racemic camphor (*Chem. Zeit.*, 1905, 29, 1202). It has since been found possible to obtain pure *l*-camphoric acid, but not pure *d*-camphoric acid, from the racemic acid by crystallisation of the quinine salts. Attempts are being made to resolve the racemic camphor into its components through the corresponding borneols. *r*-Campholide, $C_{10}H_{16}O_2$, prepared by the reduction of *r*-camphoric anhydride in alcoholic solution with sodium, or, better still, by means of nickel and hydrogen, crystallises in short, thick needles, m. p. 211.5—212° (corr.). It combines with hydrogen bromide, forming *r*-bromocampholic acid, $C_{10}H_{17}O_2Br$, rhombic plates, m. p. 178—179°, and when heated with potassium cyanide at 230—240° yields *r*-cyanocampholic acid, which is converted on hydrolysis into *r*-homocamphoric acid, $C_9H_{16}(CO_2H)_2$, obtained as feathery crystals, m. p. 231—232° (corr.). The calcium salt, $C_{11}H_{16}O_4Ca \cdot 5H_2O$, is a crystalline powder, which, when distilled with calcium hydroxide, yields *r*-camphor, m. p. 178—178.5° (corr.). W. H. G.

Constituents of Ethereal Oils. Carvenene, $C_{10}H_{16}$, and "Pure" Terpinene. FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 4474—4479).—Emphasis is laid on the great differences in the physical properties of the "pure" terpinenes obtained by various methods by the author (*Abstr.*, 1907, i, 714), Wallach (*Abstr.*, 1907, i, 64; 1908, i, 813), and Harries and Majima (*Abstr.*, 1908, i, 733). In order to throw some light, therefore, on the constitution of terpineine, the author has prepared pure carvenene by reducing chlorocarvenene, and finds that the hydrocarbon so obtained, which must have the formula $CPi^{\beta} \begin{smallmatrix} \text{CH} & - & \text{CH} \\ \text{CH}_2 & \cdot & \text{CH}_2 \end{smallmatrix} CMe$, exhibits an exaltation of 1.5 units (compare Brühl, *Abstr.*, 1908, ii, 1002). It is thus definitely shown that two cyclic conjugate ethylene linkings produce a marked exaltation, consequently the two terpenes, $\Delta^{1:3}$ - and $\Delta^{1:4}$ -dihydrocymene, must differ considerably in their physical constants. The identity of carvenene with terpinene has not yet been definitely settled.

The chlorocarvenene described by Klages and Kraith (*Abstr.*, 1900, i, 42) was impure. The pure substance has b. p. 95—98°/10 mm., D_{20}^{20} 0.994, n_D 1.51700, and mol. ref. 51.90; that is, it exhibits an exaltation of 1.71 units. It is readily reduced by sodium and alcohol to carvenene, a colourless liquid, b. p. 61—63°/10 mm., 179.5—180.5°/735 mm., D_{20}^{20} 0.844, and n_D 1.49100 (compare Harries and Majima, *loc. cit.*). The carvenene so prepared reacts slowly with nitrous acid, yielding terpinene nitrosite. W. H. G.

Aliphatic Terpenes and their Derivatives. III. C. J. ENKLAAR (*Rec. trav. chim.*, 1908, 27, 422—434. Compare Abstr., 1908, i, 664).—In the present communication the author describes the preparation and properties of the ozonides of ocimene (van Romburgh, Abstr., 1901, i, 220), *allo*-ocimene, and dihydro-ocimene. These ozonides are of somewhat variable composition, the amount of oxygen depending on the time during which the hydrocarbons are exposed to ozone.

Ocimene ozonide, $C_{10}H_{16}O_9$, occurs as a pale yellow, viscous oil, which explodes when heated or when brought into contact with concentrated sulphuric acid. When treated with water, decomposition occurs, with formation of acetone, acetic acid, malonic acid, methylglyoxal, and possibly malonaldehyde. *allo-Ocimene ozonide*, $C_{10}H_{16}O_9$, is an explosive oil rapidly decomposed by water with formation of acetone, pyruvic acid, and probably malonaldehyde.

Dihydro-ocimene ozonide, under the same conditions, gives acetone, acetic acid, lævulic acid, and probably lævulinaldehyde, and malonaldehyde. An insoluble yellow resin was also obtained in the decomposition of these ozonides by water; further treatment with ozone converts this into an ozonide.

A table is given showing the specific refractions for the α - and γ -hydrogen lines and the *D*-sodium line, and also the molecular refractions for the different rays of these three hydrocarbons. The molecular dispersions between the α - and γ -lines diverge considerably from the values calculated from Conrady's data. W. O. W.

Ethereal Oils. HEINRICH HAENSEL (*Huensel's Half-Yearly Report, October, 1908*. Compare Abstr., 1908, i, 665).—*Angelica oil* when free from terpene has $D^{15} 0.9508$, $n_D - 3.16^\circ$, acid number 0, ester number 87.3, after acetylation 168.1. *Oil of Mugwort*, from the fresh plant *Artemisia vulgaris* (yield 0.0263%), is dark brown and smells strongly aromatic; $D^{20} 0.9279$. The addition of 90% alcohol causes separation of small, colourless plates, which give a decided aldehyde reaction with ammoniacal silver solution. *Birch-bark oil*, from *Betula alba*, has $D^{20} 0.9003$, $n_D - 12.08^\circ$, acid number 9.1, ester number 11.4, after acetylation 36.5. The sesquiterpene isolated from this was colourless and nearly odourless; it has b. p. $255-256^\circ/744$ mm., $D^{20} 0.8844$, $n_D - 0.5^\circ$; in glacial acetic acid it gives a cherry-red coloration with bromine, and combines with 1 mol. hydrogen chloride when in absolute ethereal solution. The resulting dark-coloured hydrochloride, $D^{20} 0.9753$, when boiled with anhydrous sodium acetate and acetic acid, yields a hydrocarbon, b. p. $258-260^\circ/747$ mm., $D^{20} 0.8898$. *Coriander oil* (*loc. cit.*) is for the most part *d*-linalool, accompanied by small quantities of esters of this alcohol. *Cynoglossum oil*, prepared from the leaves of *Cynoglossum officinale* (yield 0.107%), is dark brown with powerful camomile-like odour; it partly solidifies when cooled, is soluble in all proportions of 90% alcohol, and has $D^{20} 0.9412$. *Siberian pine needle oil*, from *Abies sibirica*, has $D^{20} 0.9767$, $n_D - 38.30^\circ$, soluble 1 : 14.2 in 63% alcohol. *Guaiacum-wood oil* from *Bulnesia Sarmienti*.—Only about one-half of the guaiol contained in this oil is found by acetylation; it

appears to be a tertiary alcohol, in agreement with its behaviour towards phthalic anhydride. The guaiene obtained by warming the oil for an hour with three times its weight of anhydrous formic acid has b. p. 135—138°/14 mm., D^{20}_D 0.9182, and is most probably a mixture of sesquiterpenes (compare Gandurin, this vol., i, 98). *Oil of Lavender*, when free from terpene, has D^{20}_D 0.8898, α_D -6.44°, and is soluble 1:0.95 in 80% alcohol. *Oil of Lovage*, from *Levisticum officinale*, becomes slightly changed when kept; it then contains myristic acid, small quantities of an aldehyde possessing an odour resembling that of octaldehyde, and also larger quantities of a brown resin, which decomposes when warmed under reduced pressure. *Ginger-grass oil*, from *Andropogon Schoenanthus*, is optically inactive, has D^{20}_D 0.8851, and dissolves in 3.5 parts of 60% alcohol. *Italian Peppermint oil*, crude and purified, has respectively D^{20}_D 0.9035 and 0.9032, α_D -19.80° and -18.10°, ester number 11.2 and 9.1, after acetylation 154.4 and 145.9, content of esterified menthol 3% and 2.54%, content of free menthol 45.16% and 42.66%. *Hungarian oil of Juniper*.— D^{20}_D 0.8672, α_D -12°, saponification value 5.9, after acetylation 20.9, and contains according to the phthalic anhydride test about 5% of a primary alcohol, $C_{10}H_{18}O$. The Italian oil has D^{20}_D 0.8658, α_D -9.82°, saponification value 6.1; after acetylation, D^{20}_D 0.8732, α_D -7.21°, saponification value 21.3; after saponification and repeated acetylation a reversal of optical rotation appears to take place. In the higher boiling fractions, phthalic anhydride indicates the presence of small quantities of a primary alcohol, $C_{10}H_{18}O$; the terpene fractions do not contain nopinene. Olibanol from *oil of Frankincense* (*loc. cit.*) has b. p. 217°/20 mm., 333—334°/751 mm., D^{20}_D 0.9596, α_D -71.50°; when warmed with an equal weight of molten zinc chloride, a dark green oil is obtained, b. p. 315—318°/749 mm., D^{20}_D 0.9400. Olibanol is only slightly oxidised by potassium permanganate in alkaline solution, but in glacial acetic acid solution it is completely oxidised by chromic acid. J. V. E.

Essential Oils. SCHIMMEL & Co. (*Semi-Annual Report*, Nov., 1908, 5—232. Compare Abstr., 1908, i, 666).—A résumé of information regarding essential oils accumulated during the period April to November 1908. Much of the matter recorded has appeared in other journals and has been abstracted already.

Cinnamon-bark oil.—Four samples from Mahé Islands, Seychelles, had D^{15}_D 0.9464—0.9670, $[\alpha]_D$ -2°30' to -5°10', n^{20}_D 1.52843—1.53271, and contained from 25 to 35% of cinnamaldehyde and 6 to 15% "phenols." All the usual constituents of cinnamon-bark oil were present, and in addition a small amount of camphor (compare *Bull. Imp. Inst.*, 1908, 6, 111). *Clove-leaf oil*.—Clove leaves from the Seychelles yielded 4.5% of oil (*loc. cit.*); this had D^{15}_D 1.0489, $[\alpha]_D$ -1°35', eugenol 87%. *African Copaiba balsam* (oleo-resin) had D^{15}_D 0.9919, $[\alpha]_D$ -2°15', acid number 61.4, saponification number 68.5, and was not completely soluble in 98% alcohol. It contained 46.5% of volatile oil, having D^{15}_D 0.9215, $[\alpha]_D$ +22°26', and acid number 2.2. *Dalbergia cumingiana* oil, obtained to the extent of 0.5% from the wood, had D^{26}_D 0.891, $[\alpha]^{26}_D$ -4°31', ester number 5, acetyl ester number

115. No aldehydes were present (*Jaarboek Dept. Landb. Ned. Ind.*, 1906, 45). *Dill herb oil*, from Spanish herb, was greenish-blue, had D^{15} 0.9062, n_D^{20} 1.49185, and was dextrorotatory. It contained *d*- α -phellandrene, terpinene, carvone, dillapiol (? dillisoapiol), and dipentene or limonene (?).

Lemon oil.—The chief constants of oils from different districts in Sicily are recorded; they had D^{15} 0.8569—0.8610, $[\alpha]_D^{20} + 56^\circ 50'$ to $+ 62^\circ 40'$, left from 2.2 to 3.6% residue on evaporation, and contained 4.3 to 7.1% citral. All these oils contained traces of pinene, which is a natural constituent of lemon oil. *Eucalyptus Rudderi* leaves and twigs furnished 0.309% of reddish-brown oil, having D^{15} 0.942, $[\alpha]_D - 8.5^\circ$, and n_D^{20} 1.4898. The oil contained cineol and aromadendral, but no pinene or phellandrene (Baker and Smith, *Proc. Linn. Soc., N.S.W.*, 1906, 31, 714). *European Wormseed oil* contains α -pinene, terpinene, terpineol and terpinenol, and a sesquiterpene (b. p. 250° approx.) (compare Schindel-Meiser, *Apoth. Zeit.*, 1907, 22, 876). *Foeniculum officinale* stalks and leaves, grown in Java yielded an oil having D^{26} 0.970, $[\alpha]_D^{26} + 4^\circ 50'$, b. p. $227-235^\circ$, m. p. 12.8° . A second sample of oil had D^{15} 0.9837, $[\alpha]_D + 5^\circ 34'$, m. p. 16.2° . Both oils probably contain much anethole (*Jaarboek Dept. Landb. Ned. Ind.*, 1906, 45). *Hyptis suaveolens* oil from Java had $[\alpha]_D - 1^\circ 56'$ and saponification number 17. The yield was 1% and no aldehydes were present (*loc. cit.*, p. 46).

Andropogon citratus oil is contained in largest quantity in the leaves, and diminishes as the leaves age, becoming at the same time richer in citral. The leaf sheaths contain a little oil, and the thick roots 0.35 to 0.5%. A sample of "*Cochin China lemon grass*" oil produced in Barbados had D^{15} 0.900, $[\alpha]_D - 1^\circ$, aldehydes 85.5 (neutral sulphite method). The "acid sulphite" and "neutral sulphite" processes for estimation of citral in lemon grass oil give results differing by from 2 to 5%, so that the process of estimation should always be stated. Methylheptenol has been detected in *linalos oil*. *Monarda didyma* oil from the half-faded petals was pale yellow, and had D^{15} 0.8665, $[\alpha]_D - 7^\circ 30'$, n_D^{20} 1.46892, and acid number 2.4: the yield was 0.32%. The dry leaves and stems furnished 0.096% of a lemon-yellow, more soluble oil having D^{15} 0.8855, $[\alpha]_D - 32^\circ 38'$, n_D^{20} 1.46892, and acid number 5.5. Both oils had the odour of lavender.

Nutmeg flowers grown in Java yielded 7.6% of oil having D^{20} 0.942, $[\alpha]^{26} + 7^\circ$, and b. p. $155-285^\circ$. Fresh nutmegs furnished 3.8% of oil having D^{26} 0.940, $[\alpha]_D^{26} + 10^\circ 20'$, and b. p. $155-285^\circ$ (de Jong "*Teysmannia*" 1907, 8). Condensed water from the distillation of *orris root oil* contained acetaldehyde, methyl alcohol, diacetyl, and furfuraldehyde. *Pastinaca oil* was found to contain heptic and hexoic acids (*Apoth. Zeit.*, 1907, 22, 144). The physical constants of a number of Singapore and Java patchouli oils are recorded.

Italian peppermint oil, distilled from plants grown from Mitcham seed, had D^{15} 0.9090, $[\alpha]_D - 21^\circ 12'$, n_D^{20} 1.46248, and contained "total" menthol 50.5%, and menthone 17.2%. Java "*peppermint*" oil had D^{26} 0.974, $[\alpha]_D^{26}$ $12^\circ 28'$, and "total menthol" 44.4% (*Jaarboek Dept. Landb. Ned. Ind.*, 1906, 45), but doubt is expressed as to the validity of the above composition.

Poplar bud oil.—Two samples had D^{15} 0.8957 to 0.8991, $[\alpha]_D + 5^\circ 16'$ to $+5^\circ 45'$, acid number 2.8–6.4, and ester number 8.2–8.9. Acetylation experiments showed that the oil contained but little "alcohols." *East African sandalwood oil*, from *Osyris tenuifolia*?—The yield from the wood was 4.86%. The oil had D^{15} 0.9477, $[\alpha]_D - 42^\circ 50'$, n_D^{20} 1.52191, ester number 11.1, acetyl ester number 72.8. The odour recalled those of vetiver and gurjun balsam oils. *Thuja plicata*.—The leaves and twigs yielded 0.8 to 1.4% of bright yellow oil, which possessed a camphoraceous odour, and had D^{25} 0.9305, $[\alpha]_D^{25} - 6.9^\circ$, acid number 0.518, saponification number 5.7, and acetyl ester number 6.2. It contained pinene, thujone, fenchone, and esters of borneol. *Ylang-ylang oil*, from Madagascar, had D^{15} 0.9577, $[\alpha]_D - 49^\circ 55'$, n_D^{20} 1.51254, acid number 1.8, ester number 113.2, acetyl ester number 160.2. Samples from Mahé Island, Seychelles, had D^{15} 0.924–0.958 and $[\alpha]_D - 18^\circ 46'$ to $45^\circ 27'$ (compare *Bull. Imp. Inst.*, 1908, 6, 110).

Artemisia arborescens yielded 0.62% of a dark blue oil, possessing an odour like that of French wormwood oil, and having D^{15} 0.9458 and acid number 9.8. "Mumuta" grass tubers (*Andropogon*, sp.), from Samoa, gave 1.05% of an oil with an odour like that of vetiver oil, and having D^{15} 0.9845, $[\alpha]_D + 41^\circ 50'$, n_D^{20} 1.51505, acid number 0.9, ester number 13.3, and acetyl ester number 65.2. From "Nuanua" leaves (*Nelitris*, sp.), from Samoa, 0.63% of oil was obtained. This had an odour like that of ambergris, and had D^{15} 0.9025, $[\alpha]_D + 9^\circ 30'$, n_D^{20} 1.48490, acid number 2.2, and ester number 7.4. "Usi" leaves (*Evodia hortensis*), from Samoa, yielded 0.09% of a brown oil with a quinone-like odour, and had D^{15} 0.9450, $[\alpha]_D - 10^\circ$, and n_D^{20} 1.49685.

"Maali" resin, from Samoa, resembled elemi, and gave 16.08% of a bright green solid oil with a faintly balsamic odour. It had m. p. $65-80^\circ$, $[\alpha]_D + 7^\circ 15'$, saponification number 3.3, and acetyl ester number 46.6. It contained *maalyl alcohol*, $C_{15}H_{26}O$, m. p. 105° , $[\alpha]_D + 18.33^\circ$, b. p. 260° (approx.), which crystallised from alcohol in silky needles, often several inches in length, and formed with resorcinol a complex condensation product, m. p. 62° , and with chromic anhydride a red additive product, $(C_{15}H_{26}O)_2 \cdot CrO_3$, m. p. 111° . On treatment with acetic anhydride, or, better, formic acid, maalyl alcohol is converted into a *sesquiterpene*, $C_{15}H_{24}$, D^{15} 0.9190, $[\alpha]_D + 121^\circ 20'$, n_D 1.52252, b. p. $270.8-271^\circ/754$ mm., which gives an indigo-blue coloration with sulphuric acid in acetic acid. No derivatives of the sesquiterpene could be prepared. The residue of the oil appears to consist of a solution of maalyl alcohol in a levorotatory sesquiterpene.

Artemisia indica (?), of Java, yielded 0.28% of a bright brown oil, having D^{26} 0.949, $[\alpha]_D^{26} + 57^\circ 2'$, saponification number 99, acetyl ester number 228 (corresponding with 75.6% of thujyl alcohol). No thujone could be detected (*Jaarboek Dept. Landb. Ned. Ind.*, 1906, 44). *Lantana odorata*, from Jamaica, gave 0.16% of lemon-yellow oil, having an odour of hyssop and ambergris, and having D^{15} 0.9149, $[\alpha]_D - 1^\circ 36'$, n_D^{20} 1.49630, ester number 4.7, acetyl ester number 51.0. *Tagetes patula*, flowers from Mexico, yielded 0.1% of a golden-yellow oil, having D^{15} 0.8856, $[\alpha]_D - 5^\circ 35'$, n_D^{20} 1.49714, acid number 2.0, ester number 18.7, acetyl ester number 74.3.

The report concludes with a critical résumé of descriptions of essential oils in various pharmacopeias, notes on recent chemical, biological, and physical research work on terpenes and their derivatives, and a memoir on the history, botany, preparation, and composition of Japanese peppermint oil by N. Inouye. T. A. H.

Oxidation Products of Artemisin. ENRICO RIMINI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 590—597).—The arteminic acid described by Horst (Abstr., 1902, i, 387) as an oxidation product of artemisin is in reality a mixture of santonin and artemisin, its formation being due to the use of impure artemisin.

When artemisin is oxidised by alkaline permanganate (about 5 atoms of oxygen) in presence of ice, it yields a *ketonic acid*, $C_{15}H_{22}O_8$, in the form of a pale yellow syrup, which reduces ammoniacal silver nitrate solution and Fehling's solution in the cold, and yields iodoform with potassium hydroxide and iodine. The *diphenylhydrazone* of this acid, $C_{15}H_{22}O_8(N_2HPh)_2$, forms chrome-yellow crystals, m. p. 116—118° (decomp.).

If a large excess of permanganate is employed, the oxidation of artemisin (1 mol.) yields oxalic acid (1 mol.). T. H. P.

Rhein. OTTO A. OESTERLE and ED. TISZA (*Chem. Zentr.*, 1908, ii, 1929—1930; from *Schweiz Woch. Chem. Pharm.*, 1908, 46, 701—703. Compare Hesse, Abstr., 1900, i, 41).—When crystallised about twenty times from pyridine, and sublimed in a cathode ray vacuum, this substance was obtained in small, yellow needles or compact, dark-coloured crystals, m. p. 321—321·5°, which gave on analysis 63·98, 63·71% C, and 2·88, 2·81% H, corresponding with $C_{15}H_8O_6$, the formula suggested by Tschirch and Heuberger (Abstr., 1903, i, 108). When acetylated in pyridine solution, no higher acetyl derivative was obtained than the diacetate. When heated with propionic anhydride, a pyridine solution of rhein yields a lemon-yellow, crystalline *propionate*, m. p. 223—224°; analysis gave 68·21% C, and 4·43% H. Benzoylation of rhein appears to result in the formation of at least two products, which have not yet been separated.

Methylation with methyl sulphate gives several *methyl ethers*, of which one, insoluble in hot potassium hydroxide, crystallises in long, pale yellow needles, m. p. 288°. The conclusion is drawn that rhein is not a simple substance, but a mixture. J. V. E.

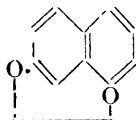
The Green Pigment of Bile. MAURICE PIETTRE (*Compt. rend.*, 1908, 147, 1492—1495).—Bilirubin crystallises from benzyl chloride in long prisms, often arranged in bundles; it crystallises still better from a mixture of chloroform and carbon tetrachloride. The formation of biliverdin is not simply an oxidation, for a green coloration is also produced when the halogens, the halogen acids in glacial acetic acid, trichloroacetic acid, chloral, bromal, etc., act on bilirubin.

G. B.

Establishment of the Oxonium Theory. HERMAN DECKER and THEODOR VON FELLEBERG (*Annalen*, 1909, **364**, 1—44).—The salts of benzopyryonium, naphthapyryonium, and dibenzopyryonium, can only be regarded as compounds containing quadrivalent oxygen, and the authors consider that the existence of quadrivalent basic oxygen is thereby established on as firm a basis as that of quinquevalent nitrogen, quadrivalent sulphur, and tervalent iodine. The compounds regarded by Collie and Tickle, Baeyer and Villiger, Hewitt and Werner, Fosse, etc., as oxonium salts, in spite of doubts which have been expressed as to this formulation, are correctly so constituted, and this also applies to Kehrman's azoxonium compounds. The authors are in entire agreement with the views of Archibald and McIntosh (*Trans.*, 1904, **85**, 919) on this subject, and they discuss at length the general resemblance between oxonium and ammonium compounds. It is pointed out that the secondary valencies of oxygen are usually brought into play at a lower temperature than in the case of nitrogen; thus oxonium compounds often decompose, or even cannot exist, at a temperature at which ammonium compounds are quite stable. In this respect quadrivalent sulphur occupies a position intermediate between nitrogen and oxygen. The formation of alkylammonium salts, as in the expression: $\text{HI} + \text{NH}_2\text{Me} \rightleftharpoons \text{NH}_3\text{MeI} \rightleftharpoons \text{NH}_3 + \text{MeI}$, whereby the quaternary compound may decompose in two directions (to which phenomenon the term "heterospasis" is applied), has its counterpart in the case of oxygen compounds, and the formation of oxonium intermediate compounds, with their possibility of heterospasis, in many cases throws light on hitherto incompletely explained reactions.

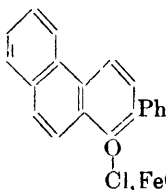
The synthesis of benzopyryonium derivatives is effected conveniently by condensing salicylaldehyde and its derivatives in presence of sulphuric or hydrochloric acid with an aliphatic or aromatic aldehyde or ketone containing an acidic methylene group next to the carbinol group. Solutions of such oxonium salts in 10—15% hydrochloric acid are mostly yellow, and on dilution, or by partial neutralisation, become colourless and deposit the corresponding colourless carbinol. Benzopyryonium ferrichloride is best prepared by shaking salicylaldehyde (2 mols.) and acetaldehyde (1 mol.) with 70% sulphuric acid and warming the mixture for three-quarters of an hour on the water-bath. After precipitating tar with hydrochloric acid, solid ferric chloride, is added. In moist air it becomes black, loses hydrogen chloride, and coumarin is formed. 2-Methylbenzopyryonium salts (*Abstr.*, 1907, i, 1064) are similarly prepared by the condensation of salicylaldehyde and acetone. The condensation of methyl ethyl ketone and salicylaldehyde in presence of sodium hydroxide leads to the formation of *o*-hydroxystyryl ethyl ketone, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{COEt}$, in small, yellow crystals, m. p. 101° (corr.), and a small amount of a compound, $\text{C}_{23}\text{H}_{22}\text{O}_3$, in yellow leaflets, m. p. $246\text{—}247^\circ$ (corr.). The former, on warming with fuming hydrochloric acid and adding ferric chloride, yields 2-ethylbenzopyryonium ferrichloride, $\text{C}_{11}\text{H}_{11}\text{OCl}\cdot\text{FeCl}_3$, in flesh-coloured crusts, m. p. $68\text{—}70^\circ$ (corr.), after sintering at 65° . The salt becomes green on exposure to light, and decomposes under the influence of moisture. When salicylaldehyde and methyl ethyl

ketone are subjected to the action of hydrogen chloride and ferric chloride added to the purified product, 2:3-dimethylbenzopyryronium ferrichloride, $C_{11}H_{11}OCl, FeCl_3$, is formed in long, yellow needles, m. p. 117—118° (corr.), after sintering at 112°. On dissolving this in acetone and pouring into water, the base, probably dimethylbenzopyranol, is precipitated. 2-isoPropylbenzopyryronium ferrichloride, $C_{12}H_{13}OCl, FeCl_3$, prepared by condensing salicylaldehyde and valeraldehyde in presence of hydrogen chloride, and subsequently adding ferric chloride, forms long, yellow needles, m. p. 75·5—76·5° (corr.). 3-Methyl-2-ethylbenzopyryronium ferrichloride, $C_{12}H_{13}OCl, FeCl_3$, similarly prepared from salicylaldehyde and diethyl ketone, forms golden leaflets, m. p. 86·5—87·5° (corr.). With water it yields 3-methyl-2-ethylbenzopyranol, $C_{12}H_{14}O_2$, in small, colourless needles, m. p. 70—72° (corr.). The condensation of salicylaldehyde and dipropyl ketone results in the production of a compound, $C_{21}H_{20}O_2$, colourless, glistening leaflets, m. p. 106—107° (corr.), and, on adding ferric chloride to the filtrate from this, 3-ethyl-2-propylbenzopyryronium ferrichloride, $C_{14}H_{17}OCl, FeCl_3$, in yellow, glistening leaflets, m. p. 55°, which with water gives 3-ethyl-2-propylbenzopyranol, in colourless needles, m. p. 74—76°. 2-Phenylbenzopyryronium ferrichloride is obtained in a 70% yield by condensing salicylaldehyde and acetophenone. 2:3-Diphenylbenzopyryronium ferrichloride, $C_{21}H_{15}OCl, FeCl_3$, similarly obtained from salicylaldehyde and deoxybenzoin, crystallises in long, yellow needles, m. p. 123—124° (corr.). With water this yields 2:3-diphenylbenzopyranol, $C_{21}H_{16}O_2$, in colourless needles, m. p. 121—122° (corr.). On boiling this with methyl or ethyl alcohol, the corresponding ether is formed. 7-Hydroxy-2-phenylbenzopyryronium chloride has the formula $C_{15}H_{15}O_4Cl$ (Perkin, Robinson, and Turner, Trans., 1898, 93, 1098, give $C_{15}H_{13}O_3Cl$). On heating at 140° in a current of hydrogen chloride, the compound, $C_{15}H_{11}O_3Cl$, is formed. The picrate of the pyryronium base turns brown at 190° and begins to sinter; it is not completely melted at 270° (Bulow and Sicherer, Abstr., 1902, i, 113, give m. p. 232—233°). The ferrichloride forms small, yellow needles containing $1C_2H_4O_2$ (from acetic acid), m. p. 162—163° (corr.), after previous sintering.



As a consequence of their work on benzopyryronium salts, the authors consider that salts of phenacetin, resacetin, gallacetin, quinacetin, isobrasilein, isohæmatein, fluorescein, and coerulein are to be looked on as benzopyryronium salts, and suggest that the free bases contain the annexed chromogen.

2-Phenyl-naphthapyryronium ferrichloride (annexed formula), prepared by condensing β -naphthaldehyde and acetophenone and precipitating with ferric chloride, forms small, dark yellow needles, m. p. 187·5° (corr.). On pouring into water, the colourless carbinol separates. 2:3-Diphenyl-naphthapyryronium ferrichloride,



$C_{25}H_{17}OCl, FeCl_3$, similarly prepared from β -naphthaldehyde and deoxybenzoin, crystallises in small, slender, yellow needles, m. p. 205—206° (corr.); the carbinol base forms two picrates, that

with two mols. of picric acid forms dark-coloured crystals, m. p. 118—120°, and that with 1 mol. of picric acid gives smaller crystals, m. p. 161° (decomp.), after sintering at 145°. J. C. C.

Cheiroline, the Alkaloid containing Sulphur obtained from Wallflower Seeds. WILHELM SCHNEIDER (*Ber.*, 1908, 41, 4466—4470).—The formula assigned by Wagner to cheiroline (*Abstr.*, 1908, i, 202) is incorrect; it should be $C_9H_{16}O_5N_2S_2$. Cheiroline is practically a neutral substance, and is optically inactive; it gives a white precipitate with mercuric chloride, and when warmed with an alkaline solution of lead oxide yields lead sulphide, and with an ammoniacal silver solution forms a mirror and silver sulphide. When the solution obtained by boiling the alkaloid (1 mol.) with dilute aqueous sodium hydroxide is acidified, it evolves hydrogen sulphide (1 mol.) and carbon dioxide (about 1.4 mols.). The solution then contains a base, $C_4H_{11}O_2NS$, which is obtained as an exceedingly deliquescent, crystalline mass; the *hydrochloride*, $C_4H_{11}O_2NS \cdot HCl$, crystallises in almost colourless, deliquescent, prismatic needles, m. p. 145—146°. The base when treated with sodium ethoxide and methyl iodide yields a quaternary *methiodide*, $C_7H_{18}O_2NIS$, obtained as glistening, silky scales, m. p. 183°; it is therefore probable that the base is a primary base.

Since cheiroline readily parts with a carbon atom and a sulphur atom, yielding a strong base, it is probable that these atoms are connected to the two nitrogen atoms as in thiocarbamide.

W. H. G.

Ergot of Rye. ERNST VAHLEN (*Archiv exp. Path. Pharm.*, 1908, 60, 42—75).—The author controverts the statement of Barger and Dale (*Abstr.*, 1908, i, 204) that the crystalline product, clavin, previously isolated from ergot, is a mixture of leucine and aspartic acid. He shows that by means of cupric acetate or hydroxide it can be resolved into two constituents, one of which gives an insoluble copper salt, whereas the other gives a soluble salt. The latter is a weakly basic substance of the formula $C_5H_{11}O_2N$, m. p. 258—260°, and does not give precipitates with the ordinary alkaloidal reagents; the former is *L*-leucine. For these reasons, the formula $C_{11}H_{24}O_4N_2$ is assigned to clavin. Clavin, leucine, and the clavin base are all very similar to one another in their crystalline form, solubility in solvents, and capacity for subliming, and the clavin is regarded as the leucine salt of the base.

The author also criticises Dale's experiment on the physiological action, and maintains, in opposition to Dale, that clavin has a specific action on the uterus.

Experiments were also carried out to determine the physiological action of the alkaloids, ergotinine, and hydroergotinine, which were isolated and described by Kraft. The latter has been assumed to be identical with the so-called ergotoxine, the water-soluble, amorphous alkaloid isolated by Barger and Carr (*Trans.*, 1907, 91, 337). It was found that more than 16 decigrams per kilo. was the toxic dose of hydroergotinine for cats, whereas, according to Dale (*Abstr.*, 1907, i, 79), 1.5 mg. of ergotoxine phosphate was a toxic dose for the same

animals. For these reasons, the chemical identity of hydroergotine and ergotoxine cannot be regarded as proved. It is suggested that both might be contaminated with varying quantities of a highly toxic substance. Ergotinine is relatively non-toxic when compared with hydroergotinine.

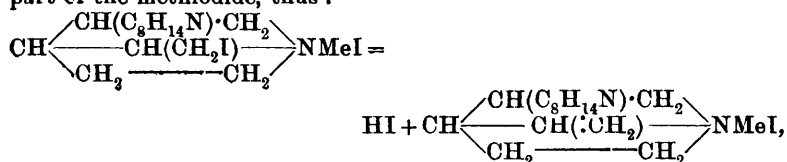
An experiment was made with the crystalline secalaminosulphonic acid, which was isolated by Kraft. It was found, when injected into a frog, to be physiologically inert. It is not, therefore, the active principle in the preparations described as sclerotic and ergotic acids.

S. B. S.

apoMorphine Hydrochloride. DAVID B. DOTT (*Pharm. J.*, 1908, [iv], 27, 801).—Experiments have been made which indicate that apomorphine hydrochloride has the composition represented by the formula $C_{34}H_{36}O_5N_2 \cdot 2HCl \cdot 2H_2O$, in which it is assumed that apomorphine is formed by the condensation of 2 mols. of morphine with elimination of 1 mol. of water.

E. G.

Action of Acids on Di-iodo- α -methylsparteine. AMAND VALEUR (*Compt. rend.*, 1908, 147, 1318—1319. Compare Abstr., 1908, i, 1006).—When iodoisoparteine methiodide is heated with either dilute sulphuric, hydrochloric, or acetic acid and the solution cooled, the product is invariably *iodoisoparteine methiodide hydriodide*, $C_{15}H_{25}N_2MeI_2 \cdot HI$, m. p. 198°, which regenerates iodoisoparteine methiodide when treated with sodium carbonate. The reaction is probably to be explained by the separation of hydrogen iodide from part of the methiodide, thus:



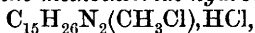
and the subsequent action of the liberated hydrogen iodide on the unchanged methiodide. This view is supported by the fact that the mother liquors from the action of dilute acetic acid on the methiodide contain a small quantity of a substance containing approximately the proportion of iodine required by the above formula. Moreover, when iodoisoparteine methiodide is heated in a sealed tube with dilute sodium hydroxide solution at 125—130°, α -methylsparteine is formed, probably according to the reaction $C_{15}H_{25}N_2MeI_2 + 2NaOH = C_{15}H_{25}N_2Me + 2NaI + O + H_2O$, the oxygen liberated serving to oxidise part of the α -methylsparteine produced.

E. H.

Relation between α -Methylsparteine and isoSparteine. Reciprocal Transformation of these Bases. II. isoSparteine-methosulphate and Some Salts of this Base. III. Action of Alkalis on isoSparteinemethosulphate. Methylisoparteinium Hydroxide. AMAND VALEUR (*Bull. Soc. chim.*, 1909, [iv], 5, 31—37, 37—40, 40—42).—The first paper is theoretical, and gives an interpretation of results recorded in the second and third papers and other

work (Abstr., 1908, i, 1006) on the basis of the formulæ previously assigned to sparteine, α -methylsparteine, and isosparteine (Abstr., 1905, i, 659, 717; 1908, i, 206). Most of this work has been published already (*loc. cit.*, and 1908, i, 736).

isoSparteine methosulphate (*loc. cit.*) dissolves in 1.5 parts of water, and the solution is slightly bitter, neutral to litmus, and does not reduce potassium permanganate. The anhydrous salt has m. p. 140—140.5°. *isoSparteine methochloride hydrochloride*,



m. p. 192—193° (decomp.), $[\alpha]_{\text{D}} - 19.75^\circ$, obtained by adding barium chloride to the solution of the methosulphate, separates from alcohol on addition of acetone, in transparent, deliquescent crystals. *isoSparteine methobromide hydrobromide*, m. p. 193° (decomp.), $[\alpha]_{\text{D}} - 15.38^\circ$, similarly obtained, is crystalline and very soluble in water. Its solution, on addition of sodium hydroxide, deposits an oil, which soon crystallises, and is probably *isosparteine methobromide*. *isoSparteine methiodide hydriodide* (Abstr., 1908, i, 44) has $[\alpha]_{\text{D}} - 11.80^\circ$, and crystallises from alcohol with H_2O .

Sparteine methosulphate, $\text{C}_{15}\text{H}_{26}\text{N}_2\text{Me} \cdot \text{HSO}_4 \cdot 7\text{H}_2\text{O}$, $[\alpha]_{\text{D}} - 24.54^\circ$, obtained by the addition of the necessary quantity of sulphuric acid to α -methylsparteinium hydroxide, crystallises from water on addition of alcohol and acetone. The solution is slightly acid to litmus, and does not reduce permanganate.

The transformation of *isosparteine* into α -methylsparteine described previously (Abstr., 1908, i, 736) may be used for the recovery of α -methylsparteine from the mixture of bases obtained in methylating sparteine (Abstr., 1908, i, 44). The mixture is treated with sulphuric acid, whereby the α -methylsparteine is converted into *isosparteine methosulphate*, the other bases remaining unchanged. The latter are washed out with ether, and the residual methosulphate converted into α -methylsparteinium hydroxide by the action of baryta, and this into α -methylsparteine.

T. A. H.

Strychnos Alkaloids. II. New Method for the Preparation of Sulphonic Acids. HERMANN LEUCHS and WILHELM SCHNEIDER (*Ber.*, 1908, 41, 4393—4396. Compare Abstr., 1908, i, 563).—It is extremely difficult to obtain strychninesulphonic acids by the direct action of sulphuric acid on the alkaloid, but *strychninesulphonic acid*, $\text{C}_{21}\text{H}_{22}\text{O}_5\text{N}_2\text{S}$, is readily formed when sulphur dioxide is passed into warm water (60°) in which finely-divided strychnine and manganese dioxide are suspended. The acid crystallises from hot water in colourless needles containing water of crystallisation, which is given up at 105°. The dried acid is extremely hygroscopic, and has m. p. 350—360° (decomp.). It dissolves readily in dilute alkalis, but not in 20% hydrochloric acid. The solution in sodium hydroxide has $[\alpha]_{\text{D}}^{20} - 233^\circ$. A hot solution of the sodium salt deposits the free acid when cooled.

J. J. S.

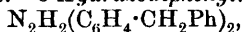
Aqueous Solutions of Pyridine. ÉMILE BAUD (*Compt. rend.*, 1909, 148, 96—98).—From determinations of the electro-capillary maxima of mixtures of water and pyridine, Gouy (Abstr., 1906, ii, 725) deduced the existence of a compound of these substances. To

the same end the author has studied the freezing temperatures, contractions in volume, refractive indices, and heats of dissolution of similar mixtures. The curve obtained by plotting the solidification temperatures of mixtures of pyridine and water against their percentage composition consists sensibly of four straight lines: the first, extending from 0 to 55% of pyridine, representing the separation of ice; the second, from 55 to 77% of pyridine, that of a hydrate; the third, from 77 to 83% of pyridine, of another hydrate, whilst the fourth represents the separation of pure pyridine. The temperature reaches a minimum for 83% of pyridine ($C_5H_5N + 0.9H_2O$), which is accordingly the composition of a eutectic mixture. As the crystallisation curves of the hydrates intersect before the maximum, the composition of these hydrates cannot be deduced; all that can be concluded is that one contains more than $3.6H_2O$ and the other more than $1.3H_2O$ per molecule of pyridine. The curve drawn with percentages of pyridine by weight as abscissæ, and the contractions in volume of these mixtures as ordinates, exhibits a maximum for the mixture of the composition $C_5H_5N, 2H_2O$. The index of refraction curve has a maximum also at the mixture of this composition. The heat of dissolution of pure pyridine in a large excess of water diminishes with rise in temperature according to the expression $Q = 2.800 - 0.044(t - 12.5)$. Determination of the heats of dissolution of the mixtures of water and pyridine permits of the calculation of the heats of formation of the latter. By calculating the results with reference to the addition of increasing quantities of water to a molecule of pyridine, a smooth curve is obtained exhibiting a change of direction at $2H_2O$ and $6H_2O$, whilst calculation of the heats for the same volume of mixture gives a curve showing a maximum for $C_5H_5N, 2H_2O$.

The conclusion is drawn that aqueous pyridine solutions contain at least two hydrates, $C_5H_5N, 2H_2O$ and $C_5H_5N, 6H_2O$, dissociated at the ordinary temperature, the more complex being the more dissociated.

E. H.

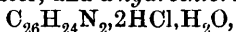
Alkaline Reduction of *o*-Nitrodiphenylmethane. PAUL CARRÉ (*Compt. rend.*, 1909, 148, 101—103*).—When *o*-nitrodiphenylmethane (Geigy and Königs, Abstr., 1885, 1236) is reduced by gradually adding zinc dust to its boiling solution in alcoholic soda, only 15—20% of *o*-hydrazodiphenylmethane is formed, the main product being *o*-aminodiphenylmethane. *o*-Hydrazodiphenylmethane,



crystallises in white lamellæ, m. p. 148—149°. It is oxidised by mercuric oxide to *o*-azodiphenylmethane, $N_2(C_6H_4 \cdot CH_2Ph)_2$, which exists in two forms. The α -modification crystallises from acetic acid in red needles, m. p. 116—117°, which, on melting, are transformed into the β -modification, m. p. 124—125°. The latter, when recrystallised from acetic acid, regenerates the α -compound, whilst crystallisation of either from alcohol gives a mixture of the two forms. When *o*-hydrazodiphenylmethane is treated with dilute acids, it undergoes the benzidine transformation, giving 2 : 2'-dibenzyl-4 : 4'-diaminodiphenyl, $C_{12}H_6(CH_2Ph)_2(NH_2)_2$, which crystallises in long, white

* and *Bull. Soc. chim.*, 1909, [iv], 5, 119—121.

needles, m. p. 136° , and forms a *sulphate*, $C_{26}H_{24}N_2 \cdot H_2SO_4$, also crystallising in long, white needles, m. p. 255° (decomp.), rapidly dissociated by boiling water, and a *hydrochloride*,



crystallising in white needles, m. p. 214° (decomp.), hydrolysed by water.

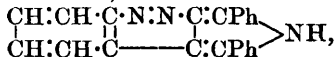
o-Aminodiphenylmethane, $NH_2 \cdot C_6H_4 \cdot CH_2Ph$, prepared by Fischer and Schutte (Abstr., 1894, i, 200), but not obtained by them in a crystalline form, crystallises from ether in large, light yellow prisms, m. p. 52° , b. p. $190-191^{\circ}/22$ mm., $172-173^{\circ}/12$ mm. Its *hydrochloride*, $C_{13}H_{13}N \cdot HCl$, crystallises in white needles, m. p. 137° (decomp.), which are dissociated by boiling water. The amine, when heated with phenylthiocarbimide, gives *α -phenyl- β -o-diphenylmethane-thiocarbamide*, $NHPh \cdot CS \cdot NH \cdot C_6H_4 \cdot CH_2Ph$, a white, crystalline powder, m. p. 138° . E. H.

Reaction of Phenylhydrazine and α -Halogen Aryl Derivatives.

GUIDO GOLDSCHMIEDT (*Gazzetta*, 1908, 38, ii, 634—638).—The results obtained by Ponzio and Valente (Abstr., 1908, i, 458) had been published previously by Ofner (Abstr., 1904, i, 818) and Flaschner (Abstr., 1905, i, 936). T. H. P.

Transformations of Diazopyrroles. FRANCESCO ANGELICO (*Atti R. Accad. Lincei*, 1908, [x], 17, ii, 655—662).—Castellana and D'Angelo (Abstr., 1905, i, 646) found that prolonged boiling of diazophenylindole with dilute sulphuric acid converts it into the corresponding azo-derivative.

The author finds that diazotriphenylpyrrole does not undergo a similar transformation under the same conditions, but that it is converted into an isomeric compound,



which acts both as an acid and as a base, dissolves readily in alcoholic potassium hydroxide solution, giving a violet solution, and separates in cinnabar-red scales; with strong acids it gives insoluble blue salts. When treated with ethyl iodide in presence of sodium ethoxide, it is converted into the *ethyl* derivative, $C_{22}H_{14}N_3Et$, which crystallises from alcohol in shining, indigo-blue needles, m. p. 181° . By the action of nitric acid on an acetic acid solution of the compound, $C_{22}H_{15}N_3$, the

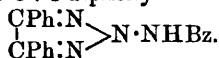
latter is converted into a *diketone*, $\begin{array}{c} CH:CH \cdot C \cdot N=N \\ | \qquad \qquad \qquad | \\ CH:CH \cdot C \cdot CBz:CBz \end{array}$, which separates

from alcohol in brownish-yellow crystals, m. p. 163° , dissolves in concentrated sulphuric acid, giving a blue solution, and is converted by hydrazine into the corresponding *azine*, $C_{22}H_{14}N_4$, crystallising from alcohol in golden-yellow needles, m. p. 240° , and subliming undecomposed.

Reduction of the diketone by means of zinc dust and acetic acid yields the compound, $\begin{array}{c} CH:CH \cdot C \cdot N:N \cdot C:CPH \\ | \qquad \qquad \qquad | \\ CH:CH \cdot C \text{---} C:CPH \end{array} > O$, which crystallises from acetic acid in shining, red needles, m. p. 195° , and is oxidised to the diketone by the action of nitric acid. T. H. P.

Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XXV. *N*-Amino-osotriazoles. ROBERT STOLLÉ (*J. pr. Chem.*, 1908, [ii], 78, 544—546. Compare Abstr., 1907, i, 654).—The author now draws the conclusion that the compound obtained by the complete hydrolysis of 2:3-dibenzoyl-5:6-diphenyl-2:3-dihydro-1:2:3:4-tetrazine, which was thought previously to be 5:6-diphenyl-2:3-dihydro-1:2:3:4-tetrazine (Abstr., 1905, i, 97), is 1-amino-3:4-diphenyl-1:2:5-triazole, $\begin{matrix} \text{CPh:N} \\ \text{CPh:N} \end{matrix} > \text{N} \cdot \text{NH}_2$, since when

it is benzoylated it yields a compound isomeric with the dibenzoyl derivative just mentioned, but having m. p. 151° ; this compound is 1-dibenzoylamino-3:4-diphenyl-1:2:5-triazole, $\begin{matrix} \text{CPh:N} \\ \text{CPh:N} \end{matrix} > \text{N} \cdot \text{NBz}_2$. It is also formed when 2:3-dibenzoyl-5:6-diphenyl-2:3-dihydro-1:2:3:4-tetrazine is heated at about 190° , and by the benzoylation of the compound obtained by eliminating one of the benzoyl groups from the above dibenzoyltetrazine; the latter compound must be therefore 1-benzoylamino-3:4-diphenyl-1:2:5-triazole,



It has also been shown that 2:3-dibenzoyl-5:6-dimethyl-2:3-dihydro-1:2:3:4-tetrazine when heated at about 150° passes into 1-dibenzoylamino-3:4-dimethyl-1:2:5-triazole, $\begin{matrix} \text{CMe:N} \\ \text{CMe:N} \end{matrix} > \text{N} \cdot \text{NBz}_2$, m. p. 114° .

W. H. G.

Addition of Hydrogen Chloride to Organic Bases and Azo-compounds. ANTONI KORCZYŃSKI (*Ber.*, 1908, 41, 4379—4381. Compare Abstr., 1908, i, 977; Scholl and Escales, *ibid.*, 1898, i, 182).—The absorption of hydrogen chloride by organic amines and azo-derivatives has been examined at various temperatures, and in an apparatus similar to that used by Ley and Wiegner. The maximum number of molecules of hydrogen chloride absorbed is not a function of the strength of the base. At -75° aniline, *p*-toluidine, and *o*- and *m*-nitroanilines form salts with 3HCl, and dibromo-*p*-toluidine and *p*-nitroaniline with 2HCl. At the ordinary temperature, azobenzene, *p*-hydroxyazobenzene, *p*-methoxyazobenzene and aminoazobenzene absorb 2HCl, and dimethylaminoazobenzene, 3HCl.

J. J. S.

The Combination of Iodine in Iodothyreoglobulin, and some Observations on Iodothyryn. ADOLF OSWALD (*Arch. exp. Path. Pharm.*, 1908, 60, 115—130).—The degradation of iodothyreoglobulin by pancreatin and barium hydroxide solution was studied. By means of the former, a small amount of a substance was obtained, which deposited from the digest, and was soluble in alkalis, but insoluble in acids; it contained 3—4.5% iodine, and was in many respects similar to Baumann's iodothyryn; the greater part of the iodine found in the digest was not in combination with organic substances. By scission with barium hydroxide, also, only a small

amount of an organic iodine compound was obtained, which was soluble in acids, and was probably unchanged thyreoglobulin.

S. B. S.

The Mono-amino-acids of Paramucin. FRITZ PREGL (*Zeitsch. physiol. Chem.*, 1908, 58, 229—232).—After acid hydrolysis, paramucin yields glucosamine, diamino-acids in traces, leucine, alanine, proline, phenyl-alanine, aspartic acid, glutamic acid, tyrosine, and tryptophan. Quantitative data are not given.

W. D. H.

Hydrolysis of Glutokyrin. MAX SIEGFRIED and O. PILZ (*Zeitsch. physiol. Chem.*, 1908, 58, 215—228).—Glutokyrin β -sulphate was prepared from gelatin; the phosphotungstic acid precipitate from it contains 80% of its nitrogen. Arginine, lysine, and glutamic acid were found in the cleavage products after hydrolysis. Histidine and glycine were not obtained.

W. D. H.

Molecular Analysis of Proteins. ALEXANDRE ÉTARD and ANTONY VILA (*Compt. rend.*, 1908, 147, 1323—1324. Compare Abstr., 1908, i, 584).—The use of anhydrous methyl alcohol is advocated for separating and drying the mixtures of amino-acids formed in protein hydrolysis. A solution of barium hydroxide in anhydrous methyl alcohol is employed for precipitating the acidic substances thus obtained.

G. B.

The Influence of Acids, Alkalis, Neutral Salts, and Carbohydrates on Trypsin. T. KUDO (*Biochem. Zeitsch.*, 1909, 15, 473—500).—Tryptic digestion with "pancreatin Rhenania" proceeds best in a neutral medium. It is inhibited by alkalis and acids, especially organic acids. Sodium carbonate has a very small destructive influence on the ferment, acetic acid is indifferent, other organic acids destroy it, and mineral acids are rather more powerful in this direction. The destructive action is independent of their valency or concentration. Various salts have an inhibitory action, but in most cases a slight one. Starch is also inhibitory, but the sugars have little or no effect.

W. D. H.

The Adsorption of Diastase and Catalase by Colloidal Protein and by Normal Lead Phosphate. AMOS W. PETERS (*J. Biol. Chem.*, 1908, 5, 367—380).—A method of concentration of enzymes is described, in which the enzyme is adsorbed from solution by the addition of lead phosphate suspended in water, or by peptone suspended in 50% acetone. Almost the whole of the enzyme is adsorbed, and remains active in spite of the presence of the adsorbed precipitate, from which it can only be separated to a slight extent by washing with water. The diastase employed was obtained from germinating wheat, from autolysed liver, and from liquid bacterial cultures. The action of diastase is accelerated by the presence of lead phosphate, but not, for instance, by that of zinc phosphate; the reason for the acceleration is unknown.

G. B.

Organic Chemistry.

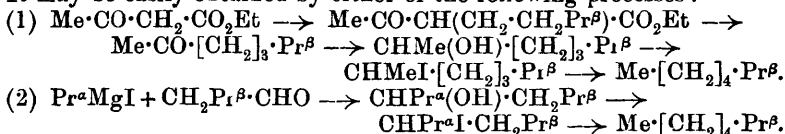
Chemical Action of the Electric Discharge at Low Temperatures. E. BRINER and E. L. DURAND (*J. Chim. Phys.*, 1909, 7, 1—30).—Most of the results described in this paper have been published already (Abstr., 1907, ii, 759; 1908, ii, 101, 940). By the action of the electric spark on a mixture of nitrogen and ethane at -78° , carbon, hydrogen, nitric acid, ammonia, and higher hydrocarbons are obtained, the latter being formed by polymerisation. In similar experiments with a mixture of nitrogen and acetylene, similar products were obtained, but in the latter case the proportion of hydrogen cyanide predominates over that of the ammonia.

In the action of the silent discharge on ethane alone at -78° , no carbon is liberated, but there is considerable formation of higher hydrocarbons. Under similar conditions, a mixture of equal volumes of nitrogen and ethane also gives a relatively high proportion of higher hydrocarbons, and less hydrogen cyanide than when the spark discharge is used.

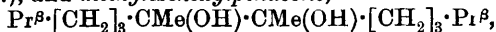
The effect of the electric discharge is very complicated, and it appears that the laws of chemical statics are not applicable; kinetic and atomic considerations afford a better guide to the phenomena.

G. S.

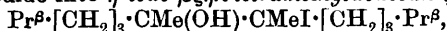
isoOctane [β -Methylheptane]. LATHAM CLARKE (*J. Amer. Chem. Soc.*, 1909, 31, 107—116. Compare Abstr., 1907, i, 169).— β -Methylheptane is the ninth hydrocarbon of the series C_8H_{18} to be prepared. It may be easily obtained by either of the following processes:



Methyl isohexyl ketone has b. p. $165^{\circ}/764$ mm.; Welt gives b. p. 167 — 168° (Abstr., 1895, i, 202). It is reduced by sodium and ethyl alcohol to methylisohexylcarbinol, b. p. $176^{\circ}/765$ mm. (compare Welt, *loc. cit.*), and methylisohexylpinacone,



a liquid, b. p. 293 — $295^{\circ}/765$ mm. The latter compound is converted by hydrogen iodide into η -iodo- $\beta\zeta\eta\lambda$ -tetramethyldodecan- ζ -ol,



an unstable, colourless oil (compare Clarke and Shreve, Abstr., 1906, i, 473). Methylisohexylcarbinol is converted by red phosphorus and iodine into ζ -iodo- β -methylheptane, a colourless, heavy oil, which, when reduced with a zinc-copper couple, yields isooctane (β -methylheptane), $\text{CH}_3\cdot[\text{CH}_2]_4\cdot\text{Pr}^\beta$, a colourless liquid, b. p. $116^{\circ}/761$ mm., D_{15}^{25} 0.7035, n_D^{25} 1.3944. The reduction may also be effected by acting on the iodo-octane with magnesium in dry ether, and treating the organo-magnesium compound with water.

Propyl magnesium iodide and *isovaleraldehyde* interact in dry ether, forming an additive product, which, when treated with water, yields β -methyl- δ -heptanol, $\text{CHPr}^{\alpha}(\text{OH})\cdot\text{CH}_2\text{Pr}^{\beta}$, a colourless liquid, b. p. $164^{\circ}/760$ mm. If the reacting substances are not quite dry, *isoamyl* alcohol and a *glycol*, $\text{CH}_2\text{Pr}^{\beta}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Pr}^{\beta}$, a colourless, viscid oil, b. p. $238\text{--}242^{\circ}/760$ mm., are formed. β -Methyl- δ -heptanol is converted by red phosphorus and iodine into δ -iodo- β -methylheptane, which is reduced by a zinc-copper couple to β -methylheptane.

W. H. G.

Production of Iodoform [from Carbon Dioxide]. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1909, [vi], 29, 54—55).—Potassium hypochlorite added gradually to an aqueous solution containing ammonia, potassium hydroxide, 10% of potassium iodide, and 5% of potassium carbonate, forms nitrogen iodide, which at first disappears on shaking. When the disappearance becomes slow, a large excess of ammonia is added, which causes an almost immediate precipitation of iodoform.

G. B.

Reactions between Iodoform and Silver Fluoride and Chloride. WILLIAM OECHSNER DE CONINCK (*Bull. Soc. chim.*, 1909, [iv], 5, 62—63. Compare Auger, *Abstr.*, 1908, i, 494).—On gently heating silver chloride and iodoform in the correct proportions suspended in dilute alcohol, the following interaction takes place: $3\text{AgCl} + \text{CHI}_3 = 3\text{AgI} + \text{CHCl}_3$. No gas is evolved, whereas if silver fluoride is taken (as Auger has shown) the products are carbon monoxide and hydrogen fluoride with a little carbon dioxide: $3\text{AgF} + \text{CHI}_3 + \text{H}_2\text{O} = 3\text{AgI} + 3\text{HF} + \text{CO}$.

R. J. C.

Preparation of Absolute Alcohol. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. Chim. suc. dist.*, 1909, 26, 580).—Ninety to 95% alcohol is digested with aluminium foil in presence of mercuric chloride and then distilled. The product consists of absolute alcohol free from aldehydes and acetals.

L. DE K.

Butane- β -ol [Methylethylcarbinol] and its Tartrates. J. RICHÉ (*J. Pharm. Chim.*, 1909, [vi], 29, 57—60).—This alcohol, synthesised from acetaldehyde by Grignard's reaction, could not be resolved into its optical antipodes by fractional esterification with tartaric acid.

G. B.

Pinacolyl Alcohols. MAURICE DELACRE (*Bull. Soc. chim.*, 1909, [iv], 5, 109—113).—The author questions the accuracy of the following conclusions given in L. Henry's recent papers on pinacolyl alcohols (*Abstr.*, 1907, i, 374; 1908, i, 881; this vol., i, 79).—(1) That the haloid esters of *sec*-pinacolyl alcohol (methyl*tert*-butylcarbinol) undergo isomerisation when heated, yielding haloid esters of *tert*-pinacolyl alcohol (dimethylisopropylcarbinol); (2) that since on dehydration with acetic anhydride both pinacolyl alcohols yield a mixture of $\beta\gamma$ -dimethyl- Δ^{β} -butylene and $\beta\gamma$ -dimethyl- Δ^{α} -butylene, in which the former largely preponderates, it may be assumed

generally that the hydroxyl of a :C(OH)\cdot group placed near a :CH\cdot and a $\text{\cdot CH}_2\text{\cdot}$ group exhibits a marked, but not exclusive, preference for the H of the :CH\cdot group, and (3) that in the dehydration of dimethylisopropylcarbinol by acetic anhydride containing sulphuric acid, the anhydride acts by first forming dimethylisopropylcarbiny acetate, which is more readily dehydrated than the parent alcohol.

The author contends that the first statement is refuted by the results given in his previous papers (Abstr., 1907, i, 578; 1908, i, 243), and that the second conclusion is inadmissible since the relative proportions of the two hydrocarbons formed vary with the conditions of the experiment. The validity of the third point he has examined by treating dimethylisopropylcarbiny acetate with dilute sulphuric acid, and finds that the acetate is scarcely dehydrated at all under conditions in which the alcohol undergoes complete dehydration (Abstr., 1906, i, 921). T. A. H.

ψ -Butylethylene Glycol. F. CLAESSENS (*Bull. Soc. chim.*, 1909, [iv], 5, 113—118).— ψ -Butylethylene ($\gamma\gamma$ -dimethyl- Δ^a -butylene, $\text{CMe}_3\text{\cdot CH\cdot CH}_2$),

described by Delacre (Abstr., 1902, i, 79), furnishes a liquid *dibromide*, b. p. 91—92°/14 mm. (approx.), 203°/762 mm. (decomp.), D_0^{20} 1.616, which becomes coloured on keeping, is readily soluble in organic solvents, and when heated with potassium acetate and acetic acid in a closed tube at 200° is converted into *bromo- $\gamma\gamma$ -dimethyl- Δ^a -butylene*, b. p. 120—130°, D_0^{20} 1.165, which was not obtained pure.

On oxidation with permanganate, $\gamma\gamma$ -dimethyl- Δ^a -butylene yields trimethylacetic acid, and is therefore an exception to Wagner's rule that, on careful oxidation with permanganate, ethylenic hydrocarbons yield the corresponding glycols (Abstr., 1888, i, 665). With iodine and yellow mercuric oxide the hydrocarbon yields the corresponding *iodohydrin*, D_0^{20} 1.481, which decomposes at 110°, but is volatile in steam. On treatment with potassium hydroxide solution, this yields the corresponding *glycol*, $\text{CMe}_3\text{\cdot CH(OH)\cdot CH}_2\text{\cdot OH}$, D_0^{20} 0.940, b. p. 205—206°, m. p. 32—33°, which is crystalline and hygroscopic. The glycol dissolves in hydrochloric acid, from which it can be recovered unchanged. With acetyl chloride it yields, apart from a small quantity of a chlorinated compound, a *diacetyl* derivative, b. p. 213—215°, D_0^{20} 1.014, which is a liquid of pleasant odour and readily soluble in water, alcohol or ether. Couturier's hydrocarbon, $\beta\gamma$ -dimethyl- Δ^a -butylene (Abstr., 1893, i, 244, and Delacre, Abstr., 1902, i, 79), can also be converted into the corresponding glycol through the iodohydrin. This glycol furnishes a chloroacetate on treatment with acetyl chloride, and dissolves in hydrochloric acid, yielding a chlorinated product which decomposes on distillation. T. A. H.

New Method for Preparation of Ethers. JEAN B. SENDERENS (*Compt. rend.*, 1909, 148, 227—229).—The author has recorded previously the decomposition of alcohols into ethylenic hydrocarbons and water by the catalytic action of precipitated alumina at 300° (Abstr., 1908, i, 494, 495; ii, 166). It is now found that this substance at a lower temperature can effect the quantitative dehydration of

alcohols with production of the corresponding ethers. Thus alcohol in the state of vapour is passed over alumina (prepared by acidifying a solution of sodium aluminate) at 240—260°, and the products passed through a Y-tube cooled in ice. It is not necessary to use absolute alcohol. The products condense to a liquid which separates into two layers; the upper layer consists of ethyl ether in a state of greater purity than commercial "rectified ether." Methyl ether and propyl ether have been prepared in the same manner. W. O. W.

Action of Acids on Sodium Ethyl Thiosulphate. III. AUGUST GUTMANN (*Ber.*, 1909, 42, 228—232. Compare Abstr., 1907, i, 671; 1908, i, 497).—The action of alkalis on sodium ethyl thiosulphate is represented thus: $\text{NaEtS}_2\text{O}_3 + \text{KOH} = \text{NaKSO}_3 + \text{EtSOH}$. Bunte (*Ber.*, 1874, 646) represents the corresponding acid hydrolysis in the following manner: $\text{NaEtS}_2\text{O}_3 + \text{H}_2\text{O} = \text{NaHSO}_4 + \text{EtSH}$. The author finds that sulphurous acid is also produced whether the reaction is carried out in concentrated or dilute solution, or in presence of much or little acid. The other products are ethyl sulphide, sulphuric acid, and ethyl mercaptan. Probably the change in acid solution, as in alkaline, is at first: $\text{HEtS}_2\text{O}_3 + \text{H}_2\text{O} = \text{SO}_2 + \text{H}_2\text{O} + \text{EtS}\cdot\text{OH}$.

Subsequently in acid solution the sulphurous acid reacts with one or two molecules of thioethyl hydroperoxide, thus: $\text{EtS}\cdot\text{OH} + \text{SO}_2 = \text{EtSH} + \text{SO}_3$; $2\text{EtS}\cdot\text{OH} + \text{SO}_2 = \text{Et}_2\text{S}_2 + \text{H}_2\text{SO}_4$.

That this explanation is correct is shown by the fact that if after alkaline hydrolysis a solution of sodium ethyl thiosulphate is rendered acid and kept, sulphuric acid is formed.

In view of these results, thiosulphuric acid can no longer be given the constitution $\text{SO}_2\begin{smallmatrix} \text{OH} \\ \text{SH} \end{smallmatrix}$, ascribed to it by Bunte, but it must exist as the two isomeric forms: $\text{SO}_2\begin{smallmatrix} \text{S}\cdot\text{OH} \\ \text{H} \end{smallmatrix}$ and $\text{SO}_2\begin{smallmatrix} \text{O}\cdot\text{SH} \\ \text{H} \end{smallmatrix}$.

E. F. A.

Acid Glycerophosphates. P. CARRÉ (*Bull. Soc. chim.*, 1909, [iv], 5, 109).—With reference to a paper by Self (*Pharm. J.*, 1908, 26, 627), it is pointed out that the process described by that investigator for the preparation of barium hydrogen glyceryl phosphate, namely, the addition of sulphuric acid to barium glyceryl phosphate until the mixture is neutral to helianthin, has been shown by the present author on a previous occasion to yield a mixture of the normal glyceryl phosphate and glyceryl dihydrogen phosphate (Abstr., 1904, i, 133 215, 819). T. A. H.

The Nitrogen of Lecithin and other Phosphatides. HUGH MACLEAN (*Biochem. J.*, 1909, 4, 38—58).—The nitrogen of the commercial preparation of lecithin termed "lecithol" (Riedel, Berlin) is probably all present as choline.

In the lecithin of heart-muscle there is probably another nitrogen-containing group in addition. The base of cuorin is probably not choline. W. D. H.

Allylxanthic Acid. BERNARDO ODDO and GIOVANNI DEL ROSSO (*Gazzetta*, 1909, 39, i, 11—23).—Study of allylxanthic acid and of its salts and other derivatives shows that in some ways the xanthic acids are comparable with hydrogen sulphide and with cyanic and thiocyanic acids.

Potassium, $\text{SK} \cdot \text{CS} \cdot \text{O} \cdot \text{C}_3\text{H}_5$, and *sodium allylxanthates*,
 $\text{SNa} \cdot \text{CS} \cdot \text{O} \cdot \text{C}_3\text{H}_5$,

obtained by the action of excess of carbon disulphide on a solution of potassium (or sodium) hydroxide in allyl alcohol at a low temperature, form white, gelatinous precipitates, which dry in the form of faintly yellow, silky needles. With copper sulphate these salts react according to the equations: $2\text{SK} \cdot \text{CS} \cdot \text{O} \cdot \text{C}_3\text{H}_5 + \text{CuSO}_4 = (\text{C}_3\text{H}_5 \cdot \text{O} \cdot \text{CS} \cdot \text{S})_2\text{Cu} + \text{K}_2\text{SO}_4$ and $2(\text{C}_3\text{H}_5 \cdot \text{O} \cdot \text{CS} \cdot \text{S})_2\text{Cu} = (\text{C}_3\text{H}_5 \cdot \text{O} \cdot \text{CS} \cdot \text{S})_2\text{Cu}_2 + \text{C}_3\text{H}_5 \cdot \text{O} \cdot \text{CS} \cdot \text{S} \cdot \text{S} \cdot \text{CS} \cdot \text{O} \cdot \text{C}_3\text{H}_5$

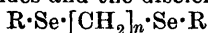
(compare Ragg, *Abstr.*, 1908, i, 604), the *cuprous allylxanthate* formed being insoluble. The allylxanthic radicle in the potassium and sodium salts may be estimated by titration with standard copper sulphate solution, using *s*-diphenylcarbazine as indicator (compare Oddo, *Abstr.*, 1903, ii, 758). The following salts of allylxanthic acid were also prepared: *silver*, $\text{C}_4\text{H}_5\text{OS}_2\text{Ag}$, *zinc*, $(\text{C}_4\text{H}_5\text{OS}_2)_2\text{Zn}$, *lead*, $(\text{C}_4\text{H}_5\text{OS}_2)_2\text{Pb}$, *nickel*, $(\text{C}_4\text{H}_5\text{OS}_2)_2\text{Ni}$, *cobalt*, $(\text{C}_4\text{H}_5\text{OS}_2)_2\text{Co}_2$, *mercury*, *cadmium*, *tin*, *bismuth*, *iron*, *platinum*, and *gold*.

Allylxanthic acid, $\text{SH} \cdot \text{CS} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2$, is obtained as a faintly yellow, unstable oil heavier than water, and, on distillation, decomposes into allyl alcohol and carbon disulphide. The *methyl ester*, $\text{SMe} \cdot \text{CS} \cdot \text{O} \cdot \text{C}_3\text{H}_5$, is a pale yellow oil, b. p. 200—203°, D^{24}_4 1.1214, with an alliaceous odour, and has the normal molecular weight in freezing benzene. The *ethyl ester*, $\text{C}_6\text{H}_{10}\text{OS}_2$, is an oil, b. p. 210—212°, D^{28}_4 1.0690, resembling the methyl derivative in odour, and having the normal molecular weight in freezing benzene. The *allyl ester*, $\text{C}_7\text{H}_{10}\text{OS}_2$, is obtained as a brownish-yellow oil, b. p. 221—223°, having a very pungent, garlic-like odour, and exhibiting normal cryoscopic behaviour in benzene.

T. H. P.

Selenomercaptans and their Derivatives. LEO TSCHUGAEFF (*Ber.*, 1909, 42, 49—54).—Ethyl, propyl, and butyl selenomercaptans have been prepared by heating on the water-bath a solution of sodium hydroselenide, obtained by saturating a 10% alcoholic solution of sodium ethoxide with hydrogen selenide with about 5% less than the calculated quantity of the alkyl iodide or bromide in an atmosphere of hydrogen. The selenomercaptans are heavy liquids with a foul, persistent odour, which are insoluble in water, react in the usual way with mercuric oxide, and yield coloured precipitates with the salts of heavy metals, particularly of lead and thallium. Selenomercaptans are extremely autoxidisable in air, yielding diselenides, $\text{R} \cdot \text{Se}_2 \cdot \text{R}$. The hydrogen of the $\cdot\text{SeH}$ group reacts with magnesium methyl iodide, methane being evolved quantitatively. Selenides, $\text{R}' \cdot \text{Se} \cdot \text{R}''$, are obtained by treating an alcoholic solution of sodium ethoxide and the selenomercaptan with an alkyl iodide or bromide, all in equal molecular quantities; in the absence of air, the yield is nearly quantitative. Diselenides of the type $\text{R} \cdot \text{Se} \cdot [\text{CH}_2]_n \cdot \text{Se} \cdot \text{R}$ result by the

action of dihaloid hydrocarbons on the sodium selenomercaptides: $2\text{NaSeR} + \text{Br}[\text{CH}_2]_n\text{Br} = \text{R}\cdot\text{Se}[\text{CH}_2]_n\cdot\text{Se}\cdot\text{R} + 2\text{NaBr}$. With ethylene dibromide, however, the main product is diethyl diselenide, ethylene being evolved. The selenides and the diselenides of the type



are colourless liquids somewhat stable in air, whilst diselenides of the type $\text{R}\cdot\text{Se}_2\cdot\text{R}$ are yellowish-red liquids, which distil undecomposed only in a vacuum.

In the accompanying table, the density, refractive index, and coefficient of expansion (α) are measured at the temperature t° .

	B. p.	t° .	$D_4^{t^\circ}$	α .	n_D .
EtSeH	53.5°	24	1.3954	0.0018	1.47715
PrSeH	84	20	1.3020	—	1.47560
BuSeH	114	24.5	1.2352	0.0012	1.47446
MeSeEt	86	23	1.3134	—	1.4820
MeSePra	114	20.4	1.2445	—	1.48121
MeSeBu ^a	141	24.5	1.1875	—	1.47710
PrSePra	159	24.3	1.1427	0.00113	1.47494
PrSe ₂ ·Pra	99/13 mm.	22.2	1.4991	0.00127	1.55535
EtSe [*] $[\text{CH}_2]_9$ SeEt	135/15 mm.	24	1.4630	0.00129	1.54892

The atomic refraction of selenium in the selenomercaptans is 10.78, in the selenides, 10.91, and in dipropyldiselenide, 11.33. C. S.

Solidification of Mixtures of Water and Soluble Fatty Acids. A. FAUCON (*Compt. rend.*, 1909, 148, 38—39).—The freezing-point curves of the systems water-formic acid, water-acetic acid, and water-propionic acid have been determined. The respective eutectic points and the molar composition of the eutectic mixtures are as follows: $\text{H}\cdot\text{CO}_2\text{H} + 1.14\text{H}_2\text{O}$, -48° ; $\text{Me}\cdot\text{CO}_2\text{H} + 2.40\text{H}_2\text{O}$, -27° ; $\text{Et}\cdot\text{CO}_2\text{H} + 0.578\text{H}_2\text{O}$, -29.4° . In no case is there evidence of chemical combination. The system butyric acid and water is being further investigated. G. S.

Behaviour of Fatty Acids in Arnold's Distillation Process. A. HEIDUSCHKA and K. PFIZENMAIER (*Pharm. Zentr.-h.*, 1909, 50, 85—86).—With reference to the publications of Dons (*Zeitsch. Nahr. Genussm.*, 1907, 14, 150) and Arnold (*ibid.*, 1908, 16, 705) on the subject of the fatty acids of butter, the author has investigated the behaviour of each of the acids, formic, acetic, propionic, butyric, hexoic, octoic, decoic, lauric, myristic, palmitic, stearic, oleic, and linoleic, when mixed with water and distilled. It was found that (1) the distillate may have a constant composition which has no relation to the composition of the mixture under distillation, or (2) its composition may vary with that of the mixture under distillation, or (3) it may exhibit a combination of (1) and (2), being of constant composition for a certain concentration of the mixture under distillation and exhibiting a proportional composition for other concentrations. A table of experimental results is given in the original. T. A. H.

Total Asymmetric Syntheses. ALFRED BYK (*Ber.*, 1909, 42, 141—142).—Mainly a criticism of Henle and Haakh's paper (this vol., i, 6). J. J. S.

General Method for the Preparation of Trialkylacetic Acids. ALBIN HALLER and ED. BAUER (*Compt. rend.*, 1909, 148, 127—132. Compare Abstr., 1908, i, 987; this vol., i, 108).—Trialkylacetophenones of the type $\text{COPh}\cdot\text{CRR}'\text{R}''$ are dissolved in benzene or toluene and boiled for five hours with sodamide. The ketone undergoes decomposition into benzene and an amide of the type $\text{CRR}'\text{R}''\cdot\text{CO}\cdot\text{NH}_2$, which is readily converted by nitrosyl sulphate into the corresponding acid, $\text{CRR}'\text{R}''\cdot\text{CO}_2\text{H}$. Attempts to bring about a similar reaction in the case of dialkylallylacetophenones, however, have not been successful. The following new compounds have been prepared in this way: *aa-dimethyl-n-butyramide*, $\text{CMe}_2\text{Et}\cdot\text{CO}\cdot\text{NH}_2$, m. p. 103—104°; *aa-dimethyl-n-valeramide*, $\text{CMe}_2\text{Pr}^a\cdot\text{CO}\cdot\text{NH}_2$, m. p. 95—96°; *aa-dimethyl-n-valeric acid*, $\text{CMe}_2\text{Pr}^a\cdot\text{CO}_2\text{H}$, b. p. 101—102°/11 mm., 190—200° under ordinary pressure; *a-methyl-a-ethyl-n-butyramide*, $\text{CMeEt}_2\cdot\text{CO}\cdot\text{NH}_2$, m. p. 78—79°; *aa-diethyl-n-butyramide*, $\text{CEt}_3\cdot\text{CONH}_2$, m. p. 108°, b. p. 148—149°/20 mm.; *aa-diethyl-n-butyric acid*, $\text{CEt}_3\cdot\text{CO}_2\text{H}$, m. p. 39·5°, b. p. 119°/14 mm., 220—222° under ordinary pressure; *a-methyl-a-ethyl-n-valeramide*, $\text{CMeEtPr}^a\cdot\text{CO}\cdot\text{NH}_2$, m. p. 46°, b. p. 134—135°/12 mm.; *a-methyl-a-ethyl-n-valeric acid*, $\text{CMeEtPr}^a\cdot\text{CO}_2\text{H}$, b. p. 215—220°. W. O. W.

Further Applications of the General Method of Hydrogenation Based on the Use of Finely-divided Metals. PAUL SABATIER and ALPHONSE MAILHE (*Ann. Chim. Phys.*, 1909, [viii], 16, 70—107).—Mainly a résumé of work already published (compare Abstr., 1905, i, 571, 635; 1906, i, 561; 1907, i, 458, 488, 490, 587, 747; 1908, i, 36, 278, 529), but the following facts have not previously been recorded: (1) unsaturated acids of the aliphatic series yield the corresponding saturated acid when directly hydrogenated in the presence of nickel; thus crotonic acid at 190° is reduced to butyric acid, and oleic or elaidic acid at 280—300° is reduced to stearic acid to the extent of 90% of that required by theory; (2) unsaturated ketones are converted into the corresponding saturated ketone by direct hydrogenation in the presence of nickel; thus mesityl oxide yields isopropylacetone (β -methylpentan- δ -one), and phorone yields diisobutyl ketone; (3) when the ketonic acids are directly hydrogenated in the presence of nickel, the ketonic group only is reduced; thus lævulic acid yields valerolactone, and ethyl acetoacetate undergoes (a) the normal reduction, yielding ethyl butyrate; (b) scission of the molecule and subsequent reduction of the products, yielding acetone, isopropyl alcohol, and propionic acid; and (c) a molecular condensation yielding solid dehydracetic acid.

Methyl *tert*.-butylamine has b. p. 54—56°, and the oxalate has m. p. 166° (not 58—60° and 160° respectively as stated previously: Abstr., 1907, i, 490). M. A. W.

Action of Ozone on Oleic Acid. CARL D. HARRIES [with WALTHER FRANK] (*Ber.*, 1909, 42, 446—458. Compare Molinari, Abstr., 1908, i, 849, and Harries, *ibid.*, 387).—Oleic acid ozonide,

after washing with sodium hydrogen carbonate solution and water, has the same composition whatever the concentration of the ozone used may be.

The formation of hydrogen peroxide by the decomposition of the ozonide with water is confirmed. The decomposition with water yields products containing 9, and not 18, carbon atoms, and the primary products are aldehydes or their peroxides, which are transformed into acids by a secondary reaction. These products have been re-investigated (compare Abstr., 1907, i, 10). Nonaldehyde peroxide, $C_9H_{18}O_2$, crystallises from light petroleum in glistening plates, m. p. 73° , and has all the characteristic properties of a peroxide. Its b. p. under reduced pressure is higher than that of nonaldehyde, but lower than that of pelargonic acid. When boiled with water it yields nonaldehyde and hydrogen peroxide. The other products isolated were pelargonic acid and the semi-aldehyde of azelaic acid, all of which are obtained from the original ethereal extract. The aqueous solution, when acidified, yields an ethereal extract from which the peroxide of the semi-aldehyde of azelaic acid, $C_9H_{16}O_4$, and azelaic acid have been isolated. The peroxide crystallises from acetone in needles, m. p. 98° , and is completely soluble in hot water, but is partly converted into the semi-aldehyde and hydrogen peroxide and partly isomerised to azelaic acid. J. J. S.

Semi-aldehyde of Succinic Acid [β -Aldehydopropionic Acid].—CARL D. HARRIES and ERNST ALEFELD (*Ber.*, 1909, 42, 159—165. Compare Harries, Abstr., 1898, i, 232).— β -Aldehydopropionic acid has been described by Perkin and Sprankling as a thick, dark yellow oil which is readily oxidised by atmospheric oxygen to succinic acid (*Trans.*, 1899, 75, 11). von Ungern-Sternberg prepared β -aldehydopropionic acid from aconic acid, and describes it as an oil solidifying to a white, crystalline mass, m. p. 147° , b. p. 234 — $236^\circ/760$ mm., which is very stable towards oxidising agents, but nevertheless has the properties of an aldehydo-acid; thus it yields a phenylhydrazone-phenylhydrazone, m. p. 182° . The conclusion drawn by this author was that Perkin and Sprankling were either not working with β -aldehydopropionic acid, or else that their statement as to the readiness with which the acid underwent oxidation was incorrect (*Diss.*, Königsberg, 1904).

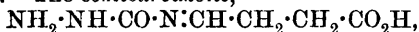
The present authors have prepared β -aldehydopropionic acid by decomposing allylacetic acid ozonide with water. They obtained it as an oil which was readily oxidised by atmospheric oxygen, forming succinic acid. The oil when kept for a few days, however, solidified to a white, crystalline mass, m. p. 147° , identical with the substance described by von Ungern-Sternberg. Mol.-wt. determinations show that the oily acid is unimolecular, whereas the solid acid is bimolecular (compare following abstract).

Allylacetic acid ozonide, $O_3 \begin{array}{c} \text{CH}_2 \\ | \\ \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$ prepared by the

action of ozone on a solution of allylacetic acid in carbon tetrachloride, is a colourless syrup, D_{21}^{21} 1.289, D_{22}^{22} 1.297, n_D^{21} 1.46552, n_D^{22} 1.47359; it is decomposed by water, yielding formic acid, form-

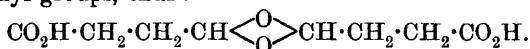
aldehyde, succinic acid, and β -aldehydopropionic acid; it is probable that the peroxide of the latter substance is formed at the same time.

The unimolecular β -aldehydopropionic acid is a colourless, viscid liquid, b. p. $134-136^\circ/14$ mm., D_{25}^{23} 1.2568, n_D^{23} 1.44873, n_a^{23} 1.44571, n_γ^{23} 1.45911; it follows from these physical constants, and from the absence of a ferric chloride reaction, that the substance is the aldehyde form of the acid. The *semicarbazone*,



crystallises in small prisms or needles, m. p. $177-178^\circ$ (decomp.); the *p*-nitrophenylhydrazone, $\text{C}_{10}\text{H}_{11}\text{O}_4\text{N}_3$, forms golden-yellow leaflets, m. p. 158° . W. H. G.

β -Aldehydopropionic Acid. CARL D. HARRIES and ALFRED HIMMELMANN (*Ber.*, 1909, 42, 166-167).—The crystalline β -aldehydopropionic acid, prepared from allylactic acid (compare preceding abstract) or from aconic acid (compare von Ungern-Sternberg, *Diss.*, Königsberg, 1904), is shown to have the bimolecular formula $(\text{C}_4\text{H}_2\text{O}_3)_2$. It yields the unimolecular variety when distilled at $134-136^\circ$ under a pressure of 14 mm. The stability of the polymerised form towards oxidising agents shows that the condensation occurs between the two carbonyl groups, thus:



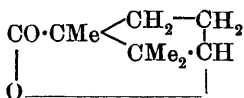
W. H. G.

Molecular Rearrangements in the Camphor Series. I. Hydroxylauronic Acid and *iso*Campholactone. WILLIAM A. NOYES and A. W. HOMBERGER (*J. Amer. Chem. Soc.*, 1909, 31, 278-281).—It has been shown (*Abstr.*, 1895, i, 295) that aminolauronic acid is converted by nitrous acid into γ -lauronic acid, laurolene, and *isocampholactone*.

When ethyl aminolauronate is treated with nitrous acid, it yields a mixture of ethyl γ -lauronolate and ethyl hydroxylauronate. *Ethyl γ -lauronolate*, $\text{C}_8\text{H}_{13} \cdot \text{CO}_2\text{Et}$, b. p. $110-115^\circ/25$ mm., has D_4^{20} 0.9514 and $[\alpha]_D^{26} + 56.6^\circ$. *Ethyl hydroxylauronate*, $\text{OH} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO}_2\text{Et}$, b. p. $150^\circ/30$ mm., has D_4^{20} 1.100 and $[\alpha]_D^{33.5} + 6.73^\circ$.

Evidence is given to show that hydroxylauronic acid has the formula $\text{CO}_2\text{H} \cdot \text{CMe} \begin{array}{c} \diagup \text{CH}_2 \diagdown \\ \diagdown \text{CH}_2 \diagup \end{array} \text{CH} \cdot \text{OH}$, which is supported by the fact that the acid is oxidised by nitric acid to active camphoronic acid.

The method of formation of *isocampholactone* suggests that it should be represented by the annexed formula. In this case the corresponding hydroxy-acid, $\text{OH} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO}_2\text{H}$, must be a stereoisomeride of hydroxylauronic acid. In order to obtain evidence on this point, *isocampholactone* was submitted to oxidation with nitric acid. The products obtained were a *lactone*, $\text{C}_8\text{H}_{12}\text{O}_4$, an acid, m. p. 228° , probably camphoronic acid, and a compound, m. p. 111° , which is probably a lactone. The *lactone*, $\text{C}_8\text{H}_{12}\text{O}_4$, m. p. 122° , b. p. 272° , is the chief product of the oxidation, and crystallises in needles. These results do not justify any conclusion with regard to the structure of *isocampholactone*. E. G.

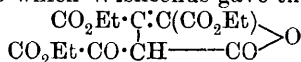


Ethyl Nitrososuccinate. JULIUS SCHMIDT and KARL TH. WIDMANN (*Ber.*, 1909, 42, 497—501).—A general method for the production of nitroso-compounds is to pass the nitrous gases from the action of nitric acid on arsenious oxide into acylcarboxylic esters. The method gives especially good results when the acyl group is attached to a tertiary carbon atom.

Ethyl acetylsuccinate when treated with the gas at 0° in a long, narrow tube, then, after two hours, evacuated in a dark glass desiccator, forms *ethyl nitrososuccinate*, $\text{CO}_2\text{Et}\cdot\text{CH}(\text{NO})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, an azure-blue liquid which cannot be distilled and is decomposed quickly by light. It is, however, pure; in a ethylene dibromide solution it is unimolecular (found 185 and 194, calc. 203), $D_4^{25} 1.20$, $n_D^{25} 1.4419$. The compound gives Liebermann's reaction, is stable in ethylene dibromide, but in alcohol or ether the cold solution is slowly decolorised, quickly when warm. This change may be due either to polymerisation or isomeric change to oximino-compounds. Potassium permanganate, Caro's acid, or hydrogen peroxide (10%) oxidise it to *ethyl nitrosuccinate*, $\text{C}_8\text{H}_{13}\text{O}_6\text{N}$, a yellow, viscous oil, which could not be distilled unchanged under diminished pressure, and explodes when quickly heated. On reduction with zinc dust and acetic acid, ethyl aspartate is formed, b. p. 126—127°/10 mm., 150—152°/25 mm. (compare Fischer, *Abstr.*, 1901, i, 193); the *picrolonate*, $\text{C}_8\text{H}_{15}\text{O}_4\text{N}$, $\text{C}_{10}\text{H}_8\text{O}_5\text{N}_4$, forms yellow crystals, m. p. 290°.

W. R.

Products of Hydrolysis of Ethyl Dioxalylsuccinate. *isoPyromucic Acid.* EDMOND E. BLAISE and HENRI GAULT (*Compt. rend.*, 1909, 148, 176—179. Compare *Abstr.*, 1908, i, 713).—The authors consider that their experiments on the production of *isopyromucic acid* by the removal of 1CO_2 from the product of hydrolysis of ethyl oxalylsuccinate furnish evidence against the constitutions ascribed by Wislicenus to the substances this author obtained by the action of alkalis on the ester (*Abstr.*, 1895, i, 506). Thus the compound to which Wislicenus gave the formula



should be represented as a δ -lactone, $\begin{array}{c} \text{CO}_2\text{Et}\cdot\text{C}=\text{C}(\text{CO}_2\text{Et}) \\ | \\ \text{CO}_2\text{Et}\cdot\text{C}:\text{C}(\text{OH})\cdot\text{CO} \end{array} > \text{O}$; the substance obtained from this by hydrolysis would then have the formula $\text{CO}_2\text{H}\cdot\text{C}(\text{OH})\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{Et}$, which agrees more closely with the properties of the compound than the ketonic structure put forward by Wislicenus.

W. O. W.

Lævulinlaldehyde. CARL D. HARRIES and MAX BOEGEMANN (*Ber.*, 1909, 42, 439—446. Compare *Abstr.*, 1905, i, 364; 1906, i, 833).—The aldehyde was prepared by the action of water on methylheptenone ozonide (*Abstr.*, 1906, i, 226). It dissolves readily in water, and reduces cold Fehling's solution. Its molecular weight, as determined by the cryoscopic method in benzene solution, proves it to be unimolecular, and its molecular dispersion agrees with the ketoaldoic constitution. Its dielectric constant, as determined by Nernst's

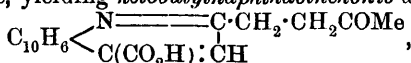
method, is high, namely, 32 at 18°, whereas the constant for succinaldehyde is 28.5 at 20°.

The dioxime has m. p. 76°; the *disemicarbazone*, $C_7H_{14}O_2N_6$, crystallises from methyl alcohol in colourless plates or prisms, m. p. 178—180°.

The diphenylhydrazone has not been obtained; phenylhydrazine reacts with an acetic acid solution of the aldehyde yielding an oil, which with hydrochloric acid forms phenylmethyldihydropyridazine. As this compound is sparingly soluble, it can be made use of in estimating the aldehyde.

The *di-p-nitrophenylhydrazone*, $C_{17}H_{18}O_4N_6$, crystallises in brown plates, m. p. 106°.

The aldehyde reacts with an alcoholic solution of pyruvic acid and β -naphthylamine, yielding *ketobutyl-naphthacinchonic acid*,



which is sparingly soluble in all ordinary solvents.

Lævulinaldehyde differs from succinaldehyde, which also contains carbonyl groups in the $\alpha\delta$ -positions, in the following points: (1) it does not polymerise; (2) it does not give Angeli's reaction with benzsulph-hydroxamic acid (Abstr., 1904, ii, 330), and (3) it is not readily converted into acetals by Laisen's method.

When reduced with a large excess of aluminium amalgam and ether, it yields γ -amylene glycol and Lipp's methyldihydrofuran (Abstr., 1889, 843).

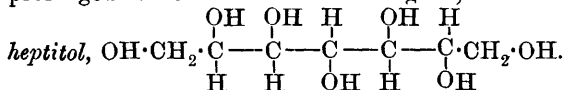
J. J. S.

Certain Numerical Relations in the Sugar Group.
C. S. HUDSON (*J. Amer. Chem. Soc.*, 1909, 31, 66—86).—On the assumption that the known α - and β -forms of dextrose and the related mutarotating sugars are the partial stereoisomerides indicated by the lactonic formula of Tollens, it is shown: (1) that the difference between the molecular rotations of the α - and β -forms of all the aldehyde sugars, and all their derivatives in which the added substance is not joined directly to the end asymmetric carbon atom, is a nearly constant quantity; (2) that the α - and β -forms of those derivatives of any aldose sugar in which only the end carbon atom is affected (*e.g.*, glucosides) have molecular rotations the sum of which is equal to the sum for the α - and β -forms of the aldose, and it is shown from the available data that these deductions are valid. On this basis, the following rules are proposed for the naming of the α - and β -forms of the sugars: The names are to be so selected that for all sugars which are genetically related to *d*-glucose the subtraction of the rotation of the β -form from that of the α -form gives a positive difference, and for all sugars genetically related to *l*-glucose a negative difference. When the end carbon atom is affected, the above rule is modified as follows: The names of the α - and β -forms are to be so selected that the difference of their molecular rotations is equal to, and of the same sign as, the similar difference for the forms of the similar derivative of that glucose (*d* or *l*) to which the first sugar is genetically related.

The equilibrium constant for the reversible reaction between the α - and β -forms of the aldohexoses and allied disaccharides is approximately constant and equal to 1.5, a rule which permits of the calculation of the rotation of the unknown forms of certain sugars. From measurements of the "thermal lag" (compare Abstr., 1908, ii, 665), it is shown that in all cases the α -form of the sugar is favoured by an increase in temperature.

A formula is deduced which allows of the calculation of the rotatory power of the unknown forms of many of the natural and synthetic glucosides. The influence of the end groups of the glucosides on the rotation of the carbon atom to which they are attached depends mainly on the weight of the group. G. S.

Preparation and Properties of β -Glucoheptitol. L. H. PHILIPPE (*Compt. rend.*, 1908, 147, 1481—1483).—The author has submitted Fischer's β -glucoheptose (Abstr., 1892, 1164) to the prolonged action of sodium amalgam; he thus obtains β -gluco-



This compound forms small, rectangular tablets, m. p. 130—131° on the Maquenne block; $[\alpha]_D + 48'$ in aqueous solution. Its rotatory power serves to distinguish it from the isomeric α -glucoheptitol (*loc. cit.*). Acetic anhydride in presence of zinc chloride converts it into a resinous *hepta-acetyl* derivative, $\text{C}_7\text{H}_9(\text{OAc})_7$, m. p. about 50°; $[\alpha]_D^{13} + 34.8^\circ$. The *heptabenzoyl* derivative, $\text{C}_7\text{H}_9(\text{OBz})_7$, forms prismatic needles, m. p. 182°. The *tribenzylidene* derivative, $\text{C}_7\text{H}_{10}\text{O}_7(\text{C}_7\text{H}_6)_3$, crystallises in very slender needles, m. p. about 230°. A *formalacetal* derivative has also been prepared. W. O. W.

Hydrolysis of Maltose by Citric Acid. JOSEPH PIERAERTS (*Bull. Assoc. Chim. suc. dist.*, 1909, 26, 562—573).—Hydrated maltose may be converted completely into 2 mols. of dextrose by boiling 50 c.c. of a 2½% solution with 10 c.c. of 20% citric acid for about thirty hours in a reflux apparatus. The time may be reduced to two hours and a-half by heating at a pressure of 1½ atm. As soon as the maltose is converted into dextrose, the liquid assumes a yellow colour, which darkens on prolonged heating. L. DE K.

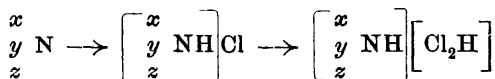
Formation of Hydrocelluloses by means of Sulphuric Acid. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1909, 22, 155—156. Compare Büttner and Neuman (this vol., i, 86).—The author claims that elementary analyses are not sufficiently accurate to serve for the clear diagnosis of different hydrocelluloses. The reducing powers are much more accurate criteria. Both acids and alkalis hydrolyse hydrocelluloses. J. J. S.

Acid Haloid Salts. FELIX KAUFLEDER and E. KUNZ (*Ber.*, 1909, 42, 385—392. Compare Scholl and Escales. Abstr., 1898, i, 182; Korczyński, this vol., i, 123).—It is shown that a large number of

mono-amines combine with dry hydrogen chloride or bromide at the ordinary temperature, forming dihydrochlorides and dihydrobromides. The stability of the dihydrochloride depends largely on the degree of alkylation; thus tertiary and quaternary bases regularly form dihydrochlorides, whilst of the secondary bases only dimethylamine forms a dihydrochloride. Dihydrochlorides of methylamine, methyl-aniline, aniline, acetanilide, methyl-*o*-toluidine, diphenylamine, and tribenzylamine could not be obtained at the ordinary temperature.

When a compound contains several nitrogen atoms, it is found that each nitrogen atom reacts independently.

The conclusion is drawn that the compounds are in all cases ammonium salts of perhalogen hydrides. This is supported by the fact that the change of *p*-nitrosodimethylaniline hydrochloride into the dihydrochloride is not accompanied by a change of colour, as in the formation of the former from the base itself. The following formulation :



shows that in the conversion of the hydrochloride into the dihydrochloride, only the colourless anion undergoes alteration, whilst the ammonium part of the molecule, which imparts the colour to the substance, remains unchanged.

The following salts were prepared by passing the dry halogen hydride over the base or its normal haloid salt. They are all hygroscopic substances, and readily part with hydrogen chloride or bromide. *Dimethylamine dihydrochloride* is a white, crystalline substance. *Tetramethylammonium chloride hydrochloride*, $\text{NMe}_4\text{Cl}\cdot\text{HCl}$, forms a white, crystalline mass. *m-Nitrodimethylaniline dihydrochloride*, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2\cdot 2\text{HCl}$, is a yellowish-white, crystalline mass. *p-Nitrosodimethylaniline dihydrochloride* is a yellow powder. *Dimethyl-*o*-toluidine dihydrochloride* was obtained as an oily liquid. *Diethylaniline dihydrochloride*, $\text{C}_{10}\text{H}_{15}\text{N}\cdot 2\text{HCl}$, forms colourless crystals, which solidify at 47° . *p-Nitrosodiethylaniline dihydrochloride* is a yellow powder. *Pyridine dihydrochloride*, $\text{C}_5\text{H}_5\text{N}\cdot 2\text{HCl}$, forms large, white prisms, m. p. $46\cdot 7^\circ$. *Quinoline dihydrochloride*, $\text{C}_9\text{H}_7\text{N}\cdot 2\text{HCl}$, is a crystalline mass having the same freezing point as the pyridine compound. *Tetramethyldiaminodiphenylmethane tetrahydrochloride*, $\text{C}_{17}\text{H}_{22}\text{N}_2\cdot 4\text{HCl}$, is a brown solid. *Tetramethyldiaminodiphenyl ketone tetrahydrochloride* is obtained only at 0° . *p-Azotoluene dihydrochloride*, $\text{C}_{14}\text{H}_{14}\text{N}_2\cdot 2\text{HCl}$, is a chocolate-brown solid. *Diethylaminoazobenzene dihydrochloride* has the same red colour as the mono-hydrochloride. *Diethylaminoazobenzene- β -naphthalene pentahydrochloride* resembles potassium permanganate in colour.

Pyridine dihydrobromide, $\text{C}_5\text{H}_5\text{N}\cdot 2\text{HBr}$, *quinoline dihydrobromide*, and *diethylaminoazobenzene pentahydrobromide* were also prepared.

W. H. G.

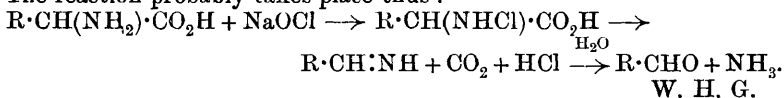
***d*-Propylenediamine and Derivatives of the Optically Active Propylenediamines.** LEO TSCHUGAEFF and W. SOKOLOFF (*Ber.*, 1909, 42, 55—58. Compare Abstr., 1907, i, 896).—The data

previously given for *l*-propylenediamine are to be corrected to D_4^{25} 0.8612 and $[\alpha]_D - 29.65^\circ$.

Cobalt-tri-l-propylenediamine iodide, $[\text{CoPn}_3]\text{I}_3$, prepared in a similar manner to the racemic iodide (Pfeiffer and Gassmann, Abstr., 1906, ii, 614), separates from hot water in brownish-yellow needles containing $2\text{H}_2\text{O}$, is much more soluble than the racemic iodide, and for a sample dried at 100° shows $[\alpha]_D + 23.63^\circ$ for p 3.38 and D_4^{25} 1.0156.

d-Propylenediamine, separated from the racemic base or from the non-crystallisable syrup remaining after the preparation of the *l*-isomeride (*loc. cit.*) by means of the *d*-propylenediamine hydrogen *l*-tartrate, has b. p. 120.5° , D_4^{25} 0.8584, and $[\alpha]_D + 29.78^\circ$, and yields, like the *l*-isomeride (*loc. cit.*), a *platinum di-d-propylenediamine chloride*, $[\text{PtPn}_2]\text{Cl}_2$, which has $[\alpha]_D - 46.45^\circ$ for p 8.27 and D_4^{25} 1.0445, from which the *nitrate*, $[\text{PtPn}_2](\text{NO}_3)_2$, is obtained, having $[\alpha]_D - 40.55^\circ$ for p 8.36 and D_4^{25} 1.0465. C. S.

Degradation of α -Amino-acids to Aliphatic Aldehydes by means of Sodium Hypochlorite. KURT LANGHELD (*Ber.*, 1909, 42, 392—393).—Raschig has shown (Abstr., 1908, ii, 30) that chloroamine is formed by the interaction of sodium hypochlorite and ammonia. A similar reaction appears to take place between sodium hypochlorite and α -amino-acids; an intermediate product is formed, which does not colour aqueous aniline, and decomposes when the solution is warmed at 40 — 50° , yielding ammonia, carbon dioxide, and an aliphatic aldehyde containing one carbon atom less than the acid. The reaction probably takes place thus:



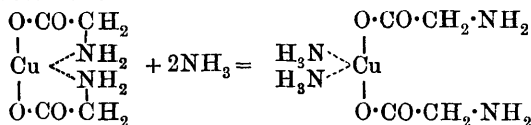
Internally Complex Salts. HEINRICH LEY (*Ber.*, 1909, 42, 354—376).—In the internally complex copper salts of α -amino-acids the union of the metal to oxygen by a principal, and to nitrogen by a supplementary, valency linking (Abstr., 1905, i, 175) causes the properties, especially the colour and the dissociation, of these complex salts to differ from those of ordinary salts.

The electrolytic and the hydrolytic dissociation of copper glycine and of copper α -alanine are very small; the solutions can be boiled without deposition of copper hydroxide. Such stability is not shown by the copper salts of all α -amino-acids, those of piperidinoacetic or diethylaminoacetic acid (of the type $\text{NR}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$) being slightly electrolytically, but considerably hydrolytically, dissociated; a complex nickel piperidinoacetate cannot be prepared by reason of its great hydrolytic dissociation. The complex copper salts of β -amino-acids are moderately hydrolytically dissociated, and in dilute solutions precipitation of copper hydroxide occurs. Complex copper salts of δ -amino-acids, the formation of which would require the production of a seven-membered ring, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CO}\cdot\text{O} \\ \text{CH}_2\cdot\text{NH}_2 \end{smallmatrix}\rangle\text{Cu}$, cannot be obtained (compare Tschugaeff, Abstr., 1907, i, 392).

The fact that glycine can displace the metal from salts of stronger

$(\text{NH}_2 \cdot \text{R} \cdot \text{CO}_2)_2\text{M} + 2\text{HX}$, where $\text{M} = \text{Cu}, \text{Ni}, \text{Co}$, or Zn , proceeding almost entirely from left to right in consequence of the very slight electrolytic dissociation of the complex salt. (The equation only partly represents what occurs; in addition, the acid HX forms a salt with the amino-acid. Since the salt formation is very small with acetic acid, the author uses acetates in the following experiments.) Conductivity measurements give some idea of what is happening in the reaction. The difference Δ between the conductivities of the metallic acetate before and after the addition of the amino-acid is approximately a measure of the complex salt formation, because if $(\text{NH}_2 \cdot \text{R} \cdot \text{CO}_2)_2\text{M}$ is largely formed, the conductivity of the solution will approach that of acetic acid, whilst the conductivity will be mainly due to the metallic acetate if complex salt formation is only small. In this way it is shown that barium, manganese, and cadmium have little tendency to form complex salts, and copper and nickel have a great tendency; the tendencies of cobalt and zinc are about the same, and much smaller than that of nickel. With nickel acetate and different amino-acids, the formation of internally complex salts decreases from glycine through α - and β -aminopropionic acids to piperidinoacetic acid; with copper acetate and γ -aminobutyric acid, negative values of Δ , that is, an increase of the conductivity, are observed, which is explained by the fact that a partial formation of basic copper acetate occurs in consequence of the large basic k value of the amphoteric electrolyte.

The abnormal colour of complex salts has been examined spectrometrically. The complex copper salts of glycine, β -aminopropionic acid, methylglycine, benzylglycine, $\alpha\alpha$ -dimethylglycine, α -phenylglycine, diethylglycine, and piperidinoacetic acid are all blue in the solid state and violet-blue in solution. The substitution of methylene hydrogen by phenyl does not produce any essential colour change. The replacement of aminic hydrogen by an aromatic group causes a great change in the absorption, internally complex copper anilinoacetate and its homologues being intensely green in the solid and the dissolved states. The addition of ammonium hydroxide to copper anilinoacetate causes a colour change from green to blue, probably by reason of the conversion of the internally complex salt into an ordinary complex salt; a similar conversion occurs with ammonium hydroxide and copper glycine, although here no essential colour change is observed:



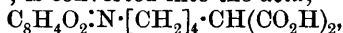
The decomposition of metallic acetates by amino-acids is accompanied by colour change when internally complex salts are formed; nickel acetate becomes distinctly blue by the addition of glycine or α - or β -aminopropionic acid. It is noteworthy that the colour of cobalt acetate is unchanged by the addition of glycine, and also that solid cobalt anilinoacetate has the normal red colour.

It is well known that the strengths of amino-acids are increased by

the introduction of acyl groups. The metallic salts of aceturic acid (acetyl glycine) are strongly dissociated, and do not behave as internally complex salts, copper acetate and nickel acetate having the normal blue and green colours respectively. The ultraviolet absorption spectra of aqueous copper acetate in the presence of increasing amounts of ammonia indicate that $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{H}_3\text{O}_2)_2$ and $\text{Cu}(\text{NH}_3)_4(\text{C}_2\text{H}_3\text{O}_2)_2$ respectively are present according as the concentration of the ammonia is small or large, thus confirming the results of the partition experiments previously described (*loc. cit.*).

The paper concludes with some remarks on the migration of cations of type $\text{CO}_2\text{H}\cdot\text{R}\cdot\text{NH}_3$. C. S.

Some Derivatives of δ -Aminocaproic [Hexoic] Acid. AUGUST ALBERT (*Ber.*, 1909, 42, 556—558).—Ethyl δ -phthaliminobutylmalonate (Abstr., 1899, i, 595), which crystallises from petroleum in needles, m. p. 46° , is converted into the acid,



by warming for a short time with hydriodic acid; it crystallises from a mixture of ethyl acetate and benzene in needles, m. p. 127° , decomposing into ϵ -phthaliminohexoic acid (Abstr., 1908, i, 649). As the yield of the latter was only 16%, another method for its preparation was devised. ϵ -Chlorohexonitriles is obtained in 32% yield by heating pentamethylene chloride and potassium cyanide in aqueous alcohol solution for seven hours (compare von Braun and Steindorff, Abstr., 1905, i, 206). The portion b. p. 242 — 250° , when heated with potassium phthalimide at 210° , is converted into crude ϵ -phthaliminohexonitrile. This oil, when heated with double its volume of sulphuric acid for ten minutes at 100° , yields a mixture of ϵ -phthaliminohexoamide, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot[\text{CH}_2]_5\cdot\text{CO}\cdot\text{NH}_2$, which crystallises from alcohol in leaflets, m. p. 158° , and the corresponding acid. The yield from the pentamethylene chloride is 12%.

Red phosphorus and bromine convert phthaliminohexoic acid into α -bromo- ϵ -phthaliminohexoic acid, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot[\text{CH}_2]_4\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, which forms crystals, m. p. 153 — 153.5° . An attempt to prepare $\alpha\epsilon$ -diaminohexoic acid from this failed through lack of material.

W. R.

The Nature of Hofmann's Bromoacetamide. MAURICE FRANÇOIS (*Compt. rend.*, 1909, 148, 173—176; *J. Pharm. Chim.*, 1909, [vi], 29, 145—151. Compare this vol., i, 13).—The substance to which Hofmann (Abstr., 1882, 950) ascribed the constitution $\text{CH}_3\cdot\text{CO}\cdot\text{NHBr}\cdot\text{H}_2\text{O}$ has been prepared by evaporating below 30° an aqueous solution of acetamide and pure hypobromous acid. The conclusion is drawn that the compound is *acetamide hypobromite*,



and that Hofmann's bromoacetamide, which arises from this by dehydration, should be regarded as a secondary amide of hypobromous acid. W. O. W.

Action of Nitrogen on Commercial Barium Carbide. OTTO KÜHLING and O. BERKOLD (*Zeitsch. angew. Chem.*, 1909, 22, 193—197).—The influence of barium chloride on the absorption of

nitrogen by a heated mixture of barium carbonate and charcoal has already been determined (Abstr., 1908, i, 143), and the investigation has been extended to barium carbide. Moissan (Abstr., 1894, i, 314) has already shown that this compound only combines with traces of nitrogen at 1200°, but the effect of other substances was not ascertained. The barium carbide used in the experiments had the following composition: Ba, 49.86; Ca, 17.11; Fe + Al, 2.62; "carbide" carbon, 7.62; Na, 0.85; Cl, 0.18; insoluble matter, 9.76; P, S, O, and CO₂, 12.00% (by difference), and the material therefore probably contains both calcium and barium carbides as well as their oxides.

The absorption of nitrogen with this material begins at 500—600°, and there is an increase in the nitrogen absorbed as the temperature rises to 920—930°, when the maximum amount is absorbed, the percentage of cyanide formed at 920—930° being 18.4, that of cyanamide 19.4. With 10% barium chloride the maximum absorption is attained at this temperature also, but with 20 and 30% of added chloride the maximum had not been reached at 1120—1130°. With the larger amount of chloride at the latter temperature, the yield of cyanide was somewhat greater (21.6%), the yield of cyanamide somewhat less (17.9%).

W. R.

Preparation of Cyanuric Acid from Carbamide. REINHOLD VON WALTHER (*J. pr. Chem.*, 1909, [ii], 79, 126—128).—Cyanuric acid is obtained in 62% yield by heating carbamide with twice its weight of anhydrous zinc chloride at 220°, decomposing the cold product with hydrochloric acid, and recrystallising the precipitate from hot water.

C. S.

Molybdenum Hexathiocyanate Salts. ARTHUR ROSENHEIM (*Ber.*, 1909, 42, 149—152).—Largely polemical. A reply to Maas and Sand (Abstr., 1908, i, 961; compare also *ibid.*, i, 397, 513, 614). It is suggested that many of the thiocyanate values obtained by Sand and Maas are low, owing to the oxidising action of the nitric acid used.

When a thiocyanate is boiled with sodium hydroxide solution, a small amount of ammonia is liberated, but the amount is so small that the error introduced into the estimation of ammonia would scarcely affect the formula deduced from the experimental data.

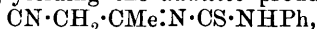
The *sodium* salt, Na₃Mo(SCN)₆·12H₂O, forms golden-yellow crystals, and agrees in composition with the sodium salts of other complex thiocyanates.

J. J. S.

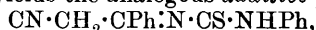
Dimolecular Nitriles. CARL W. HÜBNER (*J. pr. Chem.*, 1909, [ii], 79, 66—71).—This investigation was carried out with the object of filling some gaps in the chemistry of the dinitriles. Only one of the three condensation products obtained by von Meyer (Abstr., 1895, i, 582) by the action of phenylcarbimide on diacetonitrile [β -iminobutyronitrile] in benzene, namely, that having m. p. 148° (von Meyer gives m. p. 150°), is formed when ether is employed as the solvent. Benzacetodinitrile [β -iminophenylpropionitrile] and phenylcarbimide

also interact at the ordinary temperature in ethereal solution, yielding the analogous additive product, m. p. 190° (compare von Meyer, *loc. cit.*).

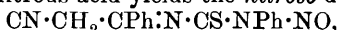
Phenylthiocarbimide reacts in a similar manner with β -iminobutyronitrile at 140 — 150° , yielding the *additive* product,



which crystallises in small, orange-yellow needles, m. p. 192° . β -Iminophenylpropionitrile yields the analogous *additive* product,



small, lemon-yellow needles, m. p. 166° , which, when heated under pressure at 140 — 150° with alcoholic ammonia and lead oxide, yields the *guanidine* derivative, $\text{C}_{16}\text{H}_{13}\text{N}_3\cdot\text{NH}$, white leaflets, m. p. 178° , and when treated with nitrous acid yields the *nitroso*-derivative,



lemon-yellow needles, m. p. 231° .

The additive product obtained by heating β -iminobutyronitrile with dicyanodiamide at 150° (compare von Meyer, *loc. cit.*) has the formula $\text{C}_6\text{H}_9\text{ON}_5$; it forms a *platinichloride*, $(\text{C}_6\text{H}_9\text{ON}_5)_2\cdot\text{H}_2\text{PtCl}_6$, which crystallises in golden-yellow needles, m. p. 240° (decomp.).

W. H. G.

Action of Cyanogen on Sulphurous Acid. DANIEL VORLANDER (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1907, ii, 92).—The action of cyanogen on sulphurous acid is similar to that of the halogens, but occurs more slowly: $\text{C}_2\text{N}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} = 2\text{HCN} + \text{H}_2\text{SO}_4$. With equivalent quantities in 0.1 to 0.2% solution, the amounts of cyanogen reduced and of sulphurous acid oxidised are initially equivalent. With a large excess of cyanogen, 94% of the sulphurous acid is oxidised after four to five days, but when the acid is in excess, only 23% of the cyanogen is reduced in seven to eight days. C. S.

Production of White Ferrous Ferrocyanide. ROBERT L. TAYLOR (*Mem. Manchester Phil. Soc.*, 1908–09, 53, vi).—A creamy-white precipitate is obtained on adding potassium ferrocyanide to a solution of a ferrous salt which has been thoroughly reduced by hyposulphurous acid or sodium hyposulphite, $\text{Na}_2\text{S}_2\text{O}_4$. Hyposulphurous acid will even reduce [precipitated Prussian blue to the white, ferrous compound. R. J. C.

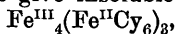
Prussian Blue and Turnbull's Blue. I. ERICH MÜLLER and THEOPHIL STANISCH (*J. pr. Chem.*, 1909, [ii], 79, 81–102).—In a solution containing ferric and ferrocyanogen ions or ferrous and ferricyanogen ions, the value of the equilibrium constant:

$$K(=[\text{Fe}^{+++}][\text{FeCy}_6^{''''}]/[\text{Fe}^{++}][\text{FeCy}_6^{'''}]),$$

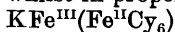
calculated from electrochemical data (Abegg, *Abstr.*, 1903, ii, 628; Schaum, *Abstr.*, 1900, ii, 2), is about 10^{-5} , and therefore either solution will contain practically only ferrous and ferricyanogen ions. Consequently, the precipitates obtained from ferric chloride and potassium ferrocyanide, or from ferrous chloride and potassium ferricyanide, should be identical. The preceding reasoning, however, is inaccurate, since it assumes that all the ions remain in solution. The

authors agree with Hofmann (Abstr., 1905, i, 38) that the preceding precipitates are ferrocyanides, but deny that soluble and insoluble Prussian blue are identical respectively with soluble and insoluble Turnbull's blue. They object that Hofmann actually isolated the precipitates, which probably changed during the process, and only determined the iron and cyanogen or the ratio Fe:CN, which cannot give accurate information as to the composition of these complex and very similar blue ferrocyanogen compounds (compare Messner, Abstr., 1895, i, 486). The authors determine the compositions by a method which does not involve the separation of the precipitates from the mother liquor, and also estimate the ratio of ferrous to ferric iron and of ionised and non-ionised iron. In definite volumes of, for example, standard ferric chloride and standard potassium ferrocyanide the amounts of Fe^{+++} and of $(\text{FeCy}_6)^{++++}$ are estimated by standard potassium permanganate before and after mixing, 0.1-molecular solutions being used to minimise the error due to any volume change on mixing. The decrease in the concentration of the ions represents the amounts which have disappeared from the solution to form the precipitate, but in consequence of the reaction: $\text{Fe}^{+++} + (\text{FeCy}_6)^{++++} \rightleftharpoons \text{Fe}^{++} + (\text{FeCy}_6)^{+++}$, it is not allowable to assume that the, for example, ferric iron which has disappeared from the solution occurs as such in the precipitate. However, the ratio of ferrous to ferric iron and of ionised to non-ionised iron can be estimated in the precipitate, and hence conclusions drawn as to its constitution.

The authors find that ferric chloride and potassium ferrocyanide in proportions exceeding 4:3 give insoluble Prussian blue,



whilst in proportions less than 1:1 the precipitate is a mixture of $\text{KFe}^{\text{III}}(\text{Fe}^{\text{II}}\text{Cy}_6) + \text{K}_2\text{Fe}^{\text{II}}(\text{Fe}^{\text{II}}\text{Cy}_6)$; ferrous chloride and potassium ferricyanide in proportions exceeding 4:3 yield insoluble Turnbull's blue, $\text{KFe}^{\text{II}}\text{Fe}^{\text{III}}_3(\text{Fe}^{\text{II}}\text{Cy}_6)_3$, whilst in proportions less than 1:1,



is formed. The Roman numerals denote the valency of the iron.

C. S.

cycloPropane. ALFRED PARTHEIL (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1907, ii, 159).—*cycloPropane* can be prepared by heating together finely-divided zinc, amyl alcohol, and trimethylene bromide.

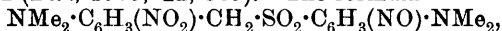
C. S.

Introduction of Iodine into the Benzene Ring. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1908, 58, 290—294. Compare Abstr., 1903, i, 450; Messinger and Vortmann, 1889, 1150; Wheeler and Jamieson, 1905, i, 350).—Fürth and Schwarz's statement (*Pflüger's Archiv*, 1908, 124, 113), that phenylalanine can yield an iodo-derivative when treated by Messinger and Vortmann's method, is refuted. Unaltered phenylalanine alone was recovered. Phenylacetic and phenylpropionic acids behave in a similar manner. The formation of iodo-derivatives only occurs when the benzene nucleus contains one or more hydroxyl groups. In certain reactions the pyrrole ring behaves as a phenol, for example, yields a tetraiodo-

derivative, and it is possible that the re-activity of tryptophan to iodine is due to the presence of the pyrrole group. J. J. S.

[Nitronitrosotetramethyldiaminophenylbenzylsulphone.]

ARTHUR BINZ (*Ber.*, 1909, 42, 385).—The formula



or a similar one in which the positions of the nitroso- and the nitro-groups are interchanged, is in better agreement with the analytical data for the nitroso-derivative obtained from tetramethyldiaminobenzylphenylsulphone than that originally given (*Abstr.*, 1908, i, 940). C. S.

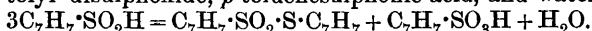
The Action of Arsenites on Toluenesulphonyl Chloride.

AUGUST GUTMANN (*Ber.*, 1909, 42, 480—483).—An aqueous solution of trisodium arsenite reacts with *p*-toluenesulphonyl chloride, yielding sodium toluenesulphinat and trisodium arsenate. It is suggested that the chloride first reacts with the alkali, yielding sodium hydroperoxide, $\text{NaO} \cdot \text{OH}$, which then oxidises the arsenite to arsenate. The formula $\text{R} \cdot \text{SO} \cdot \text{OCl}$ for the sulphonyl chloride is accepted.

Sodium arsenite has no action on sodium *p*-toluenesulphonate. An alkaline solution of sodium sulphite reacts with the sulphonyl chloride in much the same manner as the arsenite, and is oxidised to sulphate.

J. J. S.

p-Toluenesulphinic Acid. A. HEIDUSCHKA (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1907, ii, 170—172).—When ammonia is passed into an alcoholic or ethereal solution of *p*-toluenesulphinic acid, the corresponding ammonium salt is formed, whilst in benzene the reaction yields *p*-tolyl disulphoxide, *p*-toluenesulphonic acid, and water :

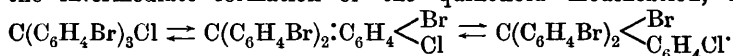


It is suggested that the ammonia acts as a base in the former, more concentrated, solutions, whilst in the dilute solution in benzene it acts as a catalyst. Primary amines show a similar behaviour ; in equal molecular quantities, they react with *p*-toluenesulphinic acid to form salts, whilst if the amine is present in less than equal molecular quantity, the acid decomposes in accordance with the preceding equation. *p*-Toluenesulphinic acid decomposes in the same way in boiling water or by melting. The decomposition may throw some light on the nature of the highly-coloured products which are obtained by fusing amine toluenesulphinates (compare Meyer, *Abstr.*, 1901, i, 264). C. S.

Triphenylmethyl. XVIII. Tautomerism in the Triphenylmethane Series. MOSES GOMBERG (*Ber.*, 1909, 42, 406—417).—It was stated previously that triphenylmethyl chloride and its analogues exist [in a benzenoid form and a quinonoid form (compare *Abstr.*, 1907, i, 504). This statement has been combated, however, by von Baeyer (*Abstr.*, 1907, i, 691) and by Tschitschibabin (*Abstr.*, 1907, i, 1022). Evidence is brought forward in the present communication in support of the author's view. A solution of tri-*p*-bromotriphenylmethyl chloride in liquid sulphur dioxide, which has been kept for

some time at 45–55° and then cooled, deposits colourless crystals, which analyses show to be composed of a mixture of tri-*p*-bromotriphenylmethyl chloride and 4-chloro-4':4''-dibromotriphenylmethyl bromide. In one experiment the isomorphous mixture contained about 85% of the latter substance.

There is little doubt that the transformation of the carbinyl chloride into the isomeric carbinyl bromide takes place owing to the intermediate formation of the quinonoid modification, thus:



Attempts to separate the pure carbinyl bromide by repeated crystallisation of the mixture were unsuccessful.

The action of liquid sulphur dioxide on 4-bromotriphenylmethyl chloride, 4:4'-dibromotriphenylmethyl chloride, 4-chloro-4':4''-dibromotriphenylmethyl chloride, and 4:4'-dichloro-4''-bromotriphenylmethyl chloride has also been studied. It is found in each case that a certain amount of the carbinyl chloride is converted into the isomeric carbinyl bromide, from which it follows that (1) part of the chlorine changes place with the bromine through the intermediate quinonoid form; (2) when the compound contains a brominated and a chlorinated benzene nucleus, it is the former which primarily changes into the quinonoid form under the influence of sulphur dioxide.

4-Chloro-4':4''-dibromotriphenylmethyl bromide forms colourless crystals, m. p. 174°. W. H. G.

Action of Nitrosobenzene on Secondary Amines. PAUL FREUNDLER and JULLARD (*Compt. rend.*, 1909, 148, 289–290. Compare Bamberger, *Abstr.*, 1896, i, 222).—Nitrosobenzene and secondary amines readily react to give azobenzene, together with smaller quantities of nitrobenzene, aniline, and possibly azoxybenzene. The greater part of the amine remains unaltered, but a portion is converted into the corresponding secondary hydroxylamine, $\text{RR}'\text{N}\cdot\text{OH}$. This reaction may be applied to differentiate between primary, secondary, and tertiary aliphatic amines. About 0.5 gram of the amine is mixed with nitrosobenzene, and when a red coloration appears, the product is distilled below 150° in a vacuum, if necessary. In the case of secondary amines, the distillate reduces silver nitrate solution in the cold, whilst with primary or tertiary amines no reducing agent is formed. A secondary hydroxylamine, however, appears to be formed when nitrosobenzene is heated for a long time with a tertiary amine.

W. O. W.

Preparation of Esters of the Cyclic Series. AUGUSTE BÉHAL (*Compt. rend.*, 1908, 147, 1478–1481).—Cyclic halogen derivatives react with organic acids, liberating hydrogen chloride, and giving rise to a cyclic ester. Thus, for example, benzyl chloride is converted into benzyl acetate when boiled for several hours with glacial acetic acid. The reaction proceeds more rapidly in presence of certain chlorides, notably those of antimony, bismuth, manganese, copper, and cobalt. The chlorides of iron, zinc, and tin have a similar action, but also

bring about the formation of resinous condensation products. The chlorides of magnesium, nickel, cadmium, mercury, chromium, barium, and strontium have no action, or else exercise a retarding effect.

Curves are given showing the influence of varying amounts of bismuth chloride, and of acetic acid on the velocity of the reaction.

W. O. W.

Formation of Hydrogen Cyanide in the Action of Nitric Acid on Phenols and Quinones. ALPHONSE SEYEWETZ and L. POIZAT (*Compt. rend.*, 1909, 148, 286—288).—Phenols and quinones containing an unsubstituted ortho- or para-position yield hydrogen cyanide when boiled with nitric acid (20%). With the exception of dimethylaniline and diethylaniline, no other aromatic compounds have been found to give the reaction, which is probably due to nitrous acid, since in presence of carbamide or aniline no hydrogen cyanide is evolved. A theoretical explanation of the reaction based on this fact is suggested.

W. O. W.

1-Methylcyclohexan-2-ol and its Derivatives. MURAT (*Ann. Chim. Phys.*, 1909, [viii], 16, 108—126).—A detailed account of the preparation and properties of certain esters, ethers, tertiary alcohols, and ethylenic hydrocarbons obtained from 1-methylcyclohexan-2-ol (Sabatier and Mailhe, *Abstr.*, 1905, i, 275).

The *hydrobromide* is less stable than the corresponding hydrochloride (Sabatier and Mailhe, *loc. cit.*), and has b. p. 118—120°/35 mm. and D_0^{20} 1.240; the *barium salt* of the *sulphate*, $(C_6H_{10}MeO \cdot SO_3)_2Ba$, has m. p. 120°; the *propionate* has b. p. 189—190°, D_0^{20} 0.9225, n_D^{20} 1.443; the *butyrate* has b. p. 104°/20 mm., D_0^{20} 0.941, D_0^{20} 0.930, n_D^{20} 1.55; the *isobutyrate* has b. p. 102°/20 mm., D_0^{20} 0.940, D_0^{20} 0.926, n_D^{20} 1.441; the *valerate* has b. p. 112—113°/24 mm., D_0^{20} 0.939, D_0^{20} 0.926, n_D^{20} 1.448; the *isovalerate* has b. p. 110—112°/20 mm., D_0^{20} 0.9375, D_0^{21} 0.926, n_D^{21} 1.447; and the *benzoate* has b. p. 200°/55 mm., D_0^{20} 1.0325, D_0^{18} 1.047, n_D^{18} 1.521.

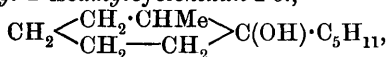
The ethers are readily obtained by the action of the alkyl iodide on the sodium derivative of the alcohol, and the following compounds were prepared: 2-ethoxy-1-methylcyclohexane, b. p. 156—158°/760 mm., D_0^{20} 0.9221, D_0^{20} 0.912, n_D^{20} 1.470; 2-amyl-1-methylcyclohexane, b. p. 177°, D_0^{20} 0.936.

When 1-methylcyclohexan-2-one is heated with acetic anhydride during several days, it yields the *acetyl* derivative of a tetrahydro-cresol, $CH_2 \begin{smallmatrix} \diagup CH_2 \cdot CHMe \\ \diagdown CH_2 - CH \end{smallmatrix} COAc$, b. p. 178°; the *tetrabromo*-derivative of the ketone, $C_6H_5MeBr_4 \cdot O$, crystallises in needles and has m. p. 76°.

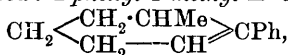
By the action of organo-magnesium derivatives on 1-methylcyclohexan-2-ol, the following tertiary alcohols were prepared: 1-methyl-2-ethylcyclohexan-2-ol, $CH_2 \begin{smallmatrix} \diagup CH_2 \cdot CHMe \\ \diagdown CH_2 - CH_2 \end{smallmatrix} CEt \cdot OH$, b. p. 181—182°/745 mm., D_0^{20} 0.9356, D_0^{20} 0.9235, n_D^{20} 1.458, forms an *acetyl*

derivative, which has b. p. 196—198°, D^0 0.946, and on dehydration by means of zinc chloride yields a mixture of methylethylcyclohexenes, b. p. 149—153°, D^0 0.829, D^{12} 0.821, which is reduced by direct hydrogenation in the presence of nickel at 200°, yielding the methylethylcyclohexane, b. p. 151°, D^0 0.7945, D^{20} 0.784, n_D^{20} 1.432;

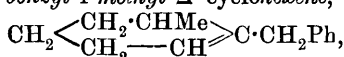
1-methyl-2-propylcyclohexan-2-ol, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{CPr} \cdot \text{OH}$, b. p. 97—98°/34 mm., D^0 0.9276, D^{20} 0.919, n_D^{20} 1.48, forms an acetyl derivative, b. p. 107—110°/30 mm., D^0 0.9650, D^{20} 0.956, n_D^{20} 1.465, and on dehydration yields a mixture of ethylenic hydrocarbons, b. p. 167—170°, D^0 0.8611, D^{20} 0.848, n_D^{20} 1.469; 1-methyl-2-tert-butylcyclohexan-2-ol, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{C(OH)} \cdot \text{CMe}_3$, b. p. 93—96°/25 mm., D^0 0.9218, D^{26} 0.908, n_D^{26} 1.465, yields on dehydration a mixture of ethylenic hydrocarbons, b. p. 183—186°/750 mm., D^0 0.864, D^{27} 0.836, n_D^{27} 1.462; 1-methyl-2-isoamylcyclohexan-2-ol,



b. p. 118—120°/22 mm., D^0 0.912, D^{17} 0.902, n_D^{17} 1.462, yields on dehydration one or more ethylenic hydrocarbons, b. p. 205—208°, D^0 0.851, D^{17} 0.845, n_D^{17} 1.471, which on direct hydrogenation in the presence of nickel at 230—250° is converted into a methylisoamylcyclohexane, b. p. 204°, D^0 0.825, D^{17} 0.812, n_D^{17} 1.454; 2-cyclohexyl-1-methylcyclohexan-2-ol, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{C(OH)} \cdot \text{C}_6\text{H}_{11}$, b. p. 146—147°/30 mm. with decomposition, D^0 0.978, D^{18} 0.969, n_D^{18} 1.501, is converted by the action of zinc chloride into an ethylenic hydrocarbon, b. p. 113—116°. Attempts to prepare corresponding tertiary alcohols by the action of 1-methylcyclohexan-2-ol on phenyl-, benzyl-, or tolylmagnesium iodide were unsuccessful, the ethylenic hydrocarbon being the only product isolated: 2-phenyl-1-methyl- Δ^2 -cyclohexene,

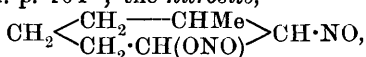


b. p. 128°/6 mm.; 2-benzyl-1-methyl- Δ^2 -cyclohexene,

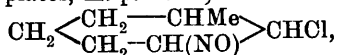


b. p. 170°/42 mm., D^0 0.99, D^{18} 0.981, n_D^{18} 1.453; 2-o-tolyl-1-methyl- Δ^2 -cyclohexene, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH} \end{smallmatrix} \text{C} \cdot \text{C}_7\text{H}_7$, b. p. 158—160°/12 mm., D^0 0.985, D^{20} 0.961, n_D^{20} 1.541.

The following derivatives of 1-methyl- Δ^2 -cyclohexene are described: the dichloro-derivative, obtained by direct chlorination, has b. p. 123—125°/20 mm., D^0 1.2300; the dibromo-derivative, similarly prepared, b. p. 128°/35 mm., D^0 1.905; Knoevenagel has described a dibromo-derivative of hexahydrotoluene, b. p. 118°/20 mm. (Abstr., 1897, i, 608); the nitrosate, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 - \text{CHMe} \\ \text{CH}_2 \cdot \text{C(NO}_2\text{H)} \end{smallmatrix} \text{CH} \cdot \text{ONO}_2$, forms brilliant prisms, m. p. 104°; the nitrosite,



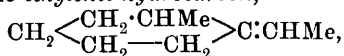
forms small, yellow plates, m. p. 103° ; the *nitrosochloride*,



is unstable.

1-Methyl- Δ^1 -cyclohexene yields a *dichloro*-derivative, b. p. $120^{\circ}/20$ mm., D_0^{20} 1.240; an unstable *dibromo*-derivative, b. p. $126\text{--}130^{\circ}/28$ mm.; a *nitrosate*, m. p. 104° ; a *nitrosite*, m. p. 102° , and a liquid *nitrosochloride*.

2-Chloro-1-methylcyclohexane reacts with magnesium, and the product condenses with acetaldehyde to form a secondary alcohol, which, on hydration, yields the *ethylenic hydrocarbon*,



b. p. $158^{\circ}/760$ mm., D_0^{20} 0.823, D_{20}^{20} 0.81, n_D^{20} 1.47.

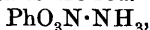
M. A. W.

Chromo-isomeric Salts of *o*-Nitrophenols. ANTONI KORCZYŃSKI (*Ber.*, 1909, 42, 167—177).—Hantzsch has shown (*Abstr.*, 1907, i, 207, 500) that the alkali salts of nitrophenols can be obtained in yellow, orange, and red modifications; the yellow and red salts are probably true isomerides, whereas the orange salts are solid solutions of the red and yellow varieties; however, the number of such isomeric salts prepared hitherto has been small. It is shown by the present investigation that the number of yellow salts of *o*-nitrophenols is quite as large as that of the red salts. The salts with amines are, as a rule, yellow, and do not differ appreciably from one another in shade; on the contrary, the red salts exhibit various shades of colour, depending on the nature of the alkali metal. Hantzsch has shown recently that the colour of the anion is not altered by union with an alkali metal in salt-formation; consequently, the yellow salts, which have precisely the same colour, must be chemically homogeneous, whereas the majority of the red salts of variable colour must be solid solutions of the red isomeride with small quantities of the yellow isomeride.

It has been found possible, by careful crystallisation from water or dilute alcohol, to separate the orange lithium salt of 2:4-dinitronaphthol into its red and yellow components.

The red and yellow salts are undoubtedly structurally identical, having the formula $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \\ \text{NO}_2 \end{array} \text{M}$; they are “chromo-isomerides,” the exact nature of the isomerism being still unknown.

The *rubidium* ($\frac{1}{2}\text{H}_2\text{O}$) and *lithium* ($\frac{1}{2}\text{H}_2\text{O}$) salts of *o*-nitrophenol are orange; the *anhydrous* salts are red. The *ammonium* salt,



prepared by passing ammonia into the molten substance, is red, and quickly passes into the orange salt, which is also obtained by the absorption of ammonia in Ley and Wiegner's apparatus (*Abstr.*, 1905, i, 749) at the ordinary temperature; at -20° , the yellow salt, $\text{PhO}_3\text{N} \cdot \text{NH}_3 \cdot \text{NH}_3$, is obtained. The *methylamine*, *dimethylamine*, *trimethylamine*, *ethylamine*, *dipropylamine*, and *benzylamine* salts, precipitated from ethereal solution, all have the same yellow colour;

the *piperidine* salt forms yellow leaflets; the *piperazine* salt crystallises in yellow needles, m. p. 74—75°.

The *anhydrous lithium*, *sodium*, *potassium*, *rubidium*, and *silver* salts of *p*-bromo-*o*-nitrophenol are red; the *lithium* salt containing H_2O is orange, and the *sodium* salt ($\frac{1}{2}\text{H}_2\text{O}$) is yellow when first precipitated; *ammonium* salts, similar to those of *o*-nitrophenol, were prepared. The salts with the organic bases mentioned above, with the exception of trimethylamine, have the same yellow colour; the *trimethylamine* salt is orange.

The *alkali* salts of 2:4-dibromo-*o*-nitrophenol are of a brighter red colour than the corresponding salts of *p*-bromo-*o*-nitrophenol; the *piperidine* and *methylamine* salts are yellow; the *ammonium*, *trimethylamine*, *dimethylamine*, *ethylamine*, *dipropylamine*, and *benzylamine* salts are orange; the *piperazine* salt, $\text{C}_6\text{H}_3\text{O}_3\text{NBr}_2\cdot\text{C}_4\text{H}_{10}\text{N}_2$, m. p. 160°, is orange; the *piperazine* salt, $(\text{C}_6\text{H}_3\text{O}_3\text{NBr}_2)_2\cdot\text{C}_4\text{H}_{10}\text{N}_2$, m. p. 185°, is scarlet.

The *lithium* and *sodium* salts of *o*-nitro-*p*-cresol, when prepared at -20° , are orange; the *potassium* ($\frac{1}{2}\text{H}_2\text{O}$), *rubidium*, and *cæsium* ($1\text{H}_2\text{O}$) salts are red, as is also the *sodium* salt when prepared at the ordinary temperature; the *thallium* and *ammonium* salts are orange; the salts with organic bases are yellow.

The *lithium* ($2\text{H}_2\text{O}$) and *potassium* ($1\text{H}_2\text{O}$) salts of bromo-*o*-nitro-*p*-cresol are blood-red; the *anhydrous lithium* salt is yellow; the *sodium*, *benzylamine*, *piperazine*, and *ethylamine* salts are orange; the *methylamine*, *dimethylamine*, *trimethylamine*, and *piperidine* salts are yellow.

The *lithium* salt of *p*-chloro-*o*-nitrophenol is orange, but the *sodium* ($1\text{H}_2\text{O}$) salt is red; the *methylamine*, *dimethylamine*, *trimethylamine*, *ethylamine*, *piperidine*, and *piperazine* salts are yellow.

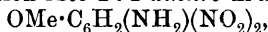
The *sodium* salt of α -nitro- β -naphthol, precipitated at low temperatures, is yellow, but quickly changes into the stable, orange form. The *dimethylamine*, *ethylamine*, and *benzylamine* salts are yellow.

The *lithium* ($1\text{H}_2\text{O}$) and *sodium* salts of 3:5-dinitro-*p*-cresol are orange; the *anhydrous potassium*, *rubidium*, and *cæsium* salts are red.

The *ammonium*, *methylamine*, *ethylamine*, *benzylamine*, *dimethylamine*, and *trimethylamine* salts of 2:4-dinitronaphthol are yellow; the *piperazine* salt crystallises in large, orange prisms, but the powdered substance is yellow; the *sodium*, *potassium*, *rubidium*, *cæsium*, and *thallium* salts are orange; the *lithium* salt ($1\text{H}_2\text{O}$) is orange, and loses its water at 160° without changing colour; the anhydrous salt absorbs $1\text{H}_2\text{O}$ from the air, and becomes carmine-red. When a solution of the salt in dilute alcohol is cautiously concentrated at 70°, it deposits at first a *carmine* salt, $1\text{H}_2\text{O}$, as microscopic leaflets or needles, after which a *yellow* salt, $1\text{H}_2\text{O}$, crystallises out in needles; both salts when dehydrated pass into the orange variety; the yellow modification generally passes spontaneously into the red form. Equivalent solutions of the two salts have the same colour and are equally intense.

W. H. G.

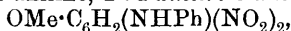
Derivatives of 2:3:4-Trinitroanisole. JAN J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 85—88. Compare Abstr., 1908, i, 978; Meldola, *Trans.*, 1902, 81, 993).—Derivatives of 2:3:4-trinitroanisole are described. The parent substance was prepared by treating 2:3-dinitroanisole with a mixture of sulphuric acid and fuming nitric acid. Crystallised from alcohol, it has m. p. 155°. Its constitution was determined by conversion into 2:4-dinitro-*m*-anisidine,



by heating in alcoholic solution with the equivalent quantity of ammonia in a sealed tube in the water-bath. It separates from alcohol in yellow crystals, m. p. 167°. When this compound is diazotised in sulphuric acid solution, and the diazo-solution poured into boiling alcohol, 2:4-dinitroanisole is obtained, proving that the parent substance is 2:3:4-dinitroanisole.

With methylamine in alcoholic solution, 2:3:4-trinitroanisole yields 2:4-dinitro-3-methylaminoanisole, $\text{OMe}\cdot\text{C}_6\text{H}_2(\text{NHMe})(\text{NO}_2)_2$, which separates from alcohol in yellow crystals, m. p. 130°. When this compound is dissolved in a mixture of nitric and sulphuric acids and the solution poured into water, 3-nitromethylamino-2:4:6-trinitroanisole, $\text{OMe}\cdot\text{C}_6\text{H}(\text{NMe}\cdot\text{NO}_2)(\text{NO}_2)_3$, separates as a sticky mass, which crystallises from methyl alcohol in colourless crystals, m. p. 99° (Romburgh, *Abstr.*, 1889, 971).

When 2:3:4-trinitroanisole in alcoholic solution is boiled with the equivalent quantity of aniline, 2:4-dinitro-3-anilinoanisole,



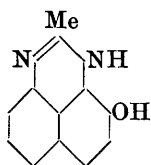
is formed. It crystallises from alcohol in reddish-brown crystals, m. p. 152°.

When 2:3:4-trinitroanisole is heated with aqueous sodium carbonate, the nitro-group at 3 is replaced by hydroxyl, yielding the monomethyl ether of 2:4-dinitroresorcinol, $\text{OMe}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{OH}$, which separates from water in light yellow crystals, m. p. 108°.

The nitro-group at 3 in 2:3:4-trinitroanisole is replaced by methoxyl by heating with sodium methoxide in methyl alcohol solution, with formation of the dimethyl ether of 2:4-dinitroresorcinol, identical with that obtained by Kauffmann and Franck (*Abstr.*, 1907, i, 1092). Crystallised from alcohol, it has m. p. 73°. When freshly prepared it is colourless, but direct sunlight turns it reddish-brown.

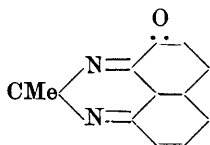
Treatment of 2:3:4-trinitroanisole with sodium ethoxide, with a view to replacing the nitro-group at 3 by ethoxyl, resulted in a complex reaction which is under investigation. A. J. W.

Derivatives of 8-Amino- β -naphthol. FRIEDRICH KEHRMANN and E. F. ENGELKE (*Ber.*, 1909, 42, 350—353).—During the course of unsuccessful attempts to prepare 8-acetylamino- β -naphthaquinone, the following new compounds have been obtained. 8-Acetylamino- β -naphthol, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NHAc}$, m. p. 164—165°, obtained from the aminonaphthol and acetic anhydride, is converted by sodium nitrite and dilute sulphuric acid into 1-nitroso-8-acetylamino- β -naphthol, m. p. 133—134° (decomp.), which separates from boiling water in golden-yellow needles. The nitroso-compound, by treatment with 3 parts of stannous chloride in 20% hydrochloric acid for twelve



(I.)

re-converted by reducing agents into the original salt, and is probably 9-quino-2-methylperimidinium (formula II).



(II.)

hours, yields yellow crystals of the *hydrochloride* of 9-hydroxy-2-methylperimidinium (formula I; compare Sachs, *Chem. Zeit.*, 1908, 30, IX for nomenclature).

Oxidation of an aqueous solution of the salt by sulphuric and chromic acids at 0° yields a substance, $C_{12}H_8ON_2$, m. p. 175° (decomp.), which crystallises in orange-yellow prisms, is

C. S.

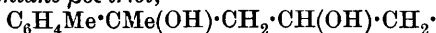
Substitution of Zinc by Magnesium in the Synthesis of Unsaturated Alcohols. W. JAWORSKY (*Ber.*, 1909, 42, 435—438. Compare *Abstr.*, 1908, i, 753).—It is found that much better yields are obtained by substituting mag-

nesium for zinc in the preparation of unsaturated alcohols by Saytzeff's method. A mixture of allyl bromide and the ketone in equivalent proportions is slowly added to magnesium ribbon (which has previously been treated for a short time with an ethereal solution of allyl bromide) immersed in absolute ether. The reaction product is subsequently treated with dilute acid, and the alcohol dried and fractionally distilled.

Diphenylallylcarbinol, $C_{16}H_{16}O$, prepared from benzophenone, allyl bromide, and magnesium, is a colourless liquid, b. p. 182—183°/32 mm. The following substances were also prepared: a viscid, yellow oil, b. p. 169°/27 mm., from piperonaldehyde; an oil, b. p. 266—272°/760 mm., from furfuraldehyde; a limpid liquid, b. p. 168—170°/760 mm. (decomp.), from mesityl oxide; a yellow oil, b. p. 165°/760 mm. (decomp.), from benzylideneacetone; a viscid, yellow oil, decomposing when boiled under 22 mm. pressure, from benzil. W. H. G.

Action of Magnesium on a Mixture of *p*-Tolyl Methyl Ketone and Allyl Iodide. E. GRISHKEWITSCH-TROCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1685—1691).—*p*-Tolylmethylallylcarbinol, $C_6H_4Me \cdot CMe(C_3H_5) \cdot OH$, obtained together with a small proportion of diallyl by the action of magnesium on a mixture of *p*-tolyl methyl ketone with allyl iodide or bromide, is a viscous, colourless liquid with a camphor-like odour and an intensely bitter taste, b. p. 128°/15 mm., 132.5—133°/30 mm., 237—240°/760 mm., D_4^{25} 0.9807, D_4^{25} 0.9832, n_D^{25} 1.5236. The alcohol readily unites with bromine (2 atoms), giving a syrupy compound, which rapidly decomposes with evolution of hydrogen bromide.

β-*p*-Tolylpentane-βδε-triol,



prepared by oxidising *p*-tolylmethylallylcarbinol by means of 1% potassium permanganate solution, crystallises from a mixture of ether and light petroleum in colourless needles, m. p. 101—103°.

β-*p*-Tolyl-β-methylhydracrylic acid, $C_6H_4Me \cdot CMe(OH) \cdot CH_2 \cdot CO_2H$, obtained by oxidising *p*-tolylmethylallylcarbinol by means of 4% potassium permanganate solution, forms acicular crystals, m. p.

102—104°. The *silver* salt, which is readily soluble in hot water, and the *calcium* and *barium* ($+2\text{H}_2\text{O}$) salts were prepared.

T. H. P.

Distribution of Cholesterol and its Allies. CHARLES DORÉE (*Bio-Chem. J.*, 1909, 4, 72—106).—Cholesterol is widely distributed in the animal kingdom, being found in representatives of all classes examined. In one or two cases analogous substances take its place, spongosterol in sponges, and so forth. The amount present varies, and the results are stated quantitatively. The same wide distribution of the phytosterols is found in the vegetable world, and these substances are probably the source of cholesterol in animals. The whole group consists of isomeric or closely related substances exhibiting the unsaturated linking and the hydroxyl group which are necessary for their antitoxic action.

W. D. H.

Fatty Acid Combinations with Cholesterol. CHARLES P. WHITE (*Proc. Physiol. Soc.*, 1908, vi; *J. Physiol.*, 38).—Cholesterol forms loose combinations with fatty acids which differ from true esters. Those with the fatty acids higher than hexoic can be obtained as fluid crystals, and give "myelin forms" and, finally, an emulsion of anisotropic globules on the addition of water. Similar combinations are formed by cholesterol with lecithin, cetyl alcohol, glycerol, mono- and di-palmitin, but not with triglycerides. The globules found in certain tissues (adrenal cortex) are of similar nature. Cholesterol may thus assist in the emulsification, absorption, and transference of fats.

W. D. H.

Agrosterol: a Cholesterol Substance in Soils. OSWALD SCHREINER and EDMUND C. SHOREY (*J. Amer. Chem. Soc.*, 1909, 31, 116—118).—The authors have isolated a cholesterol substance from Marshall clay (a soil containing 10.6% of organic matter and 0.51% of nitrogen), obtained from North Dakota, by extraction with alcohol and suitable treatment of the extract with ether and alcohol. The substance crystallises from ether in colourless needles, m. p. 237°, and from 80% alcohol in flat plates containing water of crystallisation. It is proposed to name this substance *agrosterol*, since it gives Liebermann's cholesterol reaction and has the formula $\text{C}_{26}\text{H}_{44}\text{O}$.

W. H. G.

New Synthesis of Adrenaline and Allied Compounds. KARL BOTTCHE (*Ber.*, 1909, 42, 253—266).—Barger and Jowett (*Trans.*, 1905, 87, 970) were unable to convert $\alpha\beta$ -dibromo-3:4-methylenedioxyphenylethane by means of phosphorus pentachloride into a chlorinated compound which could be decomposed to a dihydroxy-compound on hydrolysis with water; they obtained, in addition to β -bromo- α -hydroxy-3:4-methylenedioxyphenylethane, a dibromohydrin, m. p. 158°.

When, however, $2\frac{1}{2}$ to 3 mols. of phosphorus pentachloride are allowed to act on the dibromide for a considerable time at 105°, a chlorinated product is obtained, which is decomposed by water into

β-bromo-*α*-3 : 4-trihydroxyphenylethane. The halogen in this compound may be replaced by the NHMe-group, forming adrenaline.

By a similar series of reactions, *ψ*-safrole, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CMe}\cdot\text{CH}_2$, and *isosafrole*, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CH}:\text{CHMe}$, or their dichlorides or chlorohydrins, can be converted into methyladrenaline. A monobromo-adrenaline is obtained from the dibromohydrin, m. p. 158°. These three substituted adrenalines exhibit no pharmacological activity.

β-Chloro-*α*-hydroxy-3 : 4-methylenedioxyphenylethane,

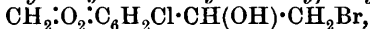


crystallises in long needles, m. p. 95°; it is prepared by acting with chlorine on a cooled solution of vinylcatechol methylene ether in carbon tetrachloride, whereby the *αβ*-dichloroethane is first obtained as a reddish-coloured oil, and this is subsequently hydrolysed by means of a mixture of acetone and water.

β-Chloro-*α*-3 : 4-trihydroxyphenylethane, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$, is prepared from the methylene ether by prolonged heating with a large excess of phosphorus pentachloride, and subsequent hydrolysis with a mixture of acetone and water. It forms needles which decompose about 100°, gives an intense green coloration with ferric chloride, and soon decomposes when kept exposed to the action of light. The carbonic ester, $\text{CO}:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CHCl}\cdot\text{CH}_2\text{Cl}$, formed as an intermediate product in its preparation, may be isolated as an oil, b. p. 190°/13 mm.

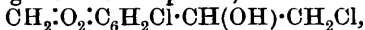
β-Bromo-*α*-3 : 4-trihydroxyphenylethane is prepared from the corresponding methylene ether in an analogous manner. It crystallises in clusters of small needles, m. p. 92–93°, decomposing to a dark violet substance, shows the same intense green coloration with ferric chloride, and decomposes even more easily than the chloro-compound. Either compound when dissolved in alcohol and shaken with a large excess of aqueous methylamine is converted into adrenaline. Although the compound prepared in this manner has not yet been obtained in the form of crystalline salts, it is very active physiologically.

Chloro-β-bromo-*α*-hydroxy-3 : 4-methylenedioxyphenylethane,



prepared by the action of sulphuryl chloride on bromohydroxy-methylenedioxyphenylethane, crystallises in well-formed, long needles, m. p. 128–129°. The halogen cannot be removed by heating with aqueous acetone. The acetate forms crystals, m. p. 89°.

The corresponding dichloro-compound,



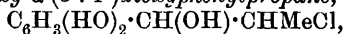
obtained by the action of sulphuryl chloride on chlorohydroxy-methylenedioxyphenylethane, separates in needles, m. p. 126–127°.

A tetrabromo-compound, prepared by the action of bromine vapour on *αβ*-dibromomethylenedioxyphenylethane, forms tiny crystals, m. p. 141–143°.

ψ-Safrole chlorohydrin, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\text{Cl}$, prepared by the action of chlorine on *ψ*-safrole, is a faintly yellow-coloured oil. It is converted by treatment with phosphorus pentachloride and subsequent hydrolysis with water into dihydroxyphenyl-*ψ*-allylchlorohydrin, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\text{Cl}$, a thin oil from which *α*-methyladrenaline is obtained as a bright golden-brown powder.

isoSafrole dichloride, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CHCl}\cdot\text{CHMeCl}$ (Hoering, Abstr., 1905, i, 903), is an oil, b. p. 164—166°/11 mm., 270°/760 mm. with much decomposition.

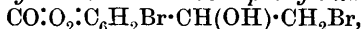
β -Chloro- α -hydroxy- α -(3:4)-dioxyphehylpropane,



forms needles, m. p. 104—105° (decomp.), and when shaken with methylamine gives rise to β -methyladrenaline, a bright yellow powder.

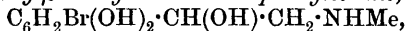
β -Bromo- α -hydroxy-3:4-dioxybromophenylethane, m. p. 157—158°, is conveniently prepared by the action of bromine on a solution of vinylcatechol methylene ether in carbon tetrachloride. The acetate has m. p. 100—101°. Oxidation with permanganate forms monobromopiperonylic acid, m. p. 201—202°.

β -Bromo- α -hydroxy-3:4-carbonatobromophenylethane,



forms glistening plates, m. p. 107°, and is converted when left in contact with acetone and water into β -bromo- α -3:4-trihydroxybromophenylethane, $\text{C}_6\text{H}_2\text{Br}(\text{OH})_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Br}$, which crystallises in lancet-like needles, m. p. 121—123°, and gives a green coloration with ferric chloride in aqueous solution.

α -3:4-Trihydroxy- β -methylaminobromophenylethane,



is obtained by the action of methylamine on the above as a light brown powder.

E. F. A.

New Syntheses of Adrenaline and Allied Compounds. HERMANN PAULY (*Ber.*, 1909, 42, 484—485).—It is claimed that Böttcher (preceding abstract) had not proved that the product obtained by him is adrenaline.

J. J. S.

Polynaphthenic Acids. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1757—1774).—Oxidation by means of air in presence of alkali serves as a means of characterising hydrocarbons and of estimating them in mixtures such as naphtha and its fractional distillates. Under the above conditions, saturated hydrocarbons give a negligible quantity of liquid oxidation products, whilst naphthenes give polynaphthenic or asphaltogenic acids, which are syrupy liquids, D 1.2, incapable of crystallising, and are not reduced to more highly hydrogenated compounds by means of sodium amalgam. These acids give the red coloration yielded by ketones with sodium nitroprusside, reduce ammoniacal silver nitrate solution and Fehling's solution, and decompose on distillation, even under greatly reduced pressure. They are soluble in alcohol, benzene, chloroform, ether, and carbon disulphide.

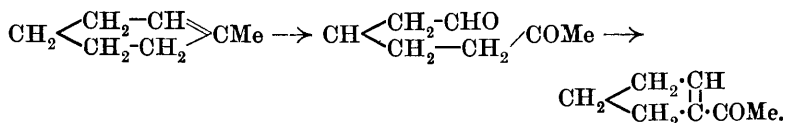
Oxidation of the fraction of "Meteor" kerosine, b. p. 169—171°, consisting of one of [the isomeric decanaphthenes, yielded a dibasic acid which, on analysis and on determination of the molecular weight cryoscopically and ebullioscopically, was found to have the formula $\text{C}_{20}\text{H}_{25}\text{O}_4$.

T. H. P.

1-Acetyl- Δ^1 -cyclopentene as an Oxidation Product of Δ^1 -cyclo-Hexeneacetic Acid. WILLIAM H. PERKIN, jun. and OTTO WALLACH (*Ber.*, 1909, 42, 145—149. Compare Wallach, Abstr., 1906, i, 176; 1907, i, 616; 1908, i, 426).—The ketone $\text{C}_7\text{H}_{10}\text{O}$ (Harding, Haworth,

and Perkin, *Trans.*, 1908, 93, 1946) has been definitely proved to be acetyl*cyclopentene*.

The fact that both Δ^1 -*cyclohexene*acetic acid and methyl- Δ^1 -*cyclohexene* yield acetyl*cyclopentene* when oxidised at 0° with permanganate proves that in this reaction a rupture of the six-membered ring occurs, and is followed by a closing of the ring to give a *cyclopentene* derivative :



The possibility of such a reaction must be borne in mind when the constitution of a cyclic compound is based on an examination of the products of oxidation with permanganate. J. J. S.

Isomeric Cinnamic Acids. EINAR BIILMANN (*Ber.*, 1909, 42, 182—188. Compare Liebermann, *Abstr.*, 1903, i, 255; Erlenmeyer, jun., *Abstr.*, 1906, i, 429).—It is shown that *allocinnamic* acid, m. p. 68°, *isocinnamic* acid, m. p. 57° (compare Liebermann, *Abstr.*, 1890, 1417), and *isocinnamic* acid, m. p. 38—46° (Erlenmeyer, sen., *Abstr.*, 1891, 200), are chemically identical and are not chemical isomerides. The three substances are trimorphous, and may be converted one into the other by simply melting the solid substance, cooling the fused mass, and inoculating with the acid required. Thus the *isocinnamic* acid, m. p. 41°, may be obtained from *allocinnamic* acid by melting this acid in a tube closed with a cotton-wool plug and subsequently cooling the fused mass in a freezing mixture; if this is heated to about 44° and inoculated with the *isocinnamic* acid, m. p. 58°, the whole mass solidifies and melts then at 58°. *alloCinnamic* acid may be obtained from this in the same manner.

Special precautions must be taken in crystallising *isocinnamic* acid, m. p. 58°, in order to prevent inoculation with *allocinnamic* acid. Thus, in order to crystallise the former in a room "infected" with the latter, it must be dissolved and the solution boiled after closing the vessel with a cotton-wool plug. This probably explains why Liebermann, having once obtained *allocinnamic* acid, could not again obtain *isocinnamic* acid, m. p. 58°.

The *isocinnamic* acid, m. p. 41°, when treated with light petroleum appears at first to dissolve, but in a few seconds the acid, m. p. 58°, crystallises out from the solution. W. H. G.

Remark on Biilmann's Discussion of the Isomeric Cinnamic Acids. EMIL ERLLENMEYER, jun. (*Ber.*, 1909, 42, 521—522. Compare Biilmann, preceding abstract).—Polemical. Biilmann's observations are not wholly in accord with those of Liebermann and the author on the three acids from *allocinnamic* acid: the fact that *allocinnamic* acid can be separated from the *iso*-acid is held to be against the idea of polymorphism. W. R.

Separation of Synthetic Cinnamic Acid into its Isomeric Components and their Re-combination into the Synthetic Acid. EMIL ERLÉNMEYER, jun. [with O. HERZ] (*Ber.*, 1909, 42, 502—513. Compare Abstr., 1906, i, 21, 176; 1907, i, 318).—It has already been shown that the synthetic acid is a mixture of storax-cinnamic acid and another acid of m. p. 128°. It has now been demonstrated that this admixed acid is not benzoic, thienylacrylic, or an alkyl- or methoxy-cinnamic acid. Fractional crystallisation is not a suitable method for obtaining this acid, but it may be obtained by fractional distillation of the ethyl esters. Ethyl storax-cinnamate has b. p. 148—151°/20 mm., whereas the ethyl ester of the synthesised acid has b. p. 152—165°/20 mm., and leaves in addition a considerable residue (10—20%). This distillate on careful refractionation gave a separation; the fraction of lowest b. p. on hydrolysis yielded "storax" acid, that of highest b. p. gave the acid, m. p. 128°, *heterocinnamic acid*. Moreover, this hetero-acid, like the cinnamic acid from storax, exists in two forms. The residue just mentioned distills at 269—271°, and on hydrolysis with cold 20% alcoholic potassium hydroxide a salt separates which yields *hetero-β-cinnamic acid* as an amorphous precipitate, m. p. 128°. It exhibits all the chemical properties of a cinnamic acid, and it separates from ethereal solution in a characteristic chalky form. It dissolves in 7—7·30 parts of 75% alcohol, whereas storax-α-cinnamic acid dissolves in 16·67 parts, and storax-β-acid in 11·31.

The hetero-β-cinnamic acid on repeated dissolution in petroleum is converted into the α-modification, which crystallises in glistening, thin leaflets, m. p. 130—131°. It dissolves in 9·40—9·54 parts of 75% alcohol, and by re-resolution in water or alcohol it is converted into the chalky isomeride.

When storax-α- and hetero-α-acids are mixed in equal proportions and crystallised from ether, the synthetic acid is reformed, also the two α-acids form mixed crystals. The hetero-β-cinnamic acid does not give a single substance; on the bottom of the vessel the β-acid is seen, and glistening leaflets on the sides. W. R.

Salt Formation and Addition Reactions of the Isomeric Acids obtained from Synthetic Cinnamic Acid, and Demonstration of their Different Chemical Behaviour. EMIL ERLÉNMEYER, jun. [with O. HERZ and G. HILGENDORFF] (*Ber.*, 1909, 42, 513—521. Compare preceding abstract).—The salts of storax-α- and hetero-β-cinnamic acid exhibit strong resemblances, yet the original acids are recovered from them unchanged; thus the diphenyloxyethylamine salt of storax-α-acid crystallises in slender needles, m. p. 177°; the salt of the hetero-β-acid crystallises similarly, m. p. 172°. Brucine forms an acid and a normal salt with the hetero-β-acid, which are very similar to those of the storax acid; they are, however, somewhat more soluble, and differ slightly in optical rotatory power (20'). A non-crystallisable syrup was obtained by mixing the two acids and attempting to prepare a solid brucine salt.

A *potassium hydrogen storax-α-cinnamate*, $C_{18}H_{15}O_4K$, is obtained from 2 mols. acid and $\frac{1}{2}$ mol. potassium carbonate, which is acid to test

paper and stable; it crystallises from alcohol (75%) in long crystals; the *potassium hydrogen* salt from the synthetic acid forms leaflets, and the similar salt from the hetero- β -acid is amorphous. Benzoic acid also forms a potassium hydrogen salt.

The properties described hitherto as descriptive of the different isomerides have all been physical. However, chemical differences also exist; the dibromide from storax- α -acid is formed more readily than that from hetero- β -acid; the ester of storax- α -acid is more rapidly hydrolysed than the hetero- β -ester, and these acids may be separated by taking advantage of the fact that hypochlorous acid forms an additive compound much more slowly with the hetero- than with the storax-acid.

The storax acid dibromide crystallises in stout crystals, m. p. 205—206°; the hetero-dibromide forms thin leaflets, m. p. 204°, whilst the dibromide from the synthetic acid is intermediate in crystalline character. By Liebermann's method all these dibromides give the original acids.

Synthetic cinnamic acid, when fractionally precipitated from its aqueous sodium salt solution, is separated into hetero- α - and - β - and storax- α -acids, which shows that these acids differ in strength also.

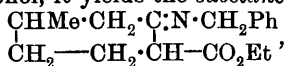
The nature of the isomerism is discussed shortly, and the opinion expressed that these isomeric phenomena are due to differences in the benzene nucleus.

W. R.

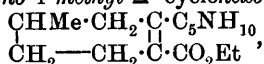
Action of Ammonia and Amines on Tetrahydrosalicylic Esters. ARTHUR KÖRZ and B. MERKEL (*J. pr. Chem.*, 1909, [ii], 79, 102—125).—Ethyl 3-amino-1-methylcyclohexane-4-carboxylate (Abstr., 1906, i, 88), which does not react with aqueous or methyl alcoholic ammonia, yields, with boiling aniline, alcohol and the substance, $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NH} \\ | \quad | \\ \text{CH}_2 - \text{CH}_2 \cdot \text{C} \cdot \text{CO} \end{array}$, m. p. 261° (decomp.), and, by heating alone at 280°, forms alcohol and the bimolecular compound, $\text{C}_{16}\text{H}_{22}\text{O}_2\text{N}_2$, m. p. above 300°.

Ethyl 1-methylcyclohexan-3-one-4-carboxylate, when heated with aminocyclohexane, yields a substance, $\text{C}_8\text{H}_{11}\text{ON}_2$, m. p. 264°, which appears to be identical with the preceding. With boiling aniline

(1 mol.), the ester yields the *anilinoanilide*, $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NHPh} \\ | \quad | \\ \text{CH}_2 - \text{CH}_2 \cdot \text{C} \cdot \text{CO} \cdot \text{NHPh} \end{array}$ m. p. 130°, whilst with benzylamine at the ordinary temperature, with or without methyl alcohol, it yields the substance,

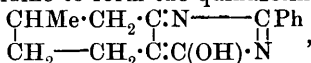


m. p. 61°, into which the attempt to introduce a second $\text{N} \cdot \text{CH}_2\text{Ph}$ group was unsuccessful. Ethyl 1-methylcyclohexan-3-one-4-carboxylate reacts (a) with the calculated amount of piperidine at the b. p. to form *ethyl 3-piperidino-1-methyl- Δ^3 -cyclohexene-4-carboxylate*,



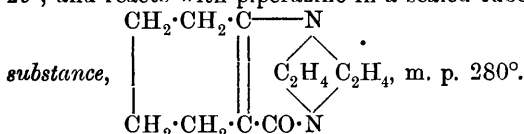
m. p. 123°; (b) with carbamide in warm dilute sodium ethoxide solution

to form the substance, $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NH} \cdot \text{CO} \\ | \quad | \\ \text{CH}_2 \text{---} \text{CH}_2 \cdot \text{C} \cdot \text{CO} \cdot \text{NH} \end{array}$; (c) with methylalcoholic benzenylamidine to form the quinazoline derivative,



m. p. 227°, and (d) with piperazine at 150° to form the substance, $\text{CH}_2 \cdot \begin{array}{c} \text{CHMe} \text{---} \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{Et}) \end{array} > \text{C} \cdot \text{C}_4\text{N}_2\text{H}_8 \cdot \text{C} < \begin{array}{c} \text{CH}_2 \text{---} \text{CHMe} \\ | \quad | \\ \text{C}(\text{CO}_2\text{Et}) \cdot \text{CH}_2 \end{array} \text{CH}_2$, m. p. 216°.

Ethyl cyclohexan-2-one-1-carboxylate, when heated with aniline, yields ethyl 2-anilino- Δ^1 -cyclohexene-1-carboxylate, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NHPh} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array}$, m. p. 29°, and reacts with piperazine in a sealed tube at 250°, forming the



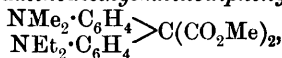
C. S.

Synthesis of β -Hydroxy- β -phenylpropionic Acid. W. N. ANDRIEWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1635—1638).—In presence of zinc, benzaldehyde and ethyl bromoacetate react, giving ethyl β -hydroxy- β -phenylpropionate (compare Daïn, *J. Russ. Phys. Chem. Soc.*, 1890, 22, 44), the changes being represented by the following equations: (1) $\text{CH}_2\text{Br} \cdot \text{CO}_2\text{Et} + \text{Zn} = \text{ZnBr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$; (2) $\text{ZnBr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} + \text{Ph} \cdot \text{CHO} = \text{ZnBr} \cdot \text{O} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$; (3) $\text{ZnBr} \cdot \text{O} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} + \text{H}_2\text{O} = \text{OH} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} + \text{ZnBr} \cdot \text{OH}$.
T. H. P.

Condensation of Mesoxalic Esters with Aromatic Tertiary Amines. ALFRED GUYOT and EDMOND MICHEL (*Compt. rend.*, 1909, 148, 229—232).—Ethyl mesoxalate readily undergoes condensation with aromatic tertiary amines. Ethyl dimethyl-*p*-aminophenyltartronate, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH})(\text{CO}_2\text{Et})_2$, prepared by heating an acetic acid solution of dimethylaniline with ethyl mesoxalate for thirty minutes, forms colourless leaflets, m. p. 76·5°. The following compounds have also been prepared: Methyl *p*-dimethylaminophenyltartronate, prisms, m. p. 115°; ethyl *p*-diethylaminophenyltartronate, $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH})(\text{CO}_2\text{Et})_2$, prisms, m. p. 45°; the methyl ester, needles, m. p. 103°. On hydrolysis with aqueous potassium hydroxide, these substances form the corresponding acids, which are unstable and have been converted into aldehydes, and also into glyoxylic acids of the type $\text{R} \cdot \text{CO} \cdot \text{CO}_2\text{H}$, and glycollic acids of the type $\text{R} \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$.

Under the influence of phosphoryl chloride, the foregoing esters undergo further condensation with aromatic tertiary amines. Thus ethyl *p*-dimethylaminophenyltartronate and dimethylaniline yield ethyl tetramethyldiaminodiphenylmalonate, $\text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2(\text{CO}_2\text{Et})_2$, white leaflets, m. p. 93°. The following compounds have been prepared in the same way: Ethyl dimethylaminodiethylaminodiphenyl-

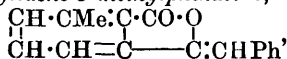
malonate, $\frac{\text{NMe}_2 \cdot \text{C}_6\text{H}_4}{\text{NEt}_2 \cdot \text{C}_6\text{H}_4} > \text{C}(\text{CO}_2\text{Et})_2$, m. p. 82° ; *ethyl tetraethyl-diaminodiphenylmalonate*, prisms, m. p. 82.5° ; the *methyl ester*, prisms, m. p. 98° ; *methyl tetramethyldiaminodiphenylmalonate*, leaflets, m. p. 166° ; *methyl dimethylaminodiethylaminodiphenylmalonate*,



needles, m. p. 121° . Alcoholic potassium hydroxide converts these esters into the corresponding tetra-alkyldiaminodiphenylacetic acids, which are unstable and have no definite m. p. (compare Weil, Abstr., 1894, i, 419). W. O. W.

***m*-Toluic Acid.** ERICH MÜLLER (*Ber.*, 1909, 42, 423—434).—A continuation of the investigations of Findelee (*Abstr.*, 1906, i, 42) and Jürgens (*Abstr.*, 1907, i, 1036). The present communication deals principally with an improved method of converting *m*-toluic acid into 3-methylphthalic acid, and of various condensation products derived from the latter substance. Experiments have also been made with the object of definitely establishing the constitutions of the four possible nitro-*m*-toluic acids.

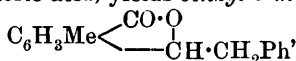
I. 3-Methylphthalic Acid.—3-Methylphthalic anhydride, when heated with phenylacetic acid in the presence of sodium acetate at 236° , yields *benzylidene-3-methylphthalide*,



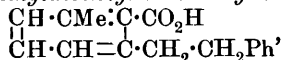
which crystallises in small leaflets, m. p. 151° , and is converted by a 10% aqueous solution of potassium hydroxide into 3-methyldeoxy-

benzoin-2-carboxylic acid, $\begin{array}{c} \text{CH} \cdot \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{H} \\ | \quad | \\ \text{CH} \cdot \text{CH} = \text{C} \cdot \text{CO} \cdot \text{CH}_2\text{Ph}' \end{array}$ crystallising with

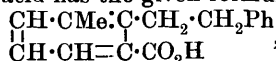
$1\text{H}_2\text{O}$ in gypsum-like crystals, m. p. $77-79^\circ$. The latter, when reduced with sodium amalgam, yields a salt of a γ -hydroxy-acid, which, when treated with hydrochloric acid, yields *benzyl-3-methylphthalide*,



which crystallises in groups of needles, m. p. $87-92^\circ$. If the salt of the γ -hydroxy-acid is heated at 212° for four hours, and then treated with dilute hydrochloric acid, it yields an oil which is undoubtedly 3-methylstilbene-2-carboxylic acid, for it is converted on reduction into 3-methyldibenzyl-2-carboxylic acid,



crystallising in nodular aggregates of rhombic prisms, m. p. $125-126^\circ$. It was shown that the acid has the given formula, and not



by V. Meyer's law of esterification (*Abstr.*, 1895, i, 228; 1896, i, 547).

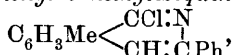
Although 3-methylphthalylglycine ethyl ester cannot be converted by Gabriel and Colman's method into an isoquinoline derivative

(compare Jürgens, *loc. cit.*), the latter may be obtained from 3-methylphthalic acid by the following method.

Benzylidene-3-methylphthalide is converted by gaseous nitrous acid into *nitrobenzylidene-3-methylphthalide*, $C_6H_5Me \begin{smallmatrix} \text{CO} \cdot O \\ \diagdown \quad \diagup \\ \text{C} : CPh \cdot NO_2 \end{smallmatrix}$,

which crystallises in yellow leaflets, m. p. 198—199° (decomp.), and is converted by hydriodic acid and red phosphorus into 3-phenyl-8-methylisocoumarin, $C_6H_5Me \begin{smallmatrix} \text{CO} \cdot O \\ \diagdown \quad \diagup \\ \text{CH} : CPh \end{smallmatrix}$, long, colourless needles, m. p. 131°.

The latter compound is converted by alcoholic ammonia into 3-phenyl-8-methylisocarbostyryl, $C_6H_5Me \begin{smallmatrix} \text{CO} \cdot NH \\ \diagdown \quad \diagup \\ \text{CH} : CPh \end{smallmatrix}$, which crystallises in small groups of needles, m. p. 231°, and is converted by boiling phosphoryl chloride into 1-chloro-3-phenyl-8-methylisoquinoline,



crystallising in needles, m. p. 64—65°. 3-Phenyl-8-methylisoquinoline, $C_{16}H_{13}N$, obtained by reducing the last-named compound with hydriodic acid and red phosphorus, has m. p. 51°; the *hydriodide*, pale yellow needles, m. p. 216—218° (decomp.); *hydrochloride*, long, slender needles, m. p. 236—240°; *chromate*, granular crystals, m. p. 164°; *platinichloride*, pale yellow needles, m. p. 221° (decomp.); *picrate*, granular crystals, m. p. 232°, and *aurichloride*, $C_{16}H_{13}N, HAuCl_4, H_2O$, microscopic needles, m. p. 211° (decomp.), were prepared.

II. *Nitration of m-Toluic Acid*.—*m*-Toluic acid when nitrated is converted into 2-nitro-*m*-toluic acid, 4-nitro-*m*-toluic acid, and 6-nitro-*m*-toluic acid. It was shown that the compound, m. p. 215—216°, is 6-nitro-*m*-toluic acid by reducing it to the amino-compound and distilling the latter with lime, whereupon *o*-toluidine was obtained.

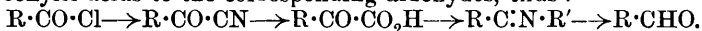
5-Amino-*m*-toluic acid, $C_8H_9O_2N$, crystallises in groups of small needles with a pink tint, m. p. 183°, and yields *m*-toluidine when distilled with lime.

Methyl 6-nitro-m-toluate has m. p. 81—82°; *methyl 5-nitro-m-toluate* crystallises in plates, m. p. 84—85°; *methyl 4-nitro-m-toluate* forms needles, m. p. 78—79°.

W. H. G.

Claisen's Acid Cyanide Synthesis. FERDINAND MAUTHNER (*Ber.*, 1909, 42, 188—195).—It has been shown previously (*Abstr.*, 1908, i, 348) that 3:4:5-trimethoxybenzoyl cyanide may be prepared from 3:4:5-trimethoxybenzoyl chloride by Claisen's synthesis. In the present communication, it is shown that the chlorides of anisic acid, veratric acid, dimethylgentisic acid, 2:3:4-trimethoxybenzoic acid, and 3:4:5-trimethoxybenzoic acid may be converted by this method into the corresponding cyanides, which when hydrolysed are first converted into amides and finally into α -ketocarboxylic acids. This method of preparation of the α -keto-acids of phenol ethers is better than that devised by Bouveault (*Abstr.*, 1897, i, 530; 1898, i, 585; 1899, i, 286), because in this case the positions of the radicles in the molecule are known. By employing Bouveault's method of converting an α -ketocarboxylic acid into the corresponding aldehyde

(Abstr., 1896, i, 649), it is possible to pass from phenol ether carboxylic acids to the corresponding aldehydes, thus :



p-Methoxybenzoyl cyanide, $\text{C}_9\text{H}_7\text{O}_2\text{N}$, prepared by the action of hydrogen cyanide on anisyl chloride in the presence of pyridine, crystallises in colourless needles, m. p. 63—64°. It is converted by cold concentrated hydrochloric acid into *p*-methoxyphenylglyoxylamide, $\text{C}_9\text{H}_9\text{O}_3\text{N}$, colourless needles, m. p. 151—152°, and *p*-methoxyphenylglyoxylic acid.

The following compounds are prepared by methods similar to those just described :

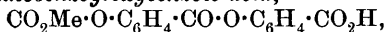
m-Methoxybenzoyl cyanide, $\text{C}_9\text{H}_7\text{O}_2\text{N}$, forms colourless crystals, m. p. 111—112°; it is not readily attacked by cold concentrated hydrochloric acid. 3:4-Dimethoxybenzoyl cyanide, $\text{C}_{10}\text{H}_9\text{O}_3\text{N}$, crystallises in colourless needles, m. p. 116—117°. 2:5-Dimethoxybenzoyl chloride, $\text{C}_9\text{H}_6\text{O}_3\text{Cl}$, prepared by the action of phosphorus pentachloride on 2:5-dimethoxybenzoic acid, is a colourless oil, b. p. 163—164°/15 mm. 2:5-Dimethoxybenzoyl cyanide, $\text{C}_{10}\text{H}_9\text{O}_3\text{N}$, forms pale yellow needles, m. p. 97—98°. 2:5-Dimethoxyphenylglyoxylamide, $\text{C}_{10}\text{H}_{11}\text{O}_4\text{N}$, crystallises in needles, m. p. 128—129°. The corresponding acid, first obtained by Bouveault as an oil, crystallises in needles, m. p. 75—76°. 2:3:4-Trimethoxybenzoyl chloride, $\text{C}_{10}\text{H}_{12}\text{O}_4\text{Cl}$, has b. p. 175—176°/11 mm., m. p. 42°. The corresponding cyanide, $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$, crystallises in colourless needles, m. p. 89—90°. 2:3:4-Trimethoxyphenylglyoxylic acid, $\text{C}_{11}\text{H}_{12}\text{O}_6$, crystallises in colourless needles, m. p. 139—140°; the amide, $\text{C}_{11}\text{H}_{13}\text{O}_5\text{N}$, forms needles, m. p. 106—107°.

3:4:5-Trimethoxybenzoyl cyanide has b. p. 178—179°/14 mm.

W. H. G.

Methyl-carbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetical Operations. II. EMIL FISCHER (*Ber.*, 1909, 42, 215—228).—The method of preparation of the chlorides of phenolcarboxylic acids described recently (Abstr., 1908, i, 892) cannot be employed with advantage when the hydroxyl group occupies a position ortho to the carboxyl group. *o*-Ethyl carbonato-benzoic acid has been prepared, however, by Hofmann (*Amer. Patent* 1639, 174 of Dec. 12, 1899) by the action of ethyl chlorocarbonate on a mixture of salicylic acid and dimethylaniline in benzene. This method has now been employed to convert the two hydroxyl groups in 2:5-dihydroxybenzoic acid and 2:4-dihydroxybenzoic acid into methyl-carbonato-groups, and from the compounds formed the corresponding chlorides have been obtained. *o*-Coumaric acid, unlike salicylic acid, adds on the methyl-carbonato-group in an aqueous alkaline solution, and yields finally the chloride, $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COCl}$.

p-Methyl-carbonatobenzoyloxybenzoic acid,



obtained by the action of *p*-methyl carbonatobenzoyl chloride on *p*-hydroxybenzoic acid, crystallises in very small, slender needles, m. p. 216—217° (corr., decomp.); it is converted by dilute aqueous ammonia into *p*-hydroxybenzoyloxybenzoic acid, m. p. about 270° (decomp.): Klepl gives m. p. 261° (Abstr., 1884, 446).

o-Methyl-carbonatobenzoic acid, $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, forms long, glistening plates, m. p. 135° (corr., decomp.); it is converted by phosphorus pentachloride into *o*-methyl-carbonatobenzoyl chloride, $\text{C}_9\text{H}_7\text{O}_4\text{Cl}$, a colourless liquid, b. p. $107-110^\circ/0.1$ mm.; the latter compound reacts with glycine or glycine ester, forming methyl-carbonatosalicyluric acid, a viscid oil which is hydrolysed by aqueous sodium hydroxide, yielding salicyluric acid (compare Bondi, Abstr., 1907, i, 766). A substance, $\text{C}_{10}\text{H}_7\text{O}_5\text{N}$, is obtained as an intermediate product in the condensation of the chloride with glycine; it crystallises in very thin, glistening, microscopic plates, m. p. 228° (corr.).

5-Methyl-carbonato-2-hydroxybenzoic acid, $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}$, obtained by the action of methyl chlorocarbonate on gentisic acid dissolved in *N*-sodium hydroxide solution, crystallises in long, colourless needles, m. p. 171° (corr.); it is converted by methyl chlorocarbonate and dimethylaniline in benzene into 2:5-dimethyl-carbonatobenzoic acid, $(\text{CO}_2\text{Me}\cdot\text{O})_2\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$, crystallising in thin plates, m. p. $144-145^\circ$ (corr., decomp.); the chloride, $\text{C}_{11}\text{H}_9\text{O}_7\text{Cl}$, forms microscopic needles, m. p. 119° (corr.).

4-Methyl-carbonato-2-hydroxybenzoic acid, $\text{C}_9\text{H}_8\text{O}_6$, crystallises in long needles, m. p. 143° (corr.). 2:4-Dimethyl-carbonatobenzoic acid, $\text{C}_{11}\text{H}_{10}\text{O}_8$, forms long needles, m. p. 159° (corr., decomp.); the corresponding chloride, $\text{C}_{11}\text{H}_9\text{O}_7\text{Cl}$, crystallises in slender needles or thin leaflets, m. p. $86-87^\circ$ (corr.).

o-Methyl-carbonatocinnamic acid, $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, crystallises in slender needles, m. p. 185° (corr.); the chloride, $\text{C}_{11}\text{H}_9\text{O}_4\text{Cl}$, forms slender, pliable needles. W. H. G.

Condensation of Aldehydes with Phenolcarboxylic Acids.

II. E. HÖST MADSEN (*Arch. Pharm.*, 1909, 247, 65-77).—An extension of the reaction described previously (Abstr., 1907, i, 423) to other aromatic aldehydes and acids.

4:4'-Dihydroxy 5:5'-dimethyltriphenylmethane-3:3'-dicarboxylic acid, m. p. 248° (approx., decomp.), obtained from benzaldehyde and *o*-cresotic acid by the general process (*loc. cit.*), crystallises with $1\text{H}_2\text{O}$ from ether on addition of light petroleum in tufts of colourless needles, and gives in alcoholic solution on addition of ferric chloride a bluish-violet coloration. The diacetyl derivative, m. p. $140-145^\circ$, separates from dilute alcohol in colourless crystals with $1\text{H}_2\text{O}$, and gives no colour immediately with ferric chloride, but yields a bluish-violet colour with this reagent after boiling with water for some minutes.

4:4'-Dihydroxy-6:6'-dimethyltriphenylmethane-3:3'-dicarboxylic acid, m. p. 271° (approx., decomp.), obtained by condensing benzaldehyde with *m*-cresotic acid, crystallises from dilute alcohol in colourless, felted needles, and is similar in solubility to the first isomeride described, but gives a redder coloration with ferric chloride. The diacetyl derivative, m. p. $240-245^\circ$ (decomp.), crystallises in colourless needles or rhomboidal plates, and gives a violet coloration with ferric chloride after boiling with water.

2:2'-Dihydroxy-5:5'-dimethyltriphenylmethane-3:3'-dicarboxylic acid, m. p. 240° (approx., decomp.), obtained from benzaldehyde and

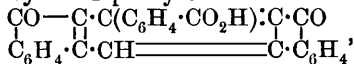
p-cresotic acid, forms a colourless, crystalline powder, and generally resembles the two isomerides described above, but is somewhat hygroscopic. The *diacetyl* derivative, m. p. 135—140°, crystallises in thin plates, and, unlike the two isomerides described above, is soluble in chloroform, ether, or hot water.

When vanillin is heated with salicylic acid in presence of hydrochloric acid by the general process, no condensation to a triphenylmethane derivative occurs, but decomposition ensues and phenols are formed. *Vanillin salicylate*, m. p. 110° (approx.), is obtained when phosphoric oxide is added to salicylic acid and vanillin dissolved in ether, and the mixture heated under a reflux apparatus during twenty-four hours. It is coloured green by ammonia, gives a violet coloration with Millon's reagent, and yields the characteristic colour reaction of salicylic acid with ferric chloride after boiling in water during a few minutes. The *oxime*, m. p. 164.5°, of the ester forms long, colourless needles.

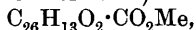
No condensation products could be obtained by the general process with (1) paraldehyde and *o*-cresotic acid, (2) acetone and *o*-cresotic acid, or (3) benzaldehyde and *o*-resorcylic acid. T. A. H.

Derivatives of Phenenytribenzoic [1:3:5-Triphenylbenzene-2':2'':2'''-tricarboxylic] Acid. GIORGIO ERRERA and A. VACCARINO (*Gazzetta*, 1909, 39, i, 1—11).—The authors have investigated further the two isomeric acids obtained by the action of concentrated sulphuric acid on phenenytribenzoic acid (compare Errera, *Abstr.*, 1908, i, 185), which are found to have m. p. 362° (instead of 349—350°) and 335—336° (instead of 321°) respectively. The quantities of the two acids obtained are always very nearly in the ratio 4 (m. p. 362°):1 (m. p. 335—336°), no matter whether the phenenytribenzoic acid is used in the crude form or after repeated crystallisation. Both are transformed slowly, but completely, into tribenzoylenebenzene under the prolonged action of concentrated sulphuric acid on the water-bath. Both acids are also esterified moderately readily by Fischer's method, the one with the lower m. p. rather more slowly than the other, probably owing to its less solubility. The observation that tribenzoylenebenzene is formed the more readily from the acid, m. p. 335—336°, leads the authors to interchange the two structural formulæ previously given (*loc. cit.*).

2:3:5:6-Dibenzoylene-1-phenylbenzene-2'-carboxylic acid,



has, therefore, m. p. 362°. Its *sodium* salt, $\text{C}_{27}\text{H}_{13}\text{O}_4\text{Na}$, H_2O , and its ethyl ester (m. p. 260°, instead of 253°) and *methyl* ester,

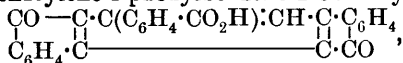


m. p. 336—337°, were prepared. Its *nitro*-derivative,



is deposited from nitrobenzene in yellow needles or large, brick-red crystals, m. p. about 429°.

3:4:5:6-Dibenzoylene-1-phenylbenzene-2-carboxylic acid,



crystallises from alcohol in pale yellow, silky needles, m. p. 335—336°. Its *ethyl* ester, $C_{26}H_{18}O_2 \cdot CO_2Et$, crystallises from light petroleum in elongated, yellow laminae, m. p. 226°, and its *methyl* ester, $C_{26}H_{18}O_2 \cdot CO_2Me$, crystallises from light petroleum in minute, yellow laminae, m. p. 248—249°; the *sodium* salt, $C_{27}H_{18}O_4Na \cdot 5H_2O$, was prepared.

Triethyl phenenyltribenzoate (compare Abstr., 1908, i, 185) separates from light petroleum in faintly yellow, prismatic crystals, m. p. 71°, belonging to the monoclinic system [FRANCESCO RANFALDI: $a:b:c = 0.48681:1:0.95873$; $\beta = 88^\circ 31' 24''$].

Trimethyl phenenyltribenzoate, $C_6H_3(C_6H_4 \cdot CO_2Me)_3$, separates from methyl alcohol as a mass of colourless crystals, m. p. 94—95°.

The great differences between these esters of phenenyltribenzoic acid and the corresponding ones of phenyl-naphthalenedicarboxylic acid (Lanser's "diphenyltetrenedicarboxylic acid") (compare Michael, Abstr., 1906, i, 518; Lanser, Abstr., 1899, i, 916) afford a further confirmation of Michael's views that these two acids are distinct.

T. H. P.

Inosic Acid. PHÆBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1909, 42, 335—338).—The authors furnish additional evidence of the constitution previously suggested for inosic acid (Abstr., 1908, i, 931). By heating a 2½% aqueous solution of the barium salt for six hours at 125—130° in a sealed tube, barium phosphate is eliminated, and from the solution, which does not contain a pentose or hypoxanthine, Haiser and Wenzel's inosine (Abstr., 1908, i, 561) has been isolated; by more prolonged heating of the barium salt, carnine itself is formed.

Haiser and Wenzel regard inosic acid and carnine as being derived from the same parent substance. The authors believe that carnine is a degradation product of inosic acid.

C. S.

Preparation of Aldehydes and Acid Anhydrides. AUGUSTE BÉHAL (*Compt. rend.*, 1909, 148, 179—182. Compare this vol., i, 145).—Benzaldehyde can be prepared by boiling for thirty-two hours a mixture of benzylidene chloride (1 mol.) and acetic acid (2 mols.). Catalysts, such as cobalt chloride, facilitate the reaction, which is probably expressed by the equation: $CHPhCl_2 + 2HOAc = Ph \cdot CHO + Ac_2O + 2HCl$. The formation of acetyl chloride, which occurs when only 1 mol. of acetic acid is employed, is probably due to the action of hydrogen chloride on the acetic anhydride.

Curves are given showing the rate of evolution of hydrogen chloride when varying amounts of acetic acid are employed. This reaction is stated to be general.

W. O. W.

Asymmetric Synthesis. PAUL FREUNDLER (*Ber.*, 1909, 42, 233—234. Compare Henle and Haakh, this vol., i, 6).—It was desired to carry out a reaction, which requires the influence of light, with a racemic compound in circularly polarised light. To this end the conversion of *r-o*-nitrobenzaldehydediamylacetal (b. p. 186—187°/11 mm.), dissolved in *r*-amyl alcohol, into amyl *o*-nitrosobenzoate was studied. The Heraeus quartz mercury lamp was used as the source of light, and screened so that the light was mainly $\lambda = 398$. Action

was continued for 400 hours, but in a single experiment no evidence of optical activity could be detected. E. F. A.

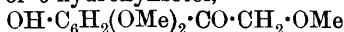
Constitution of "Dichloropiperonal." HERMANN PAULY (*Ber.*, 1909, 42, 417—422. Compare Abstr., 1907, i, 709).—Dichloropiperonal, formed by the action of sulphur chloride or sulphur dichloride on piperonaldehyde, could not be isolated in a pure state, hitherto, owing to the presence of colloidal sulphur (compare Schimmel & Co., Abstr., 1906, i, 513). It is now found that the sulphur can be removed by passing a current of chlorine into the mixture and distilling off the sulphur dichloride under reduced pressure; pure dichloropiperonal is obtained by crystallising the residue from chloroform. Since it is so readily prepared by this method, it seemed highly probable that dichloropiperonal had the formula originally given to it by Fittig and Remsen, namely, $\text{COH} \cdot \text{C}_6\text{H}_3 \cdot \text{O} \cdot \text{CCl}_2$;

nevertheless, it has been found that when this substance is reduced with zinc dust, it does not regenerate piperonaldehyde, but yields methylcatechol carbonate; thus proving the correctness of Delange's view that dichloropiperonal is really dichloromethylcatechol carbonate (Abstr., 1907, i, 700).

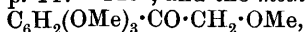
Methylcatechol carbonate, $\text{C}_8\text{H}_6\text{O}_3$, has m. p. 34—35°, b. p. 133—135·5°/26 mm., 238—241°/760 mm. It is converted by 50% aqueous pyridine into homocatechol (3:4-dihydroxytoluene), which has m. p. 65° (corr.) and b. p. 251° (corr.). Béhal and Desvignes give m. p. 51° (Abstr., 1892, 1312). W. H. G.

Crystalline Form of 3:4'-Dimethylbenzophenone. PAUL P. SCHORIGIN (*Bull. Acad. Sci. St. Petersburg*, 1909, 79—80. Compare *Ber.*, 1903, 36, 2027).—This ketone crystallises readily from alcohol in the form of long, monoclinic needles [$a:b:c = 1.0409:1:0.4154$, $\beta = 91^\circ 45'$], m. p. 82°, b. p. 328—330°/760 mm., $D_4^{20} 1.134$. Z. K.

Completely Methylated Flavone Derivatives. JOSEF HERZIG and BR. HOFMANN (*Ber.*, 1909, 42, 155—159. Compare Abstr., 1891, 1386; 1893, i, 413).—Morin reacts with methyl sulphate in the presence of a large excess of sodium hydroxide solution, yielding the *pentamethyl ether*, $\text{C}_{15}\text{H}_5\text{O}_2(\text{OMe})_5$, which crystallises from alcohol in colourless needles m. p. 154—157°. Its alcoholic solution is colourless, but turns yellow on the addition of potassium hydroxide solution. When boiled with alcoholic potash, it yields 2:4-dimethoxybenzoic acid and the *trimethyl ether* of *o*-hydroxyfisetol,



(6-hydroxy-2:4-dimethoxyphenyl methoxymethyl ketone), which separates from alcohol in compact, colourless crystals, m. p. 102—104°. The *oxime*, $\text{C}_8\text{H}_6\text{O}_2\text{N}(\text{OMe})_3$, crystallises from dilute methyl alcohol in colourless needles, m. p. 147—149°, and the *methyl ether*,

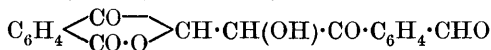


has m. p. 49—52°.

A 25% yield of quercetin pentamethyl ether (Waliaschko, Abstr., 1904, i, 760) can be obtained by treating quercetin with methyl

sulphate and sodium hydroxide and keeping for several days. When warmed with alcoholic potash, the ether yields 3:4-dimethoxybenzoic acid and the trimethyl ether of *o*-hydroxyfisetol. J. J. S.

Bisdiketohydrindene. HUGO VOSWINCKEL (*Ber.*, 1909, 42, 465—470).—Considerable amounts of Nathanson's bisdiketohydrindene (diphthalylethane) (Abstr., 1894, i, 38) are obtained in the preparation of dihydroxynaphthacenequinone (Gabriel and Leupold, Abstr., 1898, i, 482). When treated with a mixture of glacial acetic and nitric acid (1.48) at 0°, the hydrindene derivative yields a mixture of two oxidation products. The one dissolves readily in cold benzene, whereas the other is very sparingly soluble. This second compound, C₁₈H₁₂O₆, crystallises from hot chloroform in short, six-sided prisms, m. p. 211°, and the structural formula

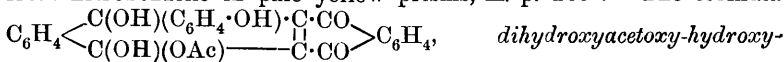


is suggested. It yields an *acetyl* derivative, C₂₀H₁₄O₇, m. p. 315°, a *benzoyl* derivative, C₂₇H₁₆O₇, m. p. 268°, and a *methyl* ether, C₁₉H₁₄O₆, which turns brown at 240° and decomposes at higher temperatures. With phenylhydrazine the oxidation product yields a complex condensation product, (C₁₈H₁₂O₆ + 5C₆H₅N₂ - 5H₂O), which crystallises from glacial acetic acid in red needles with a high metallic lustre and m. p. 209°.

The oxidation product dissolves in cold normal sodium hydroxide solution, and the immediate addition of hydrochloric acid yields an *acid*, C₁₈H₁₂O₆·2H₂O, which crystallises from glacial acetic acid in clear prisms, m. p. 240°. Its solutions in ammonia or alkali carbonates have a reddish-brown colour, and those in alkali hydroxides a reddish-brown colour which changes rapidly to blue.

Hot sodium hydroxide transforms the oxidation product into *phthalonaldehydic acid*, COH·C₆H₄·CO·CO₂H, which crystallises from water in small prisms and plates, m. p. 144°. Its *phenylhydrazone* has m. p. 229°. J. J. S.

The Naphthacene Series. II. HUGO VOSWINCKEL (*Ber.*, 1909, 42, 458—465. Compare Abstr., 1906, i, 99).—Phenol and acetic acid react with naphthacenediquinone in the presence of sulphuric acid, yielding a product, C₁₈H₈O₄·C₆H₆O·C₂H₄O₂, which crystallises from nitrobenzene in pale yellow prisms, m. p. 285°. The formula

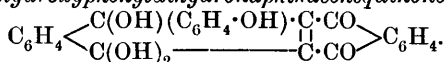


phenyldihydronaphthacenequinone is suggested. The phenolic group is firmly attached, and cannot be removed by reduction or hydrolysis, whereas the acetyl group is readily eliminated. Acetic anhydride and zinc chloride transform the condensation product into the *tetra-acetyl*

derivative, C₆H₄ $\begin{array}{c} \diagup \text{C}(\text{OAc})(\text{C}_6\text{H}_4 \cdot \text{OAc}) \cdot \text{C} \cdot \text{CO} \diagdown \\ \diagdown \text{C}(\text{OAc})_2 \text{---} \text{C} \cdot \text{CO} \diagup \end{array}$ C₆H₄, which forms pale yellow crystals, m. p. 283°.

The condensation product dissolves in dilute alkalis, yielding brownish-violet-coloured solutions, and the addition of mineral acids yields the three products:

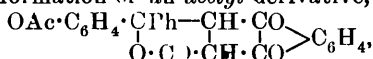
1. *Trihydroxy-phenyldihydronaphthacenequinone*,



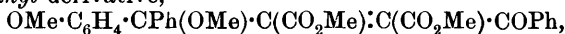
—It is insoluble in benzene, but crystallises from dilute alcohol in yellow prisms, m. p. 190°, dissolves in alkalis, giving characteristic colorations, and dyes silk an orange colour. Its solution in concentrated sulphuric acid has a reddish-violet colour, which turns to a steel-blue when warmed; with acetic anhydride and zinc chloride it yields a *monoacetyl* derivative, $\text{C}_{26}\text{H}_{18}\text{O}_7$, which separates from glacial acetic acid as a colourless, crystalline powder, m. p. 285°.

2. An *acid*, $\text{C}_6\text{H}_5\cdot\text{C(OH)(C}_6\text{H}_4\cdot\text{OH)}\cdot\text{CH—CO}$
 $\text{CO}_2\text{H}\cdot\text{C}\cdot\text{C(OH)}_2 \text{C}_6\text{H}_4$, which can be

isolated as the calcium salt. The acid separates as a flocculent mass containing water of crystallisation; when heated at 80°, it loses $0.5\text{H}_2\text{O}$, assumes a crystalline texture, and then melts at 130°. Treatment with acetic anhydride and zinc chloride leads to the elimination of water and the formation of an *acetyl* derivative,



which crystallises from glacial acetic acid in golden-yellow plates, m. p. 266°. Treatment with methyl sulphate transforms the acid into a *tetramethyl* derivative,



which forms colourless plates, m. p. 124°.

3. A *compound*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{C(C}_6\text{H}_4\cdot\text{OH)(OH)} \\ \text{CO} \end{array} \begin{array}{c} \text{CH}\cdot\text{C(OH)} \\ \text{CH}\cdot\text{C(OH)} \end{array} \text{C}_6\text{H}_4$ (?),

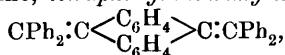
which crystallises from dilute alcohol in orange-coloured needles, m. p. 174°. It dissolves in alkali hydroxides to a violet solution, and in sulphuric acid to a pure blue solution. It yields a *monoacetyl* derivative, $\text{C}_{26}\text{H}_{18}\text{O}_6$, m. p. 172°.

Resorcinol, orcinol, and phloroglucinol condense with naphthacenediquinone and glacial acetic acid in the absence of sulphuric acid. The product obtained from resorcinol has the composition $\text{C}_{24}\text{H}_{14}\text{O}_6$, and forms a reddish-brown, crystalline powder, m. p. 234°.

Naphthacenequinhydrone, $\text{C}_{18}\text{H}_8\text{O}_4$, $\text{C}_{18}\text{H}_{10}\text{O}_4$, is obtained by the union of naphthacenediquinone with dihydroxynaphthacenequinone in nitrobenzene solution, and is identical with the compound previously described as a desmotropic modification of naphthacenediquinone.

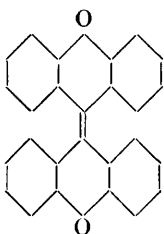
J. J. S.

Reactions of 9:10-Dihydroanthracene and of Anthranol.
 ROBERT PADOVA (*Compt. rend.*, 1909, 148, 290—292).—When 9:10-dihydroanthracene is heated at 250° for two and a-half hours with diphenyldichloromethane, *tetraphenylanthracenylilene*,

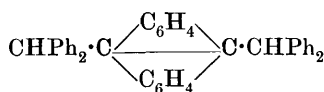


is obtained. This has m. p. 305°, and is identical with the substance

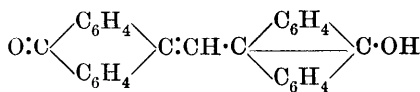
obtained by Staudinger (Abstr., 1908, i, 410) by the action of anthraquinone on diphenylketenquinoline. On reduction with sodium and benzyl alcohol, it yields the compound I (below), which has m. p. above 360° and shows an intense violet fluorescence.



Dianthraquinone (annexed formula) is said to be formed by the action of amyl nitrite on a solution of dianthrone in pyridine. The action of chloroform and alcoholic potassium hydroxide on anthranol leads to the formation of a substance crystallising in deep red prisms, m. p. above 310°. This is 10-oxanthryl-9-anthraquinonemethane (formula II). The *acetyl* derivative has m. p. 201—202°. The *benzoyl* derivative forms canary-yellow prisms, m. p. 216—218°.



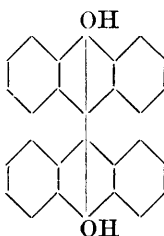
(I.)



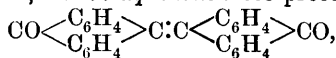
(II.)

W. O. W.

New Reduction Product of Anthraquinone. HANS MEYER (*Ber.*, 1909, 42, 143—145).—When anthraquinone is reduced with zinc dust and alkali at high temperatures and under pressure, the product is the enolic form of *dianthranol* (annexed formula) (compare Dimroth, Abstr., 1901, i, 198). It is extremely stable, and appears to exist in two forms, of which one is obtained in dark brown, glistening crystals, whilst the other is pale yellow. The m. p. is about 230°, but is not sharp. The name dianthranol is assigned to this compound, that previously described as dianthranol or dianthrone (*loc. cit.*) being regarded as the ketonic form and therefore termed dianthrone. Its solutions in aqueous alkali hydroxides are reddish-yellow. The *diacetyl* derivative forms yellow needles, m. p. 273°; the *dimethyl ether* has m. p. 245°. Both yield dihydroanthracene when reduced with hydriodic acid, and anthraquinone when oxidised with chromic acid.



Feeble oxidising agents, ferric chloride, alkaline permanganate, or a solution of iodine in potassium iodide solution, transform the phenol into *bianthrone* [better, *dianthraquinone*: see preceding abstract],



a lemon-yellow compound which is stable and sparingly soluble in most solvents. Its solutions at high temperatures have a green colour, and it is also turned green by pressure.

Prolonged heating with an alcoholic solution of hydrogen chloride transforms dianthrol into dianthrone, and alcoholic potassium hydroxide brings about the reverse change.

J. J. S.

Action of Magnesium on a Mixture of Allyl Bromide and a Terpene Ketone. W. JAVORSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1746—1748).—The author has prepared the following alcohols by

the action of magnesium on a mixture of allyl bromide and a ketonic compound under the conditions previously laid down (Abstr., 1908, i, 753).

3-Allylmenthan-3-ol, $C_{13}H_{24}O$, b. p. $130^{\circ}/22$ mm., prepared from allyl bromide and menthone.

2-Allylborneol, b. p. $130^{\circ}/20$ mm., from camphor and allyl bromide.

Δ^4 -Allyl-3-p-menthen-3-ol, $C_{13}H_{22}O$, b. p. $135^{\circ}/27$ mm., from pulegone and allyl bromide.

These three alcohols, which were obtained in about 90% yields, are colourless, mobile liquids.

Treated under the above conditions with allyl bromide, piperonal yields a thick, yellow liquid, b. p. $169-170^{\circ}/27$ mm.; furfuraldehyde, a thick, yellow liquid, b. p. $266-272^{\circ}$; menthyl oxide, a colourless, mobile liquid, b. p. $168-170^{\circ}$ (slight decomp.), with a smell like that of camphor; benzylideneacetone, an almost colourless liquid, b. p. 165° , at which temperature water is given off; benzil, a thick brown liquid, which decomposes when distilled under 22 mm. pressure. These products are under investigation.

The reaction between allyl bromide and a ketonic compound in presence of magnesium sometimes fails without apparent reason. One condition necessary for success is a slow, gentle action, any strong heating always lowering the yield of alcohol. T. H. P.

The Grignard Synthesis. Action of Magnesium Phenyl Bromide on Camphor. H. JERMAIN M. CREIGHTON (*Trans. Nova Scotia Inst. Sci.*, 1908, 11, (4), 593-597).—The interaction of ethereal magnesium phenyl bromide and camphor in equal molecular quantities at 60° leads to the formation of *phenylborneol*, $C_{10}H_{16}Ph\cdot OH$, b. p. $258-260^{\circ}$ or $143-145^{\circ}/14$ mm., $D_{20} 0.977$, $[\alpha]_D^{25} 7^{\circ}55'$, in alcoholic solution (compare Zelinsky, Abstr., 1901, i, 660). C. S.

Attempts to Resolve Racemic Camphoric Acid and *iso*-Borneol into Active Components. ERNST BECKMANN (*Ber.*, 1909, 42, 485-491. Compare Pickard and Littlebury, *Trans.*, 1907, 91, 1973).—The *isoborneol* obtained from camphene by Bertram and Walbaum's method (Abstr., 1894, i, 204) has m. p. 212° , and is slightly dextrorotatory in solution, the value for $[\alpha]_D$ varying from $+1.2^{\circ}$ to $+3.9^{\circ}$ according to the solvent used. When oxidised, the *isoborneol* yields a camphor which is slightly levorotatory, and on further oxidation a camphoric acid, which is also slightly levorotatory. No *isocamphoric* acid is formed, as treatment with acetyl chloride completely transforms the acid into its anhydride.

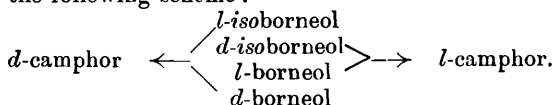
The acid obtained is mainly *r*-camphoric acid, with a slight excess of the *l*-acid, and can be resolved by repeatedly crystallising the acid cinchonidine salt from aqueous alcohol. The *d*-acid had m. p. 183° and $[\alpha]_D +44.4^{\circ}$, and the *l*-acid, m. p. $186-187^{\circ}$ and $[\alpha]_D -50.7^{\circ}$.

Attempts to resolve the *isoborneol* itself were made by conversion into the *isobornyl* hydrogen succinate, and resolution of this by means of its cinchonidine salt.

*iso*Bornyl succinate, $C_{24}H_{38}O_4$, has m. p. 37° , and resembles camphor in appearance. *iso*Bornyl hydrogen succinate, $C_{14}H_{22}O_4$, is a clear oil with an acid taste and an odour of *isoborneol*. The cinchonidine salt,

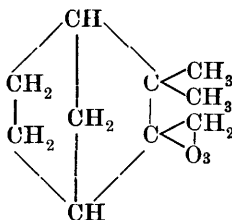
$C_{33}H_{14}O_5N_2$, crystallises from dilute alcohol in slender needles, m. p. 107° . By crystallising from its 40% alcoholic solution, nine fractions, with $[\alpha]_D$ varying from $+11.3^\circ$ to -2.5° , were obtained.

The genetic relationship of the camphors and borneols is represented by the following scheme:



J. J. S.

Components of Ethereal Oils. Constitution of Camphene. Its Oxidation with Ozone. FRIEDRICH W. SEMMLER (*Ber.*, 1909, 42, 246—252).—When ozonised, camphene forms only one ozonide, which is decomposed in two ways: on the one hand (to the extent of about 30%) into camphenilone, $C_9H_{14}O$, and this to a hydroxy-acid, δ -hydroxycamphenilonic acid, which forms a beautifully crystalline δ -lactone, $C_9H_{14}O_2$, whilst, on the other hand, acids, $C_9H_{14}O_2$, are formed.



Camphene ozonide, annexed formula, prepared by leading a stream of ozone through camphene dissolved in chloroform, is a viscid oil, which decomposes when distilled in a vacuum. Cam-

phenilone, $CH \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \\ \text{CMe}_2 \cdot \text{CO} \end{array} CH$, has m. p.

40° , D^{20}_D 0.9705. The semicarbazone, $C_9H_{14} \cdot N \cdot NH \cdot CO \cdot NH_2$, has m. p. 223° ; the oxime has m. p. 109° , b. p. $128-129^\circ/14$ mm. The nitrile, $C_9H_{13}N$, prepared by boiling the oxime with dilute sulphuric acid, has b. p. $85-90^\circ/12$ mm., D^{20}_D 0.9449, n_D 1.47348. Camphocenic acid, obtained by the action of alcoholic potassium hydroxide on the nitrile, has b. p. $145-146^\circ/11$ mm., D^{20}_D 1.020, n_D 1.4862.

δ -Hydroxycamphenilonic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}(\text{CMe}_2 \cdot \text{OH}) \\ \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \end{array} \text{CH}_2$, forms a thin syrup, b. p. $125-175^\circ/10$ mm., which decomposes, forming a solid distillate of the lactone. This has m. p. $95-96^\circ$, b. p. $126-128^\circ/10$ mm., and forms large plates; it dissolves slowly in a slight excess of potassium hydroxide, and this solution yields a colourless silver salt. The silver salt interacts with methyl iodide, forming methyl δ -hydroxycamphenilonate, b. p. $126-127^\circ/10$ mm., D^{20}_D 1.0423, n_D 1.46757. Both the acid and lactone behave as saturated compounds to permanganate. The acid, $C_9H_{14}O_2$, obtained also by the decomposition of camphene ozonide in a vacuum, is regarded as a mixture of an unsaturated monocyclic and a saturated dicyclic acid. It has b. p. $136-140^\circ/10$ mm., D^{20}_D 1.028, n_D 1.475; the methyl ester has b. p. $94-96^\circ/10$ mm., D^{20}_D 0.988, n_D 1.46261.

In view of these results, crude camphene consists to the greater part of semi-cyclic-camphene, $CH \begin{array}{c} \text{CH}_2 \text{---} \text{CH}_2 \\ \text{CH}_2 \\ \text{CMe}_2 \cdot \text{C}(\text{CH}_2) \end{array} CH$.

E. F. A.

Constituents of Ethereal Oils. Inversion of Carvenene, $C_{10}H_{16}$ (Terpinene ?), into *iso*Carvenene, $C_{10}H_{16}$ (*iso*Terpinene ?). FRIEDRICH W. SEMMLER (*Ber.*, 1909, 42, 522—527. Compare this vol., i, 110).—Carvenene has the following constants: $D^{20.2}$ 0.8443, $n_D^{20.2}$ 1.49065, which result confirms the conclusion previously arrived at that cyclic conjugated double linkings cause an exaltation in the molecular refraction (cal. 45.240, found 46.619). When carvenene is heated with alcoholic sulphuric acid for two hours, *isocarvenene*, $C_{10}H_{16}$, b. p. 59—62°/10 mm., D^{20} 0.845, n_D 1.480 (the exaltation in this case is only 0.4), and a *dicarvenene*, $C_{20}H_{32}$, b. p. 170—173°/10 mm., D^{20} 0.928, n_D 1.5175, are obtained. The physical constants for *isocarvenene* are identical with those of terpinene obtained from sabinene mono- or di-hydrochloride, and it has been found that all terpinenes are converted into a terpene by alcoholic sulphuric acid, the physical data of which agree with those of *isocarvenene*. This compound yields terpinene nitrosite identical with that obtained from carvenene. In order to investigate further the conversion of carvenene into the *iso*-compound, the action of bromine on “terpinene” from sabinene dihydrochloride in amyl alcohol-ether solution was studied; crystals of terpinol tetrabromide were deposited, thus proving that terpinol is present in the “terpinene,” which has hitherto been regarded as pure when prepared from the dihydrochloride.

Carvenene, on repeated reduction with sodium and amyl alcohol, gives *dihydrocarvenene* (Δ^2 -tetrahydrocymene), $C_{10}H_{18}$, an oil, b. p. 55—56°/12 mm., D^{20} 0.824, n_D 1.461. Oxidation of carvenene with ozone yields dimethylacetylacetone (b. p. 82—86°/10 mm.).

Carvenene is regarded as $\Delta^{1:3}$ -dihydrocymene, and *isocarvenene*, $\Delta^{1:4}$ -dihydrocymene. W. R.

Sesquiterpenes. ERNST DEUSSEN (*Ber.*, 1909, 42, 376—381; 680).

—The author is unable to say from which of the two, and possibly three, isomeric hydrocarbons present in caryophyllene (*Abstr.*, 1908, i, 353) the following substances are derived.

The oxidation of caryophyllene (α - 14°) by dilute aqueous potassium permanganate at 0° yields a glycol, $C_{15}H_{22}O_4$, m. p. 120.5° (*loc. cit.*); from the oily potassium salts remaining after the removal of the glycol, two acids have been obtained. One is a liquid monobasic acid, $C_{10}H_{16}O_3$, which forms a crystalline *semi-carbazone*, $C_{11}H_{19}O_3N_3$, m. p. 186° (slight yellow coloration), and the other is a crystalline monobasic acid, $C_8H_8O_4$, m. p. 179.5—180.5°, which sublimes without decomposition, does not form a semicarbazone, and is not identical with Baeyer's $\Delta^{2:4}$ -dihydrophthalic acid.

When a solution of caryophyllene in acetone containing a little water is cooled in a freezing mixture and oxidised by the gradual addition of powdered potassium permanganate (two atomic proportions of oxygen), a substance, $C_{10}H_{18}O_3$, m. p. 145—146°, is obtained, which separates from hot benzene in white needles, is unchanged by dilute sodium hydroxide at 100°, has a bitter-sweet taste, and

appears to be a glycol, since it is changed by dilute sulphuric acid to an amorphous, white *substance*, $C_{10}H_{16}O_2$.

[With A. LOESCHE.]—The residue remaining after the distillation in a vacuum of oil of clove stalks freed from eugenol, yields by treatment with alcohol a voluminous, white *substance*, $(C_{21}H_{30}O)_5$, m. p. 146° , which can be purified by repeated precipitation of its chloroform solution by alcohol. C. S.

Ethereal Oil of the Root Bark of *Cinnamomum zeylanicum*. A. A. L. PILGRIM (*Pharm. Weekblad*, 1909, 46, 50—54).—The chief constituent of the oil of the root bark of *Cinnamomum zeylanicum* is camphor. The other constituents are pinene, cineol, dipentene, phellandrene, eugenol, saffrole, probably carophyllene and borneol, and possibly cinnamaldehyde. The oil from the leaves contains 76% of eugenol along with pinene and cinnamaldehyde. The oil from an old sample of the stem bark contained 50% of cinnamaldehyde, and that from a specimen of young bark, 70—75%. In both, pinene, benzaldehyde, and eugenol were also present. A. J. W.

Extracts containing Glucosides. LEOPOLD ROSENTHALER and R. MEYER (*Arch. Pharm.*, 1909, 247, 28—49).—The object of this research was to determine whether in the preparation of extracts of drugs containing glucosides by exhaustion with water, as recommended by various Pharmacopeias, decomposition of the glucosides ensued, and, if so, whether this could be prevented by (1) neutralising the natural acids of the drug by adding calcium carbonate, and (2) by rendering the enzymes inactive by immersing the drug in boiling 95% alcohol.

Experiments with gentian, centaury, alder bark, cascara sagrada bark, and rhubarb showed that the first question must be answered in the affirmative, that although in none of these cases did the calcium carbonate exert any deleterious action, its protective action with respect to the glucosides was slight, and that extraction with hot alcohol is harmful in the case of centaury, is of no advantage in the case of alder bark, but is to be recommended in the cases of gentian, cascara sagrada bark, and rhubarb. The methods adopted in estimating the glucosides, etc., in these various extracts are described in detail in the original. T. A. H.

Cholesterol as an Antidote to the Saponins. ADOLF WINDAUS (*Ber.*, 1909, 42, 238—246).—The action of cholesterol as an antidote to the power of saponins to dissolve blood-corpuscles, discovered by Ransom, has been ascribed to a chemical reaction and to a physical change, such as absorption. The poisons of bees, snakes, and bacterial poisons are similarly counteracted by cholesterol. Digitonin and cholesterol, when mixed in alcoholic solution, immediately give rise to a colourless, crystalline precipitate in fine needles of *digitonin-cholesteride*, $C_{55}H_{94}O_{28} + C_{27}H_{46}O$, formed as a simple molecular compound of the two components without any elimination of water. The compound decomposes above 240° ; it is quite impossible to obtain cholesterol from it by prolonged extraction with ether.

It slowly dissociates when boiled in methyl-alcoholic solution for some hours. It is entirely without any solvent action on the blood-corpuscles. Other alcohols behave similarly to cholesterol towards digitonin. Phytosterol forms a molecular compound crystallising in thin needles; the compound with stigmasterol is even less soluble. *Digitonin- β -cholestanol* is more soluble than the cholesteride, and crystallises in stellar aggregates of needles. *α -Cholestanol* (*cyclocholesterol*) forms no such molecular compound.

Digitonin-amyl alcohol, $(C_{55}H_{94}O_{18} + C_5H_{12}O + 6H_2O)$ (compare Houdas, Abstr., 1892, 222), is more soluble than the cholesterol derivative. The air-dried product loses amyl alcohol when boiled with water.

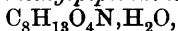
Digitonin-octyl alcohol behaves similarly. Other alcohols, linalool, geraniol, and sabinol, also combine with digitonin.

Cholesterol esters do not unite with digitonin, nor do these esters counteract the poisonous action of saponins. When digitonin-cholesteride is acetylated, it is easy to remove the cholesterol acetate.

The reaction can be used to detect small quantities of cholesterol and to separate it from mixtures, particularly in cases when cholesterol esters are also present. It is also applicable to the purification of digitonin.

Solanin-cholesteride is very sparingly soluble in alcohol, but crystallises with difficulty. *Cyclamin cholesteride* crystallises in minute needles, but the cholesterol can be extracted from this with ether. Cyclamin also gives an insoluble, crystalline additive product with octyl alcohol. From the analysis of this cholesteride, the formula $C_{36}H_{56}O_{18}$ for cyclamin is obtained. E. F. A.

Scopoline. ERNST SCHMIDT (*Arch. Pharm.*, 1909, 247, 79—80).—It was shown previously (Abstr., 1906, i, 104) that scopoline is reduced without difficulty to hydroscopoline, which contains two $-OH$ groups. Further, on oxidation with chromic acid, scopoline yields pyridine-methochloride, and from these observations the deductions are drawn that the $-OH$ group of scopoline does not lie in the pyridine nucleus, and that the same applies to the second oxygen atom, which must be present in an ether or morpholine group. In confirmation of this view, it is now shown that hydroscopoline, when carefully oxidised with chromic acid, yields a *methylpiperidinedicarboxylic acid*,



m. p. 214—216° (decomp.), which crystallises in transparent tablets and yields a crystalline, azure-blue *copper* salt. The *hydrochloride*, m. p. 224—225° (decomp.), is crystalline, and the *aurichloride* forms large, yellow leaflets.

aa'-Dimethylpyridine, on oxidation with permanganate, furnishes methylpyridinecarboxylic acid (m. p. 129°) and Ladenburg's *aa'*-pyridinedicarboxylic acid. The latter, on electrolytic reduction, furnishes two isomeric hydrogenised acids, of which *one*, m. p. 206—207°, readily passes into the *other*, m. p. 158°, and it is hoped by methylating these acids to synthesise the acid obtained by oxidising hydroscopoline. T. A. H.

The Chlorophyll Group. III. New Method of Decomposition in the Chemistry of Chlorophyll. LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1909, 16, 3—8. Compare Abstr., 1908, i, 439).—The zinc compound obtained by the action of zinc hydroxide and carbon dioxide on an alcoholic solution of chlorophyllan is termed "zinc chlorophyll." It is a complex metallic derivative of chlorophyll, which it closely resembles in properties. Treatment with acids converts the zinc compound into chlorophyllan, whereas alkalis (alcoholic potassium hydroxide) transform it into a substance analogous to alkachlorophyll, the chief difference being that the new compound contains zinc, whereas alkachlorophyll contains magnesium. The name "*zinc-phyllotaonin*" is suggested. The compound dissolves in ether, yielding a brilliant greenish-blue solution with a red fluorescence. The solution gives five characteristic absorption bands between λ 677 and λ 492. Treatment of the new compound with concentrated hydrochloric acid yields phyllotaonin or *allophyllotaonin*.
J. J. S.

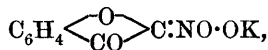
Rotation of Tannin. MAXIMILIAN NIERENSTEIN (*Chem. Zeit.*, 1909, 33, 126).—Feist's view (*ibid.*, 1908, 32, 918) that the rotatory power of tannin is due to admixture of dextrose formed by the hydrolysis of a glycolgallic acid is not accepted. Experiments show that specimens of tannin which are free from dextrose have a high rotatory power.
J. J. S.

Tannin. MAXIMILIAN NIERENSTEIN (*Ber.*, 1909, 42, 353—354. Compare Abstr., 1908, i, 40).—Since luteo-acid (pentahydroxydiphenyl-methylolidecarboxylic acid) and ellagic acid are produced by the oxidation of tannin, the author has suggested that the production of ellagic acid in plants may be due to oxidation (Abstr., 1908, i, 897). This suggestion is strengthened by the fact that the hot filtered pyridine extract of myrobalan, after dilution with water, boiling, and keeping for thirty hours, yields ellagic acid, whilst the concentrated mother liquor deposits luteo-acid, identical in all respects with that obtained synthetically from tannin.
C. S.

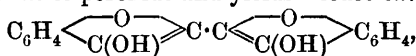
The So-called "Bloom" of Pyrogallol Tannins and Its Identity with Ellagic Acid. MAXIMILIAN NIERENSTEIN (*Chem. Zeit.*, 1909, 33, 87. Compare Abstr., 1905, i, 365, 805).—The "bloom" of some samples of sole-leather and of various pyrogallol tannin materials has been examined, and with but one exception, was conclusively shown to be ellagic acid. The exception is "white mangrove," the bloom of which is laguncurin, a yellow dye.
W. H. G.

Coumarandione, the Analogue of Isatin in the Coumarone Series. RICHARD STOERMER (*Ber.*, 1909, 42, 199—202. Compare Stoerner and Kahlert, Abstr., 1902, i, 457).—It has at last been found possible to prepare coumarandione, the lactone of *o*-hydroxybenzoyl-formic acid, which is the analogue of isatin in the coumarone series. 1-Nitro-2-diisobutylaminocoumarone, when warmed with alcoholic

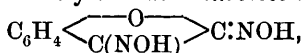
potassium hydroxide, is decomposed with the formation of *disobutylamine* and the *potassium* salt of *aci-nitrocoumaranone*,



obtained as lemon-yellow needles. When this salt is treated with an acid, it liberates nitric peroxide and yields "*leuco-oxindigo*,"



obtained as a canary-yellow precipitate, m. p. 276° (decomp.). The *leuco*-compound is oxidised by chromic acid in acetic acid into *coumarandione*, $\text{C}_8\text{H}_4\text{O}_3$, which crystallises with $1\text{H}_2\text{O}$ in small, yellow needles, m. p. 178° (decomp.), and is converted by hot, dilute hydrochloric acid into *o*-hydroxybenzoylformic acid. Coumarandione when acted on by hydroxylamine yields *diisonitrosocoumarone*,



a colourless, crystalline substance, m. p. 203–205°.

W. H. G.

***o*-Hydroxybenzoylformic Acids and Coumarandiones.** KARL FRIES (*Ber.*, 1909, 42, 234–236).—*o*-Hydroxybenzoylformic acid occurs in an anhydrous form and also as monohydrate. The *hydrate* of 2-hydroxy-4-methylbenzoylformic acid crystallises in plates, m. p. 64°; it is faintly yellow, and stable in the atmosphere. The anhydrous acid is more soluble in benzene than the hydrate; it crystallises in feather-like needles, m. p. 102°, which are almost colourless except when viewed in mass. The *hydrate* of 2-hydroxy-5-methylbenzoylformic acid forms yellow prisms, m. p. 75°; the anhydrous acid crystallises in needles, m. p. 107°. These acids lose carbon dioxide and water when heated, forming methylcoumarandiones, but the yield is small and the product difficult to purify. They are conveniently prepared by heating the hydroxybenzoylformic acids in benzene or petroleum solution with an excess of phosphoric oxide for fifteen minutes.

5-Methylcoumarandione, $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \diagup \text{CO} \diagdown \\ \text{O} \end{array} \text{CO}$, crystallises in well-formed, yellow plates, m. p. 112°. In contact with water it is slowly converted into the hydroxy-acid and goes into solution. It dissolves in concentrated sulphuric acid with a yellowish-red coloration, and on dilution the hydroxy-acid is formed. The ketone reacts immediately with *o*-phenylenediamine, but 2-hydroxy-3-*m*-hydroxy-*p*-tolylquinoxaline, and not methylcoumarophenazine, is formed.

4-Methylcoumarandione crystallises in long, golden-yellow prisms, m. p. 149°. These diketocoumarans and the hydroxy-acids give the indophenin reaction with benzene containing thiophen and concentrated sulphuric acid.

E. F. A.

Method of Preparation of Ketothionaphthens. KARL AUWERS and F. ARNDT (*Ber.*, 1909, 42, 537–545).—Starting with *p*-tolyl methyl thioether a method is described of obtaining thionaphthen derivatives by using chloroacetyl chloride.

p-Tolyl methyl thioether, $\text{C}_8\text{H}_{10}\text{S}$, from the sodium salt and methyl

sulphate, is a colourless oil, b. p. $209^{\circ}/747$ mm., $94^{\circ}/31$ mm., D_{16}^{20} 1.0302, n_D^{16} 1.57537, which, when heated with chloroacetyl chloride and aluminium chloride in carbon disulphide solution for five hours, and subsequently distilled with steam, is converted into *keto-4-methylthionaphthen*, $C_6H_4Me \begin{smallmatrix} \diagup CO \\ \diagdown S \end{smallmatrix} CH_2$. It crystallises from petroleum in colourless needles, m. p. 102° , which gradually change when moist to carmine-red. On oxidation with potassium ferricyanide in dilute alkali, "4'-dimethylthioindigotin," $C_{18}H_{12}O_9S_2$, is formed, which crystallises from nitrobenzene in brownish-red needles, m. p. over 300° .

Ketobenzylidene-methylthionaphthen, $C_6H_4Me \begin{smallmatrix} \diagup CO \\ \diagdown S \end{smallmatrix} C:CHPh$, is formed by the condensation of benzaldehyde and ketomethylthionaphthen in alcohol in the presence of hydrogen chloride, and forms long, yellow, glistening needles, m. p. 145.5° . The *dibromide*,

$C_{16}H_{12}OBr_2S$, forms stout, yellow prisms, m. p. 116° , and is re-converted into the parent substance by alkali or alcohol.

Ketobenzylidene-thionaphthen, $C_{15}H_{10}OS$, crystallises from alcohol in yellow needles, m. p. 131.5° ; its *dibromide*, $C_{15}H_{10}OBr_2S$, forms crystals, m. p. $114-115^{\circ}$.

6-Methylthiol-3-methylacetophenone, $SMe \cdot C_6H_4Me \cdot COMe$, from tolyl methyl thioether, acetyl chloride, and aluminium chloride, crystallises from light petroleum in white needles, m. p. 51.5° . It is not hydrolysed by known methods, either being recovered unchanged or suffering decomposition. The 6-thiol-3-methylacetophenone could not be obtained from the thiocresol by a similar method to the methyl ether.

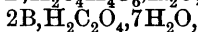
p-Tolyl chlorothioloacetate, $C_6H_4Me \cdot S \cdot CO \cdot CH_2Cl$, from thiocresol and chloroacetyl chloride, which forms snow-white crystals, m. p. 38° , could not be converted into the o-chloroacetyl isomeride (compare Fries and Finck, this vol., i, 42). The *acetyl* compound of thiocresol, $C_9H_{10}OS$, is an oil, b. p. $121^{\circ}/14$ mm. W. R.

Cinchonamine and Certain Other Rare Alkaloids. BERNARD F. HOWARD and O. CHICK (*J. Soc. Chem. Ind.*, 1909, 28, 53).—The results of trials with cinchonamine hydrochloride as a test for nitric acid and for the estimation of nitrates, by the formation of cinchonamine nitrate, which is nearly insoluble in water, especially in presence of free acid (compare Abstr., 1905. i, 102), are given. Certain data respecting cinchonamine, quinicine, cinchonicine, cupreine, and concusconine are also recorded.

Cinchonamine hydrochloride may be used for the estimation of nitrates in certain cases where other methods present difficulties, and yields results but little inferior to those given by the nitrometer process, but is unsuitable for use in presence of salts of bismuth or other metals which yield insoluble oxychlorides. In aqueous solution 1/100,000 of nitric acid can be detected, and in acetic acid, 1/500.

Cinchonamine, $C_{19}H_{24}ON_2$, $[\alpha]_D + 120^{\circ}$ in alcohol, does not contain methoxyl. Quinicine, $C_{20}H_{24}O_2N_2$, $[\alpha]_D + 38^{\circ}40'$ in chloroform, yields a

crystalline *tartrate*, $B_2H_2C_4H_4O_6$, and *oxalate*, $2B_2H_2C_2O_4 \cdot 9H_2O$, and contains one methoxyl group. Cinchonine, $C_{19}H_{22}ON_2$, $[\alpha]_D + 47^\circ 13'$, like quinine, could not be obtained crystalline; it does not contain methoxyl. The *tartrate*, $B_2H_2C_4H_4O_6 \cdot H_2O$, and *oxalate*,



are crystalline. Concusconine, $C_{23}H_{26}O_4N_2$, $[\alpha]_D + 19^\circ 34'$, was prepared from cinchonamine residues; it contains two methoxyl groups. Cupreine, $C_{19}H_{22}O_2N_2$, $[\alpha]_D - 163^\circ 45'$ in alcohol, contains no methoxyl. The amorphous *platinichloride*, $B_2H_2PtCl_6 \cdot H_2O$, was prepared, but the salt, $B_2H_2PtCl_6 \cdot 4H_2O$, referred to by L  ger could not be obtained. Cupreine sulphate, $B_2H_2SO_4$, is stated to crystallise with $6H_2O$, but this salt prepared under various conditions was found to be anhydrous. The acid sulphate, $B_2H_2SO_4 \cdot H_2O$, crystallises in short, stout, yellow prisms. The disulphate, $B_2H_2SO_4 \cdot 3H_2O$, forms short, silky needles and is deliquescent. The hydrochloride, $B_2HCl \cdot H_2O$, crystallises in small, slightly brown needles, and the dihydrochloride, B_2HCl , is also crystalline. The formul   assigned to these alkaloids were confirmed by determination of the platinum in the respective platinichlorides.

T. A. H.

Isomerism of Ephedrine and ψ -Ephedrine. HERMANN EMDE (*Arch. Pharm.*, 1909, 247, 54—55).—In a previous paper (*Abstr.*, 1908, i, 203) the author has shown that ephedrine is better represented by the formula $NHMe \cdot CHPh \cdot CHMe \cdot OH$ than by $OH \cdot CHPh \cdot CHMe \cdot NHMe$, and that ψ -ephedrine is an optical isomeride of ephedrine. Gadamer (this vol., i, 49) accepted this, but suggested that the conversion of the one isomeride into the other by the action of hydrochloric acid is probably due to racemisation in the asymmetric complex containing the hydroxyl group, rather than in that containing the methylimino-grouping. The author now points out that this explanation is not excluded by his former paper, and that he left this point as an open question.

T. A. H.

Crystallography of the Ephedrine, Damascenine, and Aconitine Groups. K. SCHWANTKE (*Zeitsch. Kryst. Min.*, 1909, 46, 73—115).— ψ -Ephedrine, rhombic $[a : b : c = 0.84492 : 1 : 1.8598]$. Ephedrine hydriodide, rhombic $[a : b : c = 0.73703 : 1 : 0.28643]$. ψ -Ephedrine hydriodide, rhombic $[a : b : c = 0.60282 : 1 : 1.3722]$. Methylephedrine methiodide, rhombic $[a : b : c = 0.97926 : 1 : 0.76088]$. Methyl- ψ -ephedrine methiodide, rhombic $[0.64227 : 1 : 1.2088]$.

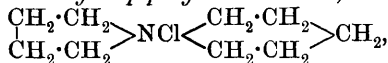
Damascenine hydrochloride, triclinic $[a : b : c = 0.66527 : 1 : 0.45318]$; $\alpha = 89^\circ 51'$; $\beta = 103^\circ 30'$; $\gamma = 89^\circ 11'$; hydrobromide, monoclinic $[a : b : c = 2.7575 : 1 : 2.4825]$; $\beta = 100^\circ 6'$; hydriodide, monoclinic $[a : b : c = 2.7519 : 1 : 2.4372]$; $\beta = 99^\circ 27'$.

Aconitine, rhombic $[a : b : c = 0.54492 : 1 : 0.38917]$; hydrobromide, rhombic $[a : b : c = 0.86455 : 1 : 1.3095]$; hydrochloride, rhombic $[a : b : c = 0.87488 : 1 : 1.3040]$. Picroaconitine could not be obtained crystalline. Methylpicroaconitine, rhombic $[a : b : c = 0.99572 : 1 : 1.31416]$. Ethylpicroaconitine, rhombic $[a : b : c = 0.97952 : 1 : 1.2700]$. Aconine hydrochloride, monoclinic $[a : b : c = 0.63461 : 1 : 1.0374]$; $\beta = 90^\circ$.

L. J. S.

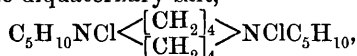
Dicyclic Quaternary Bases. AUGUST ALBERT (*Ber.*, 1909, 42, 545—556).—It has been shown by Gabriel and Colman (*Abstr.*, 1906, i, 881) that when evaporated with water γ -chloropropylpiperidine is transformed into the quaternary salt, and that the reaction is a reversible one. This paper deals with the preparation of a dicyclic quaternary salt containing one more methylene group in one of the rings. 1- δ -Phenoxybutylpiperidine, $\text{OPh} \cdot [\text{CH}_2]_4 \cdot \text{C}_5\text{NH}_{10}$, obtained by heating δ -chlorophenoxybutane with piperidine for four hours at 100° , distils at $316\text{--}320^\circ$. It is purified by means of the hydriodide, $\text{C}_{15}\text{H}_{23}\text{ON} \cdot \text{HI}$, which forms white, feathery needles, m. p. 147° ; the hydrochloride has m. p. 156° , the hydrobromide, m. p. 159° , the picrate, m. p. $120\text{--}121^\circ$, the mercurichloride, m. p. 138° , and the gold salt, m. p. 121° . When the hydrochloride is heated with hydrochloric acid in a sealed tube at 150° for five hours, 1- δ -chlorobutylpiperidine hydrochloride, $\text{CH}_2\text{Cl} \cdot [\text{CH}_2]_3 \cdot \text{C}_5\text{NH}_{10} \cdot \text{HCl}$, is formed quantitatively; it crystallises in white plates from acetone, m. p. 162° ; the aurichloride, $\text{C}_9\text{H}_{19}\text{NCl}_5\text{Au}$, has m. p. 93° , the picrate, m. p. 132° . δ -Bromobutylpiperidine hydrobromide, $\text{C}_9\text{H}_{19}\text{NBr}_2$, prepared in a similar manner, forms plates, m. p. 162.5° .

A cold ethereal solution of δ -chlorobutylpiperidine is quickly converted into tetramethylenepiperylum chloride,

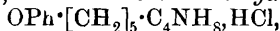


which forms white, hygroscopic leaflets; the aurichloride, $\text{C}_9\text{H}_{18}\text{NCl}_4\text{Au}$, has m. p. 245° , the picrate, $\text{C}_{15}\text{H}_{20}\text{O}_7\text{N}_4$, m. p. 232° , the mercurichloride, $\text{C}_9\text{H}_8\text{NCl}_6\text{HgCl}_2$, m. p. 229° , the platinichloride, m. p. 237° . Alkali converts δ -bromobutylpiperidine hydrobromide at once into the quaternary salt.

That it is not the diquaternary salt,



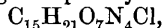
is proved by its synthesis from ϵ -chloropentylpyrrolidine, whereas if diquaternary salts were obtained in such reactions, the isomeric compound, $\text{C}_4\text{H}_8\text{NCl} \left\langle \begin{array}{c} [\text{CH}_2]_5 \\ [\text{CH}_2]_5 \end{array} \right\rangle \text{NClC}_4\text{H}_8$, would be the result. This was accomplished by heating ϵ -chlorophenoxy-pentane with pyrrolidine at 100° for four hours, when ϵ -phenoxy-pentylpyrrolidine, which distils at $317\text{--}318^\circ/760\text{ mm.}$, was obtained. The hydrochloride,



has m. p. 139° , the hydriodide, m. p. 109° , the aurichloride,



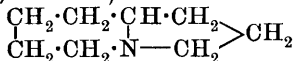
m. p. 109° , and the picrate, m. p. $99\text{--}100^\circ$. ϵ -Chloropentylpyrrolidine forms light yellow, very hygroscopic crystals; the picrate,



and picrolonate have been prepared. The base undergoes in ethereal solution isomeric change into the tetramethylpiperylum chloride. This quaternary salt does not give δ -chlorobutylpiperidine on evaporation of its aqueous solution, thus proving more stable than the trimethylene compound.

W. R

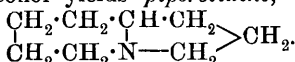
Synthesis of Inactive δ -Coniceine. KARL LÖFFLER and HANS KAIM (*Ber.*, 1909, 42, 94—107).—The constitution



suggested by Lellmann (*Abstr.*, 1890, 1328) for δ -coniceine has been confirmed by direct synthesis.

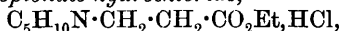
Pyridylacrylic acid (Einhorn, *Abstr.*, 1892, 77), when reduced by Ladenburg's method with sodium and alcohol, yields piperidylpropionic acid, which was isolated in the form of the hydrochloride of the ethyl ester.

The free acid when distilled under reduced pressure yields the lactim, 2-piperolidone, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \\ | \qquad \qquad | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{N} - \text{CO} \end{array} \rangle \text{CH}_2$, which on reduction with sodium and alcohol yields *piperolidine*,



This is identical with inactive δ -coniceine, which was prepared from *i*-coniine by a process similar to that used by Lellmann in the preparation of active δ -coniceine.

Ethyl piperidylpropionate hydrochloride,



crystallises from acetone in glistening, colourless needles, m. p. 122°. The *aurichloride*, $\text{C}_{10}\text{H}_{19}\text{O}_2\text{N} \cdot \text{HAuCl}_4$, forms yellow needles, m. p. 127—128°; the *platinichloride* has m. p. 127—130°. The free *ester* has b. p. 143—144°/21 mm. and D_4^{25} 1.0214, and is hydrolysed by hot hydrochloric acid to the *hydrochloride* of the acid, $\text{C}_8\text{H}_{15}\text{O}_2\text{N} \cdot \text{HCl}$, which melts at 188°. The *aurichloride*, $\text{C}_8\text{H}_{15}\text{O}_2\text{N} \cdot \text{HAuCl}_4$, has m. p. 151°, and the *platinichloride*, 197°. The *acid* crystallises from water in large, rectangular plates containing water of crystallisation. It begins to sinter at 70°, and melts at 105°, or, when anhydrous, at 147—148°.

2-Piperolidone has b. p. 126—127°/12 mm., or 263—264°/760 mm., and D_4^{25} 1.0715. The *hydrochloride* is hygroscopic; the *platinichloride*, $(\text{C}_8\text{H}_{13}\text{ON})_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$, forms large, hexagonal plates, and has m. p. 138°; the *aurichloride* is oily.

Piperolidine has b. p. 161° and D_4^{25} 0.904, and its aqueous solution is strongly alkaline. The *picrate*, $\text{C}_8\text{H}_{15}\text{N} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, has m. p. 226°; the *hydrochloride* is hygroscopic; the *aurichloride* crystallises in compact needles, m. p. 192°, after sintering at 189°; the *platinichloride* melts and decomposes at 213°; the *mercuric* salt has m. p. 235—238°. The *ethiodide* is formed immediately on the addition of ethyl iodide to an ethereal solution of the base, and the corresponding *platinichloride*, $(\text{C}_8\text{H}_{15}\text{NEt})_2 \cdot \text{PtCl}_6$, begins to decompose at 218°, and has m. p. 229—230°.

3-Hydroxy-2-piperolidone, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \\ | \qquad \qquad | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{N} - \text{CO} \end{array} \rangle \text{CH} \cdot \text{OH}$, is obtained

when Einhorn's α -pyridyllactic acid is reduced and the aqueous solution of the resulting acid evaporated. It separates from acetone in colourless crystals, m. p. 129—130°, b. p. 183—184°/18 mm. or

304—305°/760 mm. The *aurichloride*, $C_8H_{13}O_2N, HAuCl_4$, m. p. 89—90°, and the *platinichloride*, $(C_8H_{13}O_2N)_2, H_2PtCl_6$, m. p. 92—94°, are both readily soluble in water. J. J. S.

Synthesis of β -Coniceine (*l*- α -Allylpiperidine). KARL LÖFFLER and GOTTHOLD FRIEDRICH (*Ber.*, 1909, 42, 107—116).—2- β -Hydroxypropylpiperidine (Ladenburg, *Abstr.*, 1890, 68), when heated at 100° with phosphoric oxide, yields a mixture of two isomeric secondary bases, one of these is a solid, m. p. 18°. This can be resolved into active components, the *l*-form of which is identical with β -coniceine (Löffler, *Abstr.*, 1905, i, 917), which is thus shown to be *l*- α -allylpiperidine. The isomeric base, *iso*- α -allylpiperidine, which can be isolated from the alcoholic mother liquors of the picrate of the solid base, can also be resolved into active components by means of the hydrogen tartrates.

2- β -Hydroxypropylpiperidine forms a *picrate*, m. p. 111—112°, a *platinichloride*, m. p. 148—149°, and an *aurichloride*, m. p. 136—137°.

α -Allylpiperidine forms a well-defined *picrate*, $C_8H_{15}N, C_6H_3O_7N_3$, m. p. 113—114·5°. The *hydrochloride*, $C_8H_{15}N, HCl$, crystallises in glistening plates, sparingly soluble in acetone, m. p. 206—207°. The *aurichloride* has m. p. 107—108°, and the *platinichloride*, m. p. 184°. The free base has m. p. 18°, b. p. 168·5—170°/753 mm., and D_4^{25} 0·8716. It readily reduces permanganate, and yields a nitrosoamine with nitrous acid. It combines with hydrogen iodide, and the additive compound when reduced yields *a*-propylpiperidine. The *d*-tartrate of the *d*-base is less soluble than that of the *l*-base; it has m. p. 39° and $[\alpha]_D^{45} + 49\cdot89$.

iso- α -*Allylpiperidine* yields an oily *picrate*. The *hydrochloride*, $C_8H_{15}N, HCl$, has m. p. 186—187°, and is stable when exposed to the air; the *platinichloride* has m. p. 138—139°, and the base has b. p. 166·5—168·5° and D_4^{25} 0·8695. The *d*-hydrogen tartrate,

$C_8H_{15}N, C_4H_6O_6$, has m. p. 70—71°. The base from the tartrate has $[\alpha]_D + 24\cdot81^\circ$ at 15°, and the corresponding *hydrochloride*, m. p. 189—190°. The liquid base, obtained together with β -coniceine by the elimination of water from conhydrine, has $[\alpha]_D - 25\cdot5^\circ$, and its *hydrochloride* has m. p. 189—190°. This base can be partly transformed into β -coniceine by saturating with hydrogen chloride at -16°, heating in sealed tubes at 100° for several hours, and then eliminating hydrogen chloride. When reduced by Ladenburg's method, solid β -coniceine yields *l*-coniine, and this affords a simple method of passing from conhydrine to *l*-coniine. J. J. S.

Constitution of ψ -Conhydrine. KARL LÖFFLER (*Ber.*, 1909, 42, 116—124. Compare Ladenburg and Adam, *Abstr.*, 1891, 1119).— ψ -Conhydrine and conhydrine are readily separated by means of their *hydrochlorides*; the salt derived from conhydrine is extremely hygroscopic, whereas that from the ψ -base crystallises well from alcohol and has m. p. 212—213°. The ψ -base has m. p. 105—106° (not 100—102°), b. p. 236—236·5°, and $\alpha_D + 10\cdot98^\circ$ to $+ 11\cdot06^\circ$. It crystallises from anhy-

drous ether in extremely slender needles, but from moist ether in hydrated plates, m. p. about 80° . Engler and Bauer's statement (Abstr., 1894, i, 471), that ψ -conhydrine can be transformed into conhydrine by simply preparing the gold salt and decomposing this in the usual manner, is not confirmed.

ψ -Conhydrine aurichloride, $C_8H_{17}ON, AuCl_4$, has m. p. $133-134^{\circ}$, and the platinichloride forms slender, golden-yellow needles, m. p. $185-186^{\circ}$.

ψ -Conhydrine is an hydroxyconiine, since when treated with hydriodic acid a ψ -iodoconiine is obtained, which on reduction yields *d*-coniine, whereas conhydrine under similar conditions yields *l*-coniine. Conhydrine and ψ -conhydrine are not stereoisomeric, as the latter yields no trace of β -coniceine or its oily isomeride (compare preceding abstract). Similarly, when the ψ -base is transformed into the iodo-derivative and hydrogen iodide is eliminated from this, no trace of the dicyclic δ -coniceine is formed. It is shown that the hydroxyl group of the ψ -base cannot be present in the side-chain, and must thus be attached to a carbon atom of the nucleus, probably in the γ -position.

The ψ -coniceine, $C_8H_{15}N$, obtained by the action of phosphoric oxide on ψ -conhydrine at $100-120^{\circ}$, has b. p. $171-172^{\circ}$, $D_4^{15} 0.8776$, and $[\alpha]_D + 122.6^{\circ}$ at 15° . It does not dissolve readily in water, decolorises permanganate, and forms a nitrosoamine. Its hydrochloride crystallises from a mixture of alcohol and acetone, and has m. p. $205-206^{\circ}$. The platinichloride has m. p. $153-154^{\circ}$, and the aurichloride is an oil. The iodoconhydrine, obtained by the action of hydriodic acid on ψ -conhydrine, yields a hydriodide, $C_8H_{16}NI, HI$, m. p. $216-217^{\circ}$, whereas the isomeric compound, obtained by the addition of hydrogen iodide to ψ -coniceine, has m. p. 182° .
J. J. S.

ψ -Conhydrine. CARL ENGLER (Ber., 1909, 42, 559. Compare Engler and Bauer, Abstr., 1894, i, 471).—As Löffler (preceding abstract) has shown that Ladenburg and Adam's ψ -conhydrine (Abstr., 1891, i, 1119) is a solid solution of conhydrine and ψ -conhydrine, there is no foundation for the supposed conversion of the pseudo-compound into conhydrine.

W. R.

4-Picolylalkine [4- β -Hydroxyethylpyridine], 4-Pipecolylalkine [4- β -Hydroxyethylpiperidine, and Quinuclidine. KARL LÖFFLER and FRITZ STIETZEL (Ber., 1909, 42, 124-132).—4-Methylpyridine condenses readily with 40% formaldehyde solution, yielding Koenigs and Happe's trimethylol derivative (Abstr., 1903, i, 851), but with a 20% aldehyde solution at $135-140^{\circ}$ it yields the mono-methylol derivative, 4- β -hydroxyethylpyridine, $C_5NH_4 \cdot CH_2 \cdot CH_2 \cdot OH$, as a colourless syrup, $D_4^{15} 1.1016$ and b. p. $125-126^{\circ}/15$ mm. It is most readily purified by means of the picrate, $C_{13}H_{15}O_8N_4$, which forms compact, dark yellow crystals, m. p. $122-123^{\circ}$. The platinichloride forms crystalline plates, m. p. 164° (decomp.), readily soluble in water. The aurichloride has m. p. $124-125^{\circ}$. When heated with hydriodic acid and red phosphorus, 4- β -hydroxyethylpyridine yields the oily iodide, $C_5NH_4 \cdot CH_2 \cdot CH_2I$. The corresponding picrate forms long, refractive prisms, m. p. $108-110^{\circ}$, and the platinichloride forms pale yellow needles, m. p. $147-148^{\circ}$. When warmed, the iodide is readily

transformed into the isomeric *pyridonium iodide*, $\text{C} \begin{array}{c} \diagup \text{CH}-\text{CH} \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \text{CH}=\text{CH} \diagup \end{array} \text{NI}$

(compare Abstr., 1905, i, 265), which crystallises from dilute alcohol in minute, colourless needles, m. p. 216—218°. The corresponding *chloride* forms minute crystals, and the *platinichloride*, $(\text{C}_7\text{H}_8\text{N})_2\text{PtCl}_6$, an insoluble, flesh-coloured precipitate, decomposing at about 300°. It has not been found possible to transform Happe's tri-iodohydrin from the trimethylol derivative into an isomeric pyridonium salt.

4-β-Hydroxyethylpiperidine, $\text{NH} \begin{array}{c} \diagup \text{CH}_2 \cdot \text{CH}_2 \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, obtained by reducing the corresponding pyridine derivative by Ladenburg's method, has b. p. 120—125°/15 mm. or 227—228°/760 mm. and D_4^{25} 1.0059. It has an intense odour of semen. The *aurichloride*, $\text{C}_7\text{H}_{15}\text{ON} \cdot \text{HAuCl}_4$, forms large, compact crystals, m. p. 108—110°; the *picrate* is oily. With hydriodic acid and phosphorus the base yields the *hydriodide*, $\text{C}_7\text{H}_{14}\text{NI} \cdot \text{HI}$, which crystallises from hot water in needles, m. p. 158—159°. The iodo-base is readily transformed

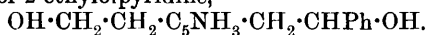
into the *quinuclidine hydriodide*, $\text{CH} \begin{array}{c} \diagup \text{CH}_2 \cdot \text{CH}_2 \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \text{CH}_2 \cdot \text{CH}_2 \diagup \end{array} \text{NHI}$, when its

etheral solution is boiled. The hydriodide forms a colourless syrup readily soluble in water. The *picrate* crystallises in slender, pale yellow needles. The *base*, $\text{C}_7\text{H}_{13}\text{N}$, has b. p. 140—141° and D_4^{23} 0.9139. It does not decolorise permanganate, and forms an *ethiodide*, which is hygroscopic. The *platinichloride*, $(\text{C}_9\text{H}_{18}\text{N})_2\text{PtCl}_6$, has m. p. 212°.

J. J. S.

Condensation of 2:6-Lutidine with Formaldehyde and Derivatives of 2-Methyl-6-methylolpyridine. KARL LÖFFLER and FRITZ THIEL (*Ber.*, 1909, 42, 132—140. Compare Koenigs and Happe, Abstr., 1903, i, 850). 2-Methyl-6-ethylolpyridine distils at 121—122°/12 mm., and has m. p. about 55°. It does not decolorise permanganate, and yields a *picrate* which crystallises in pale yellow needles, m. p. 102—102.5°. The *platinichloride* has m. p. 183—185° (decomp.).

In the preparation of the monohydroxy-derivative an appreciable amount of a *dihydroxy*-compound, $\text{C}_9\text{H}_{13}\text{O}_2\text{N}$, is formed. This crystallises from a mixture of chloroform and ether in colourless prisms, m. p. 73—74.5° and b. p. 185.5—186°/15 mm. The *picrate* crystallises from alcohol in yellow needles, m. p. 133.5—134.5°. The *platinichloride*, $(\text{C}_8\text{H}_{13}\text{O}_2\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$, has m. p. 171—173° (decomp.), and the *aurichloride*, m. p. 141—142°. When oxidised with nitric acid the base yields dipicolinic acid, and hence is presumably 2:6-*diethylolpyridine*. 2-Methyl-6-ethylolpyridine condenses with benzaldehyde at 125—130° yielding a brown oil, the *platinichloride* of which decomposes at 200—206°. This condensation product is probably 6-phenylmethylol-2-ethylolpyridine,



When heated at 125—130° with hydrobromic acid which has been saturated at 0°, the methylethylol derivative yields 2-methyl-6-bromo-

ethylpyridine. The *picrate*, $C_8H_{10}NBr, C_6H_3O_2N_3$, crystallises from benzene in slender prisms, m. p. 111° ; the *platinichloride* separates from water in compact, pointed crystals, m. p. $183-184^\circ$ (decomp.), and the *aurichloride* forms reddish-yellow needles, m. p. $159-162^\circ$ (decomp.). The free base is slowly isomerised to the *pyridonium bromide*, $\begin{array}{c} CH:CH-C-CH_2 \\ | \quad | \quad | \\ CH:CMc-NBr-CH_2 \end{array}$, which crystallises from acetone in snow-white needles, m. p. $155-156^\circ$.

2-Methyl-6-ethylpyridine is obtained when the methyl-bromoethylpyridine is reduced with zinc dust and hydrochloric acid; it is usually accompanied by a certain amount of methylvinylpyridine, which can be removed by treatment with acidified $N/100$ permanganate. The pure methylethyl derivative is a colourless liquid, b. p. $160-161.5^\circ/760$ mm. and $D^{15}_D 0.9229$. The *picrate*, $C_8H_{11}N, C_6H_3O_7N_3$, forms yellow plates, m. p. $127-127.5^\circ$; the *platinichloride*, small crystals, m. p. $188-190^\circ$ (decomp.), and the *aurichloride*, yellow needles, m. p. $127.5-128.5^\circ$.

When reduced by Ladenburg's method, the base yields two stereoisomeric 2-methyl-6-ethylpiperidines, which can be separated by means of their *hydrochlorides*, $C_8H_{17}N, HCl$. Of these, one is sparingly soluble in acetone, and forms long, snow-white needles, m. p. $153.5-154^\circ$.

The corresponding *platinichloride*, $(C_8H_{17}N)_2, H_2PtCl_6$, forms well developed prisms, m. p. $188-190^\circ$, and is readily soluble in water. The *aurichloride* has m. p. 134° , and the *picrate* forms long needles, m. p. 135° . The free base has b. p. $151-151.5^\circ/755$ mm. (corr.) and $D^{14.5}_D 0.8306$. The base can be resolved into its active components by crystallising the acid tartrates. The sparingly soluble *tartrate*, m. p. $58-59^\circ$, gives a base with $[\alpha]^{17.5}_D +13.97^\circ$. The *platinichloride* of the active base decomposes at $204-206^\circ$; the *aurichloride* has m. p. $133.5-134.5^\circ$, and the *hydrochloride*, m. p. $287-288^\circ$.

The *hydrochloride*, which is readily soluble in acetone, forms needles, m. p. $171.5-172.5^\circ$. The *platinichloride* has m. p. $196-197^\circ$, and the base, iso-2-methyl-6-ethylpiperidine, is a colourless liquid, b. p. $157-158^\circ/760$ mm. and $D 0.845$. The *picrate* has m. p. $101.5-102^\circ$, and the *aurichloride* is an oil. The base can be resolved by means of camphorsulphonic acid, but the acid tartrates are syrups. J. J. S.

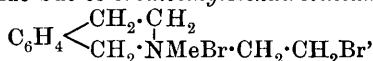
N-Hydroxydioxindole: Trioxindole. GUSTAV HELLER [with JULIUS SÖLLING] (*Ber.*, 1909, 42, 470-479).—Reissert has already prepared *N*-hydroxyindole (*Abstr.*, 1896, i, 389; this vol., i, 51). *N-Hydroxydioxindole* (*trioxindole*), $C_6H_4 \begin{array}{c} \text{CH(ON)} \\ \diagup \quad \diagdown \\ \text{N(OH)} \end{array} \text{CO}$, is obtained when ammonium *o*-nitromandelate is reduced with zinc dust and water in the presence of ammonium chloride and then acidified with hydrochloric acid. It crystallises from water in colourless prisms, sinters at 167° , and melts and decomposes at 172° . The aqueous solution has an acid reaction, gives a blue coloration with ferric chloride, and reduces Fehling's solution in the cold. Alkalis decompose the compound, and in the presence of atmospheric oxygen, anthroxanic acid is formed; if an excess of alkali is present, isatin is also formed.

Trioxindole is converted into *N*-hydroxyisatin when its acetone solution is oxidised with a dilute acetic acid solution of permanganate; acetoxydioxindole under similar conditions yields isatin. Oxidation with a hot alkaline solution of permanganate converts trioxindole into azoxybenzoic acid, and reduction with zinc dust and acetic acid yields isatyd (Heller, Abstr., 1904, i, 516).

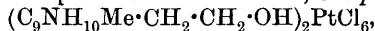
Acetoxydioxindole, $C_{10}H_9O_4N$, crystallises from benzene in prisms, which turn red at 100° and then melt at 125° . Its alkaline solutions deposit salts of isatoic acid when kept, and its aqueous solution yields isatin when boiled. The *N*-benzoyl derivative, $C_8H_6O_3N \cdot CPh$, obtained by the action of benzoyl chloride in the presence of aqueous sodium acetate solution, has m. p. 126° . A different benzoyl derivative is obtained by benzoylating in pyridine solution; it has m. p. 152° .

With hydrazine sulphate and sodium acetate solution the trioxindole yields a compound, $C_8H_9O_2N_3$, m. p. 243° , which is insoluble in alkalis; the mother liquors from the compound yield isatinhydrazone. With phenylhydrazine a compound, $C_{20}H_{17}N_5$, is obtained. It crystallises from alcohol in large, pliable plates, m. p. 226° . *Isatinosazone*, which is isomeric with this compound, crystallises from a mixture of chloroform and light petroleum in slender, reddish-brown needles, m. p. 183° (decomp.). J. J. S.

Asymmetric Nitrogen. XXXV. One-sided Addition of a Tertiary Base to a Dihalogenide. EDGAR WEDEKIND (*Ber.*, 1909, 42, 300—303).—The author attempted to synthesise an optically active compound containing two asymmetric nitrogen atoms. A completely analogous compound to tartaric acid is scarcely possible, but it was hoped to prepare one in which the nitrogen atoms were separated by one or more methylene groups. It was found, however, that interaction of ethylene bromide with *isokairolin* (*N*-methyltetrahydroisoquinoline) does not lead to the formation of ethylenebis-*isokairolinium* bromide but to *bromoethylisokairolinium bromide*,

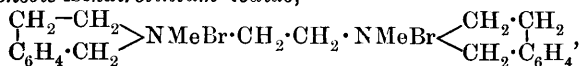


which crystallises from a mixture of alcohol and ether, decomp. 183° . This compound has no further action on *isokairolin*, and this inability to form a further additive compound is ascribed to steric hindrance. The *iodide*, $C_{12}H_{17}NBrI$, readily obtained from potassium iodide and an aqueous solution of the bromide, crystallises from ether, and if the iodide or bromide is shaken with moist silver oxide, neutralised with hydrogen chloride, and platinic chloride added, the *platinichloride*,



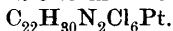
is precipitated. *N*-Ethyltetrahydroisoquinoline has no action on ethylene bromide, and ethylene iodide gives with *isokairolin* an abnormal salt.

Ethylenebis-isokairolinium iodide,



easily obtained from ethylenebistetrahydroisoquinoline (1 mol.) and

methyl iodide (2 mols.), separates from alcohol as a crystalline powder, decomp. 232° , and the free base forms the *platinichloride*,



The dicamphorsulphonate, from the iodide and silver *d*-camphorsulphonate in moist acetone, could not be resolved into fractions of differing rotatory power, and the regenerated iodide is inactive. W. R.

5-Methylisooxazole. LUDWIG CLAISEN (*Ber.*, 1909, 42, 59—68).—The substance b. p. $103\text{--}105^{\circ}/20$ mm., obtained by Schmidt and Widmann (*Abstr.*, 1908, i, 456), and designated 5-methylisooxazole, cannot be such. The author has already prepared 5-methylisooxazole, b. p. 122° or $29\text{--}30^{\circ}/20$ mm. (*Abstr.*, 1892, 1072). In the isooxazoles, as in other homologous series, the b. p. of the methyl derivative must lie between those of the parent substance and of the dimethyl derivative. *isooxazole* has b. p. 95.5° , and dimethylisooxazole, $141\text{--}142^{\circ}$. A substance of b. p. $103\text{--}105^{\circ}/20$ mm. would have b. p. above 200° under atmospheric pressure, and consequently cannot be a methylisooxazole. Moreover, Schmidt and Widmann's substance does not possess the unpleasant odour of pyridine which is so characteristic of the lower isooxazoles.

The author contributes the following new properties in connexion with the methylisooxazoles. The sesquioxime, $\text{C}_8\text{H}_{13}\text{O}_3\text{N}_3$, obtained previously (*Abstr.*, 1891, 416), is decomposed by warm *N*/2-hydrochloric acid, yielding pure 5-methylisooxazole, whilst with concentrated hydrochloric acid a mixture is obtained of 80% of 3-methylisooxazole and 20% of 5-methylisooxazole, from which the latter is easily removed by treatment with sodium ethoxide (*Abstr.*, 1904, i, 14).

5-Methylisooxazole, in aqueous-alcoholic solution, forms with platinic chloride a yellow, crystalline compound, $(\text{C}_4\text{H}_5\text{ON})_2\text{PtCl}_4$, m. p. $210\text{--}212^{\circ}$, and a white, crystalline mercurichloride, $\text{C}_4\text{H}_5\text{ON}, \text{HgCl}_2$, and cadmichloride, $\text{C}_4\text{H}_5\text{ON}, \text{CdCl}_2$, with aqueous mercuric and cadmium chlorides respectively. In dilute aqueous potassium hydroxide, 5-methylisooxazole forms a clear solution of potassium cyanoacetone, from which phenylhydrazine hydrochloride precipitates cyanoacetone-phenylhydrazone. Sodium cyanoacetone is obtained quantitatively as a white, crystalline precipitate by adding alcoholic sodium ethoxide to a dilute ethereal solution of 5-methylisooxazole, and in aqueous-alcoholic solution yields with diazobenzene chloride a yellow, crystalline phenylazocycanoacetone, and with aniline hydrochloride, cyanoacetoneanilide. 5-Methylisooxazole yields β -iminobutyronitrile by heating at 100° with alcoholic ammonia; 5-amino-1-phenyl-3-methylpyrazole by prolonged heating with phenylhydrazine, and with methyl iodide at 100° a methyl iodide, $\text{C}_4\text{H}_5\text{ONMeI}$, m. p. $125\text{--}126^{\circ}$, which in cold aqueous solution is converted by silver oxide into acetoacetylmethylamide, the *N*-benzoyl derivative of which, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NMeBz}$, m. p. 107° , is obtained by slowly warming 5-methylisooxazole and methyl sulphate at 70° , pouring the product into water, and adding a solution of potassium benzoate.

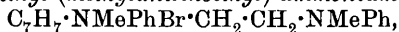
The preceding reactions are quoted by the author as additional evidence for the correctness of the constitution of his 5-methylisooxazole. C. S.

Asymmetric Nitrogen. XXXVI. Quaternary Amino-ammonium Salts, a New Type of Asymmetric Nitrogen.

EDGAR WEDEKIND and WOLDEMAR MEYER (*Ber.*, 1909, 42, 303—309).

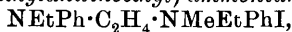
—The result of the experiments on *isokairoline* (this vol., i, 184) lead to the examination of other ditertiary bases with regard to their additional activity towards alkyl haloids. The type employed was $\text{Ph} \begin{smallmatrix} > \\ \alpha \end{smallmatrix} \text{N} \cdot [\text{CH}_2]_x \cdot \text{N} \begin{smallmatrix} < \\ \alpha \end{smallmatrix} \text{Ph}$; when $x=2$ and α is Et, benzyl bromide gives no additive compound; when $x=3$ and α is Me, then benzyl bromide is quickly taken up by both tertiary nitrogen atoms; if $x=2$ and α is Me, then only one molecule of benzyl bromide is absorbed to form a monoquaternary salt. An analogous amino-ammonium salt is formed from diphenyldimethylethylenediamine and methyl iodide; the diquaternary salt can be obtained indirectly, however, by the action of methyl sulphate and subsequent conversion of the methyl sulphate salt into di-iodide. The diquaternary or the amino-ammonium salt can be obtained from allyl iodide and diphenyldimethylpropylenediamine according to the conditions. The conclusion is drawn that the inability to form diquaternary salts in the case of dimethylene compounds is due to steric hindrance (*loc. cit.*), and that the lengthening of the chain to three methylene groups enables the latent additive activity of the other nitrogen atom to become operative. The high molecular rotatory power of the amino-ammonium salts examined is in accordance with their high degree of asymmetry.

Phenylbenzylmethyl-(methylanilinoethyl)-ammonium bromide,



from diphenyldimethylethylenediamine and benzyl bromide, is obtained in 59% yield, and is crystallised from acetone containing a little alcohol, decomp. 119—139°. Once with excess of bromide a *dibromide*, $\text{C}_{30}\text{H}_{34}\text{N}_2\text{Br}_2$, was formed, decomp. 124—125°. The amino-ammonium compound is very easily resolved into its optical antipodes, as the solubility of the *l*-base-*d*-camphorsulphonate in methyl alcohol is very much less than the *d*-compound. The extreme $[\text{M}]_D$ of the fractions for the ions were -442° and $+417^\circ$. The two camphorsulphonates form snow-white needles, decomp. 125°. The *d*-base-*d*-bromocamphorsulphonate is the less soluble salt when the bromo-compound is used. The *l*-amino ammonium *iodide*, $\text{C}_{23}\text{H}_{27}\text{N}_2\text{I}$, forms rhombic plates, decomp. 115°, $[\text{M}]_D -411.5^\circ$ in alcohol and $[\text{M}]_D -424.6^\circ$ in chloroform. The *d*-*iodide* has $[\text{M}]_D +403.2^\circ$ in alcohol, and undergoes autoracemisation in solution; the velocity constant in 50% alcohol-chloroform solution is $K=0.00024$, and in 96% alcohol, $K=0.000033$. The rate is, therefore, much slower in alcohol than in chloroform, but that it takes place in alcohol which has a high dielectric constant is surprising in the light of Wedekind and Paschke's work (*Abstr.*, 1908, i, 722). As benzyl bromide can be detected in the inactive solution, the conclusion drawn previously, that racemisation is due to decomposition and not to intramolecular change, is supported.

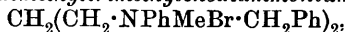
Phenylmethyllethyl-(ethylanilinoethyl)-ammonium iodide,



obtained from diphenyldiethylethylenediamine and methyl iodide in a closed tube heated at 80° for six hours, crystallises from ether, decomp.

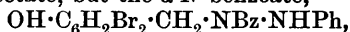
180°, and the symmetrical compound, $C_2H_4(NPhMeEtI)_2$, from diphenyl-diethylethylenediamine and methyl sulphate at 120° and precipitation by potassium iodide, is yellow, decomp. 119—120°.

Diphenyldibenzyltrimethyltrimethylenediammonium dibromide,



forms colourless crystals, decomp. 195—197°. The dicamphor-sulphonate is well characterised. W. R.

Migration and Reciprocal Displacement of Acid Groups in Acylated Dibromohydroxybenzylphenylhydrazines. KARL AUWERS (*Ber.*, 1909, 42, 267—277).—An extension of the inquiry (*Abstr.*, 1908, i, 458). It has been shown that treatment of the dibromo- α -*N*-acetyl-*o*-benzoxylbenzylphenylhydrazine, $OBz \cdot C_6H_2Br_2 \cdot CH_2 \cdot NAc \cdot NHPh$, with alcoholic potash does not yield the expected α -*N*-acetate, but the α -*N*-benzoate,



whether the hydrolysis is carried out with excess of alkali or not, or in the warm or in the cold. The *O*-radicle is usually the first to be split off, and this may then displace the acetyl group from its position, or the rule is reversed in this case, the *N*-acetyl being first hydrolysed with subsequent migration of the benzoyl group. It is, however, to be noted in this connexion that the *N*-acetates, α and β , are very stable towards alkalis (10%), whereas the *NN*-diacetate and *ONN*-triacetate give the α -*N*-acetate with a 1% alcoholic solution of potassium hydroxide; further, one molecular equivalent of alkali with the triacetate does not give the *NN*-diacetyl compound—a portion of the compound is not attacked, the remainder being hydrolysed to α -*N*-acetate.

With other esters the behaviour is quite otherwise, the *O*-propionyl- α -*N*-acetyl compound on partial hydrolysis with aniline gives α -*N*-acetate and propionanilide; alcohol potassium hydroxide giving, however, α -*N*-propionate and acetanilide. The *O*-acetyl- α -*N*-propionyl derivative is hydrolysed to α -*N*-propionate in the normal manner.

The question of whether it is the greater mass of the migratory group which displaces the other acyl radicle, or whether it depends on the space occupied by the groups, was also examined, but the results so far obtained have been meagre. The reactivity of phenylhydrazine is largely decreased by the introduction of heavy acyl groups, and *s*-benzoyl or heptoylphenylhydrazide do not react with dibromo-*o*-hydroxybenzyl bromide or its esters under ordinary conditions. Indirect methods of preparing these α -*N*-derivatives from phenylhydrazine and the corresponding ester of the bromide, whereby subsequent intramolecular change would be induced, have led to mixtures which could not be separated. The crude product, however, obtained by benzylation of the α -*N*-heptoate, on hydrolysis gave the α -*N*-benzoate, so that it would appear that the heptoyl radicle containing the same number of carbon atoms as the benzoyl group is nevertheless displaced by it.

The formyl compounds are distinguished by the easy displacement

of the formyl group; thus the action of *s*-formylphenylhydrazide and dibromobenzoxymethyl bromide leads to the formation of the α -*N*-benzoate, and an analogous result is obtained with the acetoxy-compound.

[With HUGO DANNEHL and K. MÜLLER.]—*s*-Phenyldibromo-*o*-hydroxybenzyl- α -*N*-formylhydrazine, $C_{14}H_{12}O_2N_2Br_2$, prepared by heating 2 mols. of *s*-formylphenylhydrazide with 1 mol. of dibromo-*o*-hydroxybenzyl bromide in benzene solution, crystallises from alcohol in colourless crystals, m. p. 164—165°. The α -*N*-formyl-*O*- β -*N*-diacetyl derivative, $C_{18}H_{16}O_4N_2Br_2$, is a yellow, amorphous powder, which on hydrolysis yields the α -*N*-acetate. The *O*-benzoyl- α -*N*-formyl derivative, $C_{21}H_{16}O_3N_2Br_2$, crystallises from alcohol in very slender, white needles, m. p. 154° (decomp.). The *O*-acetyl- α -*N*-propionyl derivative, $C_{18}H_{18}O_3N_2Br_2$, crystallises from alcohol in glistening leaflets, m. p. 173—174°, and is not dissolved by aqueous alkali, showing that under these conditions migration of the acetyl group to the β -*N* does not occur. The α -*N*-propionyl-*O*-benzoate, $C_{22}H_{20}O_3N_2Br_2$, forms colourless needles, m. p. 176—177°, and on hydrolysis yields the α -*N*-benzoate.

The heptoate of dibromo-*o*-hydroxybenzyl bromide, $C_{14}H_{17}O_2Br_3$, prepared by heating the bromide with heptoyl chloride for three hours at 160°, crystallises from methyl alcohol in silken needles, m. p. 41°. The α -*N*-heptoate forms slender needles, m. p. 146—148°, and is soluble in aqueous alkali.

W. R.

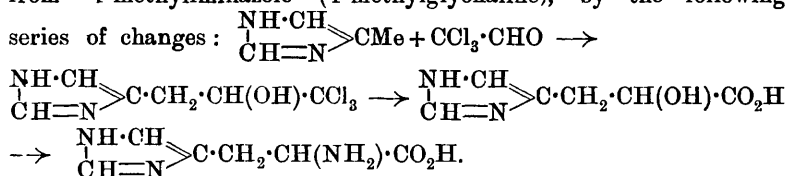
Transformation of Azines into Hydrazones. GUSTAV KNÖFFER (*Monatsh.*, 1909, 30, 29—38).—The results of the author's investigation of the behaviour of aldazines and ketazines towards phenylhydrazine show that all these azines are converted by this means into the corresponding hydrazones (compare Fulda, Abstr., 1903, i, 199; Ofter, Abstr., 1904, i, 818; Ott, Abstr., 1905, i, 376; Fürth, Abstr., 1907, i, 61). That the transformation, which takes place according to the equation: $CHR:N:N:CHR + 2NHPh \cdot NH_2 = 2CHR:N \cdot NHPh + N_2H_4$, is not a consequence of the mass action of the reagent is shown by the fact that the reacting substances were taken in approximately theoretical proportions, the conversion of the azine being practically complete. The azine, suspended in alcohol (or acetic acid), was heated with phenylhydrazine in a reflux apparatus until complete solution occurred. The following azines of aldehydes and ketones giving azines and hydrazones which are readily identified were employed.

(1) Benzaldazine. (2) Salicyldaldazine. (3) Anisaldazine. (4) Cinnamaldazine. (5) Cuminaldazine. (6) Furfuraldazine. (7) *p*-Hydroxybenzaldazine. (8) Vanillaldazine. (9) Piperonalazine. (10) *p*-, (11) *o*-, and (12) *m*-nitrobenzaldazines. (13) *p*-Dimethylaminobenzaldazine. (14) Protocatechualdazine, $C_{14}H_{12}O_4N_2$, decomp. about 245°, which is readily soluble in alcohol. (15) Resorcyldaldazine, $C_{14}H_{12}O_4N_2$, which does not melt at 310°. (16) Methylphenylketazine. (17) Methyl-*m*-nitrophenylketazine, $C_{16}H_{14}O_4N_4$, m. p. 194—195°. (18) Methyl-*p*-aminophenylketazine, $C_{16}H_{18}N_4$, which forms heavy, yellow crystals, m. p. 166°, and dissolves readily in alcohol. (19) Benzylideneacetazine, $C_{20}H_{20}N_2$, which forms yellow crystals, m. p. 160°, and with phenyl-

hydrazine yields benzylideneacetonephenylhydrazone, m. p. 159° (Fischer, Abstr., 1884, 1150, found 157°). T. H. P.

The Azoxine Analogue of apoSafranine. FRIEDRICH KEHRMANN and WERNER GRESLY (*Ber.*, 1909, 42, 347—349).—The azoxine analogue of *aposafranine* and of *apothionine* has been prepared by eliminating an amino-group from diaminophenazonium chloride (Abstr., 1903, i, 279) in the usual way, and has been isolated as the dark red, crystalline *platinichloride*, $(C_{12}H_9ON_2)_2PtCl_6$. The *chloride* and impure *nitrate* have been prepared. C. S.

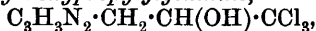
Experiments on the Synthesis of Histidine. OTTO GERNGROSS (*Ber.*, 1909, 42, 398—405).—The object of this investigation was the synthesis of histidine, which it was proposed to effect, starting from 4-methyliminazole (4-methylglyoxaline), by the following



The condensation product of 4-methylglyoxaline with chloral when hydrolysed with an aqueous alcoholic solution of sodium hydroxide yields, however, α -methoxyglyoxaline-4-propionic acid, which has not yet been converted into histidine.

2-Methylquinoline and chloral when mixed form an *additive* product, $C_{12}H_{10}ONCl_3\cdot H_2O$, which crystallises in large, glistening cubes and prisms, sinters at 56°, m. p. 63°, and dissociates into its components when kept or when dissolved in water. 4-Methylglyoxaline and chloral form a similar *additive* product, $C_6H_7ON_2Cl_3$, which crystallises in rosettes of hexagonal plates, sinters at 116°, and has m. p. 123° (decomp.).

4- $\gamma\gamma\gamma$ -Trichloro- β -hydroxypropylglyoxaline,



is prepared by heating 4-methylglyoxaline with chloral for forty-two hours at 78—80°; it crystallises in prisms, m. p. 195° (decomp.); the *hydrochloride*, $C_6H_8ON_2Cl_4$, forms stellate groups of crystals, and decomposes between 230—260°; the *nitrate* forms large, colourless, glistening prisms, decomposing above 195°; the *oxalate* forms rosettes of prisms. The base is converted by sodium hydroxide in aqueous methyl alcohol at 25° into α -methoxyglyoxaline-4-propionic acid, which crystallises in rectangular plates, turns yellow at 210°, and decomposes at 221°; the *hydrochloride*, $C_7H_{10}O_3N_2\cdot HCl$, forms small needles, sinters at 170°, and decomposes at 172°. The *methyl ester hydrochloride*, $C_8H_{12}O_3N_2\cdot HCl$, prepared by the action of hydrogen chloride on a solution of the acid in methyl alcohol, forms silky needles, which become orange-yellow at 173° and have m. p. 185° (decomp.).

α -Chloroglyoxaline-4-propionic acid, prepared from histidine by the

method of Windaus and Vogt (*Beitr. chem. Physiol. Path.*, 1907, 9, 406), has m. p. 191° and yields a *methyl ester hydrochloride*,



crystallising in large, thin, glistening plates, m. p. 140° . W. H. G.

Isatoic Anhydride (Anthranilcarboxylic Acid). ERNST MOHR (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1907, ii, 96—97).—Isatoic anhydride dissolves in an excess of cold sodium or barium hydroxide; the clear solution yields sodium or barium carbonate and anthranilate when boiled. Isatoic anhydride dissolves in water containing an equal molecular quantity of sodium hydroxide, forming a solution which probably contains the sodium derivative, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}-\text{O} \\ \diagup \quad \diagdown \\ \text{NNa} \cdot \text{CO} \end{smallmatrix}$ or $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{N}=\text{C}\cdot\text{ONa} \end{smallmatrix}$, precipitates a corresponding barium derivative on the addition of barium chloride, and regenerates isatoic anhydride when acidified. After a short time, the solution deposits isatoic anhydride, and under certain conditions contains sodium anthranoyl-anthranilate, due to the action of the anhydride or its sodium derivative on the sodium anthranilate produced. Similarly, isatoic anhydride reacts with glycine to form *o*-aminohippuric acid. C. S.

Action of Hydriodic Acid and of Iodine on Dimethylamino-antipyrine (Pyramidone). HENRI COUSIN (*Bull. Soc. chim.*, 1909, [vi], 5, 121—124; *J. Pharm. Chim.*, 1909, [vi], 29, 49—54).—Hydriodic acid acts on pyramidone, forming the *iodide*, $\text{C}_{13}\text{H}_{17}\text{ON}_3\cdot\text{HI}$, colourless prisms, m. p., indistinct, above 200° (decomp.). When iodine is added to this salt, or to the free base in alcoholic solution, the *periodide*, $\text{C}_{13}\text{H}_{17}\text{ON}_3\cdot\text{HI}\cdot\text{I}_2$, is obtained as brown needles insoluble in water. G. B.

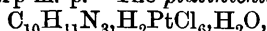
5-Amino-1-phenyl-3-methylpyrazole. ERNST MOHR [and, in part, LUDWIG SCHMIDT] (*J. pr. Chem.*, 1909, [ii], 79, 1—49).—A continuation of the researches of von Walther (*Abstr.*, 1897, i, 297). Many of the compounds described in this paper have already been investigated (compare Michaelis, *Abstr.*, 1905, i, 476; Michaelis and Klopstock, *Abstr.*, 1907, i, 735). The cyanoacetonephenyl-hydrazone, prepared by the interaction of β -aminocrotononitrile and phenylhydrazine in dilute acetic acid, has m. p. 99 — 100° (compare Burns, *Abstr.*, 1893, i, 314; von Walther, *loc. cit.*). The product obtained when the two substances are heated together, or in alcoholic solution, has m. p. 88 — 94° , and dissolves in cold concentrated sulphuric acid, forming an intense blood-red solution; the substance m. p. 99 — 100° does not give an intense coloration; these differences cannot yet be explained. Both substances when warmed with dilute hydrochloric acid at about 55° yield 5-amino-1-phenyl-3-methylpyrazole. The latter compound appears to react both as an iminopyrazolone, $\text{N}\begin{smallmatrix} \text{CMe}\cdot\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{NPh}\cdot\text{C}\cdot\text{NH} \end{smallmatrix}$, and as an aminopyrazole, $\text{N}\begin{smallmatrix} \text{CMe}\cdot\text{CH} \\ \diagup \quad \diagdown \\ \text{NPh}\cdot\text{C}\cdot\text{NH}_2 \end{smallmatrix}$, for when it is treated with sodium nitrite and

dilute hydrochloric acid it yields 4-oximino-5-imino-1-phenyl-3-methylpyrazolone (compare von Walther, *loc. cit.*) and 5-diazo-1-phenyl-3-methylpyrazole chloride; the presence of the latter in the solution is shown by the formation of an azo-dye on the addition of an alkaline solution of β -naphthol.

4-Oximino-5-imino-1-phenyl-3-methylpyrazolone appears to behave as a tautomeric substance, represented by the formulæ $\text{N} \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{NO} \\ \text{NPh} \cdot \text{C} \cdot \text{NH}_2 \end{smallmatrix}$

and $\text{N} \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{N} \cdot \text{OH} \\ \text{NPh} \cdot \text{C} \cdot \text{NH} \end{smallmatrix}$; thus it reacts both as an acid and as a base; the solid substance is bright red, the molten substance is dark green; the dilute solutions in indifferent solvents are sky-blue, the alcoholic solution is reddish-violet.

5-Amino-1-phenyl-3-methylpyrazole hydrochloride, when crystallised from hot dilute hydrochloric acid, forms long, white needles; it contains water and hydrogen chloride in a loose state of combination, and does not give a sharp m. p. The *platinichloride*,



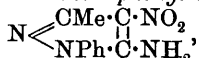
crystallises in slender, reddish-yellow needles, m. p. 169° , which when kept in the mother liquor change into compact, orange-red prisms, m. p. $176-178^\circ$ (decomp.).

1-Phenyl-3-methylpyrazole-5-azo- β -naphthol, $\text{C}_{20}\text{H}_{16}\text{ON}_4$, crystallises in glistening, bright red, microscopic needles, m. p. $209-210^\circ$.

During the preparation of 4-oximino-5-imino-1-phenyl-3-methylpyrazolone, a by-product was obtained, which is possibly 5-imino-1-phenyl-3-methyl-4:5-pyrazoquinone, $\text{N} \begin{smallmatrix} \text{CMe} \cdot \text{CO} \\ \text{NPh} \cdot \text{C} \cdot \text{NH} \end{smallmatrix}$; it crystallises in aggregates of lemon-yellow needles, m. p. $133-134^\circ$.

4:5-Diamino-1-phenyl-3-methylpyrazole condenses with benzil, yielding triphenylmethylpyrazopyrazine, $\text{N} \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{N} \cdot \text{CPh} \\ \text{NPh} \cdot \text{C} \cdot \text{N} \cdot \text{CPh} \end{smallmatrix}$, which crystallises in very pale lemon-yellow needles, m. p. 190° .

4-Oximino-5-imino-1-phenyl-3-methylpyrazolone is converted by an alkaline solution of potassium hypochlorite into 1-phenyl-3-methyl-4:5-pyrazoquinonedioxime anhydride, $\text{N} \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{N} \\ \text{NPh} \cdot \text{C} \cdot \text{N} \end{smallmatrix} > \text{O}$, straw-yellow plates, m. p. $94-95^\circ$, and by potassium permanganate in dilute sulphuric acid into 4-nitro-5-amino-1-phenyl-3-methylpyrazole,

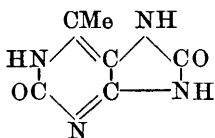


a yellowish-brown powder, m. p. $167-168^\circ$.

W. H. G.

Pyrimidines. XLI. Formation of Purine Derivatives from 4-Methylcytosine. CARL O. JOHNS (*Amer. Chem. J.*, 1909, 41, 58-65. Compare Abstr., 1908, i, 917).—When 2-oxy-6-amino-4-methylpyrimidine (4-methylcytosine) is nitrated in presence of sulphuric acid, an almost quantitative yield of 5-nitro-4-methylcytosine, $\text{N} \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{C}(\text{NH}_2) \cdot \text{C}(\text{NO}_2) \end{smallmatrix} \text{CMe}$, is obtained; it crystallises from water in

small, yellow prisms, decomp. 260—280°. The position of the nitro-group is shown by the formation of Behrend's 5-nitro-4-methyluracil when it is heated with 30% sulphuric acid in a sealed tube. When treated in a similar manner with 20% acid, cytosine and nitrocytosine give respectively uracil and nitrouracil. Attempted reduction of 5-nitro-4-methylcytosine by means of ammonium sulphide regenerated 4-methylcytosine, but aluminium amalgam reduces it to 5:6-diamino-2-oxy-4-methylpyrimidine, $\text{N} \begin{array}{c} \text{CO} \text{---} \text{NH} \\ \text{C}(\text{NH}_2) \cdot \text{C}(\text{NH}_2) \end{array} \text{CMe}$, crystallising

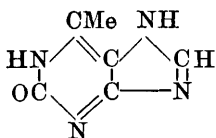


from water in long prisms containing 1 mol. H_2O , which do not melt, but decomp. at 280—285°; the picrate, decomp. 240°.

5:6-Diamino-2-oxy-4-methylpyrimidine condenses with carbamide when the anhydrous substances are heated together at 170—180°, giving 2:8-dioxy-6-methylpurine (annexed formula),

forming small, sparingly soluble crystals that do not melt below 345°.

This compound is the last of the three possible dioxypurines to be prepared. In a similar manner, by condensing with thiocarbamide, 2-oxy-8-thio-6-methylpurine is obtained; it is an almost insoluble, crystalline powder, not melting below 345°.



5:6-Diamino-2-oxy-4-methylpyrimidine when heated with formic acid yields the *monoformyl* compound, $\text{C}_5\text{H}_7\text{ON}_4\text{CHO}$, which forms minute crystals from hot water solutions, not melting below 345°. This substance gives a white, crystalline sodium salt, which loses water vigorously at 200°, leaving a porous mass, 2-oxy-6-methyl-

purine (annexed formula), readily soluble in water, crystallising therefrom in slender prisms, not melting, but decomp. at 300—345°.

J. V. E.

Synthesis of 1-Methylxanthine. MAX ENGELMANN (*Ber.*, 1909, 42, 177—182).—1-Methylxanthine was first isolated from human urine by Krüger and Salomon (*Abstr.*, 1898, i, 699). Since it had not been synthesised hitherto, the author has effected this, starting from cyanamide and methyl alcohol. Methylisocarbamide (methyl imino-carbimate), prepared from cyanamide and methyl alcohol (compare Stieglitz and McKee, *Abstr.*, 1900, i, 340), condenses with ethyl cyanoacetate in the presence of sodium ethoxide, forming 4-imino-6-oxy-2-methoxydihydropyrimidine, $\text{NH} \begin{array}{c} \text{C}(\text{OMe}) \text{:} \text{N} \\ \text{CO} \text{---} \text{CH}_2 \end{array} \text{C:NH}$, a crystalline substance, m. p. 214—216°, which, when treated with methyl sulphate and aqueous sodium hydroxide, yields 4-imino-6-oxy-2-methoxy-1-methyldihydropyrimidine, $\text{C}_6\text{H}_9\text{O}_2\text{N}_3$, colourless crystals, m. p. 206—208°. The latter substance is converted by sodium nitrite and acetic acid into 5-oximino-4-imino-6-oxy-2-methoxy-1-methyldihydropyrimidine, small, violet needles, m. p. about 145° (decomp.), which, when reduced with ammonium sulphide, yields 4:5-diamino-6-oxy-2-methoxy-1-methylpyrimidine, crystallising in needles, m. p. 160°. The latter substance is converted by hot concentrated hydrochloric acid

into 4:5-diamino-2:6-dioxy-1-methylpyrimidine, the hydrochloride of which, when heated with sodium formate and formic acid at 100° , yields 5-formylamino-4-amino-2:6-dioxy-1-methylpyrimidine, crystallising in needles which do not melt at 300° ; the crystalline sodium salt, when heated at 230 – 240° , liberates H_2O , with the formation of 1-methyl-xanthine.

W. H. G.

Action of Unsymmetrical Benzoylphenylhydrazine on *o*-Benzoquinone. WILLIAM MCPHERSON and H. J. LUCAS (*J. Amer. Chem. Soc.*, 1909, 31, 281–284).—It has been shown in earlier papers (Abstr., 1896, i, 127; 1900, i, 411; 1901, i, 572) that unsymmetrical acylphenylhydrazines react with *p*-benzoquinone to form hydrazones of the general formula $\text{O}:\text{R}:\text{N}:\text{N}:\text{AcR}'$. Willstätter and Veraguth (Abstr., 1907, i, 453) have found that, under certain conditions, these hydrazones readily undergo a rearrangement into the isomeric hydroxyazo-compounds, $\text{OAc}:\text{R}:\text{N}:\text{NR}'$, in which the acyl group is attached to the oxygen atom.

By the action of α -benzoylphenylhydrazine on *o*-benzoquinone, *o*-benzoxiazobenzene, $\text{OBz}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{NPh}$, is produced. It is probable that in this reaction the hydrazone, $\text{O}:\text{C}_6\text{H}_4\cdot\text{N}:\text{NBzPh}$, is formed first, and instantly undergoes rearrangement. *o*-Benzoxiazobenzene, m. p. 93° , crystallises in orange needles or plates, and on hydrolysis yields *o*-hydroxyazobenzene (Bamberger, Abstr., 1900, i, 531), which on benzoylation is re-converted in the original substance.

α -Benzoylphenylhydrazine reacts with tetrachloro-*o*-quinone with formation of the compound $\text{C}_6\text{Cl}_3\text{O}_2\cdot\text{NH}:\text{NBzPh}$.

E. G.

Mechanism of Coupling Reactions. HANS TH. BUCHERER (*Ber.*, 1909, 42, 47–49. Compare Dimroth and Hartmann, this vol., i, 66).—The author and Sonnenburg have found that 2-naphthol-1-sulphonic acid couples with diazotised *p*-nitroaniline in sodium acetate solution to form *p*-nitrobenzene-azo- β -naphthol, whilst in sodium carbonate solution the product of coupling is an easily soluble substance, which readily changes to the preceding compound, and is regarded as an *O*-azo-derivative, $\text{SO}_3\text{Na}\cdot\text{C}_{10}\text{H}_6\cdot\text{O}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$.

O-Azo-compounds have also been obtained from α -naphthol-6:8-disulphonic acid or salicylic acid and diazotised naphthionic acid or diazotised aniline; these compounds readily change to ordinary *o*- or *p*-hydroxyazo-compounds.

C. S.

Decomposition of Diazo-solutions. CARL G. SCHWALBE (*Ber.*, 1909, 42, 196–199. Compare Abstr., 1905, i, 618, 843).—Polemical. Mainly a reply to Cain (this vol., i, 70). Emphasis is laid on the fact that the author studied the rates of decomposition of diazo-solutions as prepared technically. The quantity of nitrous acid present in such solutions is sufficient to produce an increase in the velocity of decomposition.

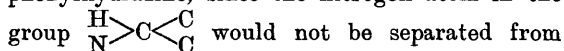
W. H. G.

Cain's Theory of Diazonium and Ammonium Salts. ARTHUR HANTZSCH (*Ber.*, 1909, 42, 394–398. Compare Abstr., 1908, i, 1021).—Polemical. A further reply to Cain (this vol., i, 70). The chief

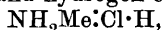
points raised are as follows: (1) Comparison of the instability of the C_6 -ring in benzoquinone towards halogens, hydrogen chloride, mild oxidising agents, etc., with the stability of the benzene nucleus in diazonium salts towards these reagents, shows that these two classes of compounds do not contain the same C_6 -ring as represented by Cain's formula; (2) contrary to Cain's statement, the double linking in the group $-N:N-$ is readily resolved by mild reducing agents, as



in the conversion of azobenzene into hydrazobenzene. A compound having the annexed formula would yield on reduction a diamine and not phenylhydrazine, since the nitrogen atom in the



the carbon atom by mild reducing agents; (3) it does not necessarily follow from the non-existence of aliphatic diazonium salts that the presence of the benzene nucleus is essential for the formation of diazonium salts. The stability of the latter is greatly influenced by substitution in the benzene ring, and it is not remarkable that the compound resulting from the total replacement of the benzene nucleus by an alkyl group decomposes spontaneously; (4) the process of ionisation of ammonium salts in the manner represented by Cain is very improbable, since in the case of trimethylethylammonium hydroxide and the corresponding nitrate, dissociated ethyl alcohol and ethyl nitrate would be formed intermediately; ethyl nitrate does not, however, form ions. Further, if the addition of alkyl halides to amines takes place thus: $R_3N + ClR \rightarrow R_3N:Cl \cdot R$, then the compound formed from methylamine and hydrogen chloride, namely,



should be isomeric with that derived from ammonia and methyl chloride, namely, $NH_3:Cl \cdot Me$.

W. H. G.

Change of Colour in Additive Reactions. DANIEL VORLÄNDER (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1907, ii, 91).—The salts of aminoazo-compounds and acids may be regarded as additive compounds or as ammonium salts. If the latter is correct, azobenzene-trimethylammonium chloride should be red; this is not the case, the azo-ammonium ion being orange-yellow, like azobenzene and aminoazobenzene.

Solutions of hydrogen chloride or bromide in benzene, carbon tetrachloride, or chloroform immediately colour dimethylaminoazobenzene. Moreover, dimethylaminoazobenzene and *p*-methoxydimethylaminoazobenzene form dark red, conducting solutions in dry, liquid sulphur dioxide, whereas the solution of aminoazobenzene is yellow and non-conducting. An additive compound with sulphur dioxide is probably formed in the former, but not in the latter, case. The author draws the conclusion that the colour of the compounds of aminoazobenzenes and acids is conditioned by an additive relation between the amine and the acid. The cause of the different colour of the acid derivatives and of the quaternary ammonium salts is attributed to the fact that, in the former, the union of the constituents is loose and of the nature

of that of a double salt, whilst in the case of the ammonium derivatives the constituents are more intimately united, as in complex salts.
C. S.

Study of the Constitution of Proteins by the Hydrolytic Action of Hydrogen Fluoride. Preparation of Definite Natural Peptides. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1909, 148, 236—238. Compare Abstr., 1908, i, 706).—The author has extended his experiments on the use of hydrogen fluoride in the hydrolysis of proteins. The 60% acid diluted with twice its volume of water effects the complete hydrolysis of gelatin with production of free amino-acids. More dilute acid, however, is incapable of bringing about such profound decomposition; the products in this case consist of diamines and certain uncrystallisable polypeptides, which have been isolated in the form of well-defined picrates, and are analogous to some synthetic polypeptides described by Fischer (Abstr., 1906, i, 73). They appear to exist in proteins in definite combination, and not to have arisen through the synthetic action of the hydrogen fluoride.

The following compounds have been isolated from the products of hydrolysis of pepsin extract. *Arginyl-arginine dipicrate*,

$C_{18}H_{38}O_4N_{12} \cdot (C_6H_3O_7N_3)_2 \cdot 2H_2O$,
m. p. 207° (corr.). *Glutamin-lysine picrate*, $C_{11}H_{21}O_5N_2 \cdot C_6H_3N_3O_7 \cdot H_2O$,
prisms, m. p. 216°. *Lysyl-lysine dipicrate*, $C_{12}H_{26}O_3N_4 \cdot (C_6H_3O_7N_3)_2$,
small tablets, m. p. 238—242°.

From gelatin, *arginyl-arginine picrate*, $C_{12}H_{26}O_3N_8 \cdot C_6H_3O_7N_3 \cdot 2H_2O$,
has been prepared. It forms needles, m. p. 213°. W. O. W.

Combining Power of Egg-white for Hydrochloric and Sulphuric Acids. HERBERT E. ROAF (*Proc. physiol. Soc.*, 1908, iv; *J. Physiol.*, 38).—Diluted egg-white was placed in a series of dialysing tubes immersed in various strengths of acid. After some days the amount of acid in the outer vessel was estimated, and it was found that with two acids (sulphuric and hydrochloric) and varying concentrations, equivalent amounts are taken up by the same quantity of protein. It was to be expected that proteins as complex amino-acids should show a definite combining power for acids and alkalis.

W. D. H.

Osmotic Pressure of Hæmoglobin. HERBERT E. ROAF (*Proc. physiol. Soc.*, 1908, i—ii; *J. Physiol.*, 38).—The experiments were made by laking red corpuscles of the cow, freed from serum, with water. The hæmoglobin was reckoned as 90% of the dry organic matter. Their object was to determine the effect of altered conditions on the "solution aggregate" of the hæmoglobin. Three determinations of osmotic pressure were made: (1) with distilled water, (2) with 0.34% sodium hydrogen carbonate, and (3) with 0.2% of sodium carbonate; the results for 1% of hæmoglobin were 5.7, 5.3, and 11.6 mm. of mercury respectively, which correspond with "aggregates" of 29787, 32035, and 14636 respectively. The osmotic pressure of protein solutions is altered by electrolytes and non-

electrolytes. Substances which prevent laking lower the osmotic pressure of hæmoglobin; hæmoglobin is more affected by electrolytes than are serum-proteins. It is possible that the osmotic changes which occur in muscular contraction may be due to alterations in the aggregation of proteins and not to liberation of inorganic salts.

W. D. H.

Nucleo-protein of the Pig's Liver. VITTORIO SCAFFIDI (*Zeitsch. physiol. Chem.*, 1909, 58, 272—281).—By boiling and precipitation with acetic or tartaric acid, a nucleo-protein was obtained from pig's liver which contains 3.48—3.73% of purine nitrogen, 2.67% of phosphorus, and a pentose. It also contains iron in quantities varying from 0.5 to 3.6%. Schmiedeberg's ferratin, which was prepared in much the same way, contained 6% of iron. W. D. H.

Action of Rennet at Various Temperatures. C. GERBER (*Compt. rend.*, 1908, 147, 1320—1322).—There are many causes which produce deviations from the law, that the times taken to curdle a given quantity of milk are inversely proportional to the amount of ferment added. The present paper is concerned with such deviations as are due to a too speedy curdling, so that the product of time and quantity of ferment is lowered. These deviations increase with the temperature, and at the same temperature they increase with the quantity of ferment added. For the same quantity of rennet, they are largest with specimens of rennet containing a high proportion of saline constituents. Calcium chloride, however (and to some extent, hydrochloric acid), has an accelerating effect which is greatest when the enzyme concentration is greatest, so that the above-mentioned negative deviation, due to the large quantity of ferment present, is annulled; the process thus becomes regular, and the law is followed. G. B.

A New Artificial Peroxydase. E. DE STOEKLIN (*Compt. rend.*, 1908, 147, 1489—1491. Compare Abstr., 1908, i, 490, 746; ii, 573).—Iron tannate can act as a peroxydase, and in conjunction with hydrogen peroxide oxidises a number of substances which are resistant to all peroxydases hitherto known. In particular, it attacks substances containing a single phenolic hydroxyl, for instance, guaiacol. It acts like a true enzyme, oxidising many times its own weight of ethyl alcohol to acetaldehyde, and it produces a black substance from tyrosine in the same way as tyrosinase. G. B.

[Effect of Adsorbents on Yeast Juice.] LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1908, 15, 217—219).—In reference to Resenscheck's work (this vol., i, 74), the authors state that they also find that the presence of negative adsorbents diminishes the fermentative capacity of yeast juice to a small extent. Positive adsorbents have a somewhat greater inhibitory influence. S. B. S.

Organic Chemistry.

The Relative Ease of Addition in the Alkylene Group.
 ARTHUR MICHAEL and ROGER F. BRUNEL (*Amer. Chem. J.*, 1909, **41**, 118—148).—Exceptions to Markownikoff's rule governing the addition of halogen acids to unsaturated hydrocarbons have been indicated by Saytzeff (*Annalen*, 1875, **179**, 296) and Linnemann (*Annalen*, 1872, **163**, 96). In a series of papers (Abstr., 1888, 1054; 1900, i, 321; 1904, ii, 164; 1906, i, 550, 551), Michael has developed the view that a general law of addition connecting the course of the process with the structure of the substances can be based on the "positive-negative" hypothesis. This positive-negative law of addition is supported by the work of Berthelot (*Compt. rend.*, 1862, **54**, 1350) and Butleroff (*Annalen*, 1875, **180**, 246; *Ber.*, 1873, **6**, 561) on ethylene, propylene, and isobutylene, whilst the observations of Butleroff (*Annalen*, 1877, **189**, 51; Abstr., 1880, 230) and Kondakoff (Abstr., 1897, i, 177) tend to confirm the existence of a maximum additive power in the series, deduced theoretically.

In order to determine where this maximum occurs, the behaviour of the butylenes, β -methyl- Δ^{β} -butylene, $\beta\gamma$ -dimethyl- Δ^{β} -butylene, and diisobutylene, towards sulphuric acid of different strengths, the halogen acids, and phosphoric acid has been studied.

At 28—29° a mixture of 1.5 parts of sulphuric acid with 1 part of water absorbs isobutylene about twelve times as fast as ψ -butylene, which is absorbed by (5:1) sulphuric acid at about the same rate as the isobutylene is absorbed by the weaker acid. At the same temperature ψ -butylene is absorbed almost twice as fast as *n*-butylene by sulphuric acid of the strength 3.5:1.

When isobutyl alcohol is dehydrated by passing its vapour through a Jena combustion tube containing pieces of a graphite crucible heated at 500°, analysis of the gas produced, by absorption with sulphuric acid shows that it contains 55% of isobutylene and 2.5—3.0% of a gas unabsorbed by bromine, whilst if the graphite is replaced by aluminium oxide, the evolved gas contains 65—70% of isobutylene and about 1% of hydrogen.

isoButylene is dissolved by sulphuric, phosphoric, and hydrochloric acids at least three times as fast as β -methyl- Δ^{β} -butylene, whilst the latter is absorbed twelve times as rapidly as $\beta\gamma$ -dimethyl- Δ^{β} -butylene by (2:1) sulphuric acid. Although $\beta\gamma$ -dimethyl- Δ^{β} -butylene dissolves readily in sulphuric acid of the strength 4:1, diisobutylene is not dissolved, but is polymerised by twelve days' contact with this acid.

Thus it is found that of all the alkylenes examined, isobutylene has the greatest additive power, the expected decrease occurring between this hydrocarbon and β -methyl- Δ^{β} -butylene. Moreover, as predicted by theory, the difference in additive power between β -methyl- Δ^{β} -butylene and $\beta\gamma$ -dimethyl- Δ^{β} -butylene is much greater than that between isobutylene and the former hydrocarbon.

E. H.

Comparative Stability of Bromoform, Chloroform, and Iodoform. WILLIAM OECHSNER DE CONINCK (*Rev. gén. Chim. pure et appl.*, 1909, 12, 81).—Bromoform or chloroform when distilled from lead nitrate alone, or from an aqueous alcoholic solution of this salt, shows no signs of decomposition. When iodoform is thus treated, the following reaction occurs: $2\text{Pb}(\text{NO}_3)_2 + 2\text{CHI}_3 + \text{O} = 2\text{PbI}_2 + \text{I}_2 + 2\text{CO}_2 + \text{H}_2\text{O} + 2\text{H}_2\text{O}$. This change takes place with the dry materials, but in alcoholic solution at 94° no decomposition is observed.

G. T. M.

Preparation of Acetylene Di- and Tetra-chlorides from Acetylene and Chlorine. J. H. LIDHOLM (D.R.-P. 204516).—The interaction of chlorine and acetylene may be controlled by employing a definite source of light, such as a quartz-mercury lamp actuated by a current of 5 amperes and 60—75 volts. A mixture of two volumes of chlorine and one of acetylene when thus illuminated reacts quite quietly, yielding chiefly acetylene tetrachloride with about 10% of the dichloride.

G. T. M.

Preparation of Trimethylene Chlorobromide and Dibromide. PIERRE BRUYLANTS (*Bull. Acad. roy. Belg.*, 1908, 1085—1094).—The cyclopropanecarboxylonitrile required for the preparation of the compounds described elsewhere (this vol., i, 226) was obtained by treating γ -chlorobutyronitrile with dry potassium hydroxide, and this compound was prepared by Henry's method, the action of potassium cyanide on trimethylene chlorobromide. The author found the methods described by Reboul (*Abstr.*, 1879, 127) and by Lermantoff (*Abstr.*, 1877, 59) for the preparation of trimethylene chlorobromide (α -chloro- γ -bromopropane) unsatisfactory; the following modification of the process, however, gave a satisfactory yield of the product, and did not involve the use of sealed tubes. Allyl chloride is saturated with moist hydrogen bromide at 20 — 22° in sunlight, and the operation repeated until the gas ceases to be absorbed. Trimethylene dibromide ($\alpha\gamma$ -dibromopropane) is similarly prepared from allyl bromide and hydrogen bromide at 30 — 35° .

M. A. W.

Preparation of Nitromethane. ANDRE WAHL (*Bull. Soc. chim.*, 1909, [iv], 5, 180—182. Compare Preibisch, this Journ., 1874, 462; Auger, *Abstr.*, 1900, i, 578, and Steinkopf, this vol., i, 78).—A solution of 100 grams of monochloroacetic acid in 100 c.c. of water is neutralised with a solution of sodium carbonate (90 grams in 150 c.c. of water), and to this is added 90 grams of sodium nitrite. The solution is warmed, gently at first, and when the reaction has set in, a current of steam is passed through and about 175 to 190 c.c. of distillate is collected. The nitromethane is decanted, and that contained in the decantation liquid is recovered by a second distillation. The yield is about 50% of the theoretical.

T. A. H.

Oxidation of Alcohols by Simultaneous Action of Ferrous Tannate and Hydrogen Peroxide. E. DE STOEKLIN (*Compt. rend.*, 1909, 148, 424—426. Compare this vol., i, 196).—The author has

studied quantitatively the oxidation of ethyl alcohol by hydrogen peroxide in presence of ferrous tannate, and gives tables showing the amount of aldehyde and acetic acid formed when 50% alcohol, and also when acetaldehyde, is submitted to oxidation in presence of varying amounts of the iron salt. The results lead to the following conclusions: (1) the alcohol is first converted into aldehyde, (2) the aldehyde undergoes further oxidation to acetic acid, (3) a portion of the aldehyde is absorbed by the ferrous tannate, (4) part of the aldehyde is probably converted into an aldehyde peroxide, (5) the amount of aldehyde and acetic acid formed increases with the weight of iron present.

It has been observed that oxidation takes place when other organic compounds are substituted for tannin in these experiments.

Methyl, ethyl, *n*-propyl, and *n*-butyl alcohols have been oxidised in the same way, but *isopropyl* and *isobutyl* alcohols, the higher alcohols, and also polyhydric alcohols, such as glycol, glycerol, and sorbitol, resist attack.

W. O. W.

Catalytic Action of Coal, Brown Coal, or Peat in the Aerial Oxidation of Organic Substances. MAX DENNSTEDT and F. HASSLER (D.R.-P. 203848).—The oxidation of many organic substances can be brought about by passing their vapours mixed with air over coal heated at 150—300°. In this way ethyl alcohol is oxidised to acetaldehyde and acetic acid, toluene to benzaldehyde and benzoic acid, naphthalene to naphthaquinone and phthalic anhydride, anthracene to anthraquinone, and borneol or *isoborneol* to camphor and camphoric acid. Brown coal and peat have a similar effect, which appears to be due to the contained iron. Accordingly, ferruginous compounds are added when the amount of iron originally present in the coal or peat is only small.

G. T. M.

Action of Ethyl Mesoxalate on Alkyl Magnesium Halides and the Synthesis of $\beta\delta$ -Dimethylpentane- $\beta\delta$ -diol. JOSEPH LEMAIRE (*Bull. Acad. roy. Belg.*, 1909, 83—159).—The primary object of the research described was the preparation of pentamethylglycerol, $\text{OH}\cdot\text{CMe}(\text{CMe}_2\cdot\text{OH})_2$, and the first method tried was the action of Grignard's reagent on ethyl mesoxalate. The latter was prepared by a modification of the method described by Curtis (*Abstr.*, 1906, i, 480). As Wieland (*Abstr.*, 1904, i, 596) by the action of dry nitrous anhydride on $\alpha\gamma$ -diphenylpropane- $\alpha\gamma$ -dione has obtained the definite intermediate compound, $\text{N}_2\text{O}_2[\text{CH}(\text{COPh})_2]_2$, which is decomposed by dilute sulphuric acid, giving $\alpha\gamma$ -diphenylpropanetrione, $\text{COPh}\cdot\text{CO}\cdot\text{COPh}$, it is suggested that in Curtis's reaction an analogous compound, $\text{N}_2\text{O}_2[\text{CH}(\text{CO}_2\text{Et})_2]_2$, is formed and decomposed by the water contained in the nitrous anhydride. When ethyl mesoxalate (1 mol.) is treated with magnesium methyl bromide (5 mols.), *dihydroxytetramethylacetone*, $\text{CO}(\text{CMe}_2\cdot\text{OH})_2$, small crystals, m. p. 117—118°, b. p. 238—240°/755 mm., is formed, the medial carbonyl group remaining unattacked. The latter observation, taken in conjunction with the fact that the medial carbonyl group in triketopentane is also stable towards Grignard's reagent, indicates that this inactivity is due in both cases

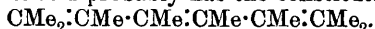
to the negative influence of the neighbouring groups. Dihydroxytetramethylacetone does not form a phenylhydrazone or a semicarbazone, and does not combine with hydrogen cyanide. The conclusion is drawn that the activity of the carbonyl group is inhibited by the two adjacent tertiary hydroxyl groups. Moreover, since the latter are attacked by phosphorus pentachloride and sulphuryl chloride, but not by acetyl and benzoyl chlorides, the behaviour of the complex :C(OH)·CO·C(OH): seems comparable with that of the carboxyl group.

Ethyl magnesium bromide (5 mols.) in ethereal solution acts on ethyl mesoxalate, giving a mixture of four substances. The chief product consists of *ethyl hydroxydiethylpyruvate*, $\text{OH·CET}_2\text{·CO·CO}_2\text{Et}$, a greenish-yellow liquid, b. p. $230\text{--}232^\circ$, D^{20}_D 1.037, n_D 1.44335, which does not solidify at -60° and does not react with phenylhydrazine or semicarbazide. The second compound is a pale green liquid, $\text{C}_6\text{H}_{11}\text{O}_2$, b. p. $140\text{--}150^\circ/755$ mm., having an agreeable odour. The third product is a golden-yellow liquid, $\text{C}_7\text{H}_{10}\text{O}_3$, b. p. $199\text{--}200^\circ/750$ mm., which forms a *semicarbazone*, m. p. 142° . The quantity obtained of the fourth substance was insufficient for identification, but it seems to be dihydroxytetraethylacetone. The conclusion is drawn that ethyl magnesium halides are more active towards ethyl mesoxalate than methyl compounds, and that the bad yield of dihydroxytetramethylacetone, when using the latter, is due to the formation of ethyl hydroxydimethylpyruvate.

Magnesium propyl bromide reacts similarly to the ethyl compound with ethyl mesoxalate.

The production of dihydroxytetramethylacetone rendered the preparation of $\beta\delta$ -dimethylpentane- $\beta\delta$ -diol desirable for purposes of comparison. Attempts to prepare this compound by the action of methyl magnesium bromide on acetylacetone, ethyl malonate, ethyl chloromalonate, ethyl acetoacetate, ethyl sodioacetoacetate, or malonyl chloride were unsuccessful.

Ethyl β -chloroisovalerate (1 mol.), prepared in the manner described by Montemartini (Abstr., 1898, i, 236), reacts with methyl magnesium bromide (2 mols.) giving (1) a liquid, b. p. $126\text{--}128^\circ$, with a camphor-like odour, which combines readily with bromine and must be either $\text{CMe}_2\text{Cl·CH}_2\text{·CMe·CH}_2$ or $\text{CMe}_2\text{·CH·CMe}_2\text{Cl}$, and (2) a liquid which is probably a mixture of the above compound and its parent chlorohydrin, $\text{CMe}_2\text{Cl·CH}_2\text{·CMe}_2\text{·OH}$. An attempt to prepare the unsaturated chlorohydrin having the second of the above two formulæ by the action of hydrogen chloride on Grignard's tetramethylallyl alcohol, $\text{CMe}_2\text{·CH·CMe}_2\text{·OH}$, gave a mixture of $\beta\delta$ -dimethyl- $\Delta^8\gamma$ -pentadiene, $\text{CMe}_2\text{·C·CMe}_2$, and a *dipolymeride* of the latter, a liquid, $\text{C}_{14}\text{H}_{24}$, b. p. $215^\circ/755$ mm., D^{20}_D 0.8533, n_D 1.4838, which combines with 3 molecules of bromine and probably has the constitution



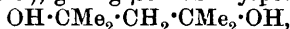
Since the latter hydrocarbon probably results from the condensation of 2 molecules of δ -chloro- $\beta\delta$ -dimethyl- Δ^8 -pentene, $\text{CMe}_2\text{Cl·CH·CMe}_2$, with elimination of hydrogen chloride, whilst the unsaturated chlorohydrin obtained by the action of methyl magnesium bromide on ethyl β -chloroisovalerate does not lose hydrogen chloride even when

treated with dilute alkali, it probably has the first of the above formulæ.

When *isobutylene* chlorohydrin, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\text{Cl}$, reacts with potassium cyanide the product consists of β -hydroxyisovaleronitrile $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CN}$, a colourless, viscous liquid, b. p. $130\text{--}132^\circ/30\text{ mm.}$, $210\text{--}212^\circ/756\text{ mm.}$, m. p. -12° , D^{20}_D 0.96762, n_D 1.42911, with an unpleasant odour, which, unlike its α -isomeride, can be distilled without decomposition. This nitrile reacts with acetyl chloride or acetic anhydride, forming the *acetate*, $\text{OAc}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CN}$, a mobile liquid, b. p. $115\text{--}120^\circ/35\text{ mm.}$, $198\text{--}200^\circ/758\text{ mm.}$, D^{18}_D 0.9951, n_D 1.4193, and with phosphorus pentachloride, giving partly a chloro-derivative and partly the unsaturated nitrile, $\text{CMe}_2\cdot\text{CH}\cdot\text{CN}$, identical with that obtained by the dehydration of α -hydroxyisovaleronitrile.

The formation of an acetate differentiates the β -hydroxyisovaleronitrile from the analogous *tert.*-butanol, which gives, not an acetate, but a chloride, and shows that the cyanogen group influences the tertiary hydroxyl even when separated from it by a methylene group. β -Hydroxyisovaleronitrile reacts with methyl magnesium bromide, giving a mixture of mesityl oxide and diacetone alcohol; it is readily hydrolysed with potassium hydroxide, giving β -hydroxyisovaleric acid, but the ester of the latter can only be obtained pure by the action of ethyl iodide on the silver salt. Ethyl β -hydroxyisovalerate, when treated with Grignard's reagent, gives $\beta\delta$ -dimethylpentane- $\beta\delta$ -diol, but, owing to the difficulty in preparing the ester, its use was abandoned in favour of the following method.

Diacetone alcohol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COMe}$ (1 mol.), prepared as described by Heintz (*Annalen*, 1875, 178, 342), reacts with magnesium methyl bromide (2 mols.), giving $\beta\delta$ -dimethylpentane- $\beta\delta$ -diol,



a viscous liquid, b. p. $113^\circ/35\text{ mm.}$, D^{20}_D 0.9206, n_D 1.4375, already prepared by Franke (*Abstr.*, 1907, i, 171, 816). This diol when distilled at atmospheric pressure is partly dehydrated, giving $\beta\delta$ -dimethyl- Δ^{α} -pentene- δ -ol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2$, a reaction entirely analogous to that undergone by the chlorohydrin, but differing from the dehydration of diacetone alcohol and β -hydroxyisovaleronitrile. The conclusion is drawn that the influence of a $\text{C}(\text{OH})$ group is different from that of a carbonyl or cyano-group on an adjacent methylene group. $\beta\delta$ -Dimethylpentane- $\beta\delta$ -diol is only very slightly oxidised to dihydroxytetramethylacetone by twenty-four hours' contact with dilute potassium permanganate solution.

Two series of reactions are suggested for the preparation of pentamethylglycerol, one starting from γ -chloro- β -butanone, the other from α -hydroxy- α -methylpropionitrile. E. H.

Preparation of Chlorohydrin from Glycerol and Sulphur Chloride. DEUTSCHE SPRENGSTOFF AKTIEN-GESELLSCHAFT (D.R.-P. 201230).—Although dichlorohydrin is the product of the action of sulphur chloride on glycerol at 100° , it has now been found possible to obtain chiefly chlorohydrin by operating with the calculated amount of the chloride at 25° and then at $50\text{--}70^\circ$. In this way 85—95% of the glycerol is converted into the monochloro-derivative,

only about 1—2% of the dichloro-compound being produced. The chief product is purified by distillation under reduced pressure.

G. T. M.

Halogen Ethers. A. KARVONEN (*Ber.*, 1909, 42, 687—692).—According to Palomaa (*Diss. Helsingfors*, 1908) the reactivity of the halogen in haloid derivatives of aliphatic ethers varies with the position of the halogen atom with respect to oxygen. Preliminary experiments show that tripropylamine does not react with ethyl β -iodoethyl ether at 100°.

Methyl β -iodoethyl ether, $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{I}$, is obtained by the action of methyl alcohol on ethylene iodide at 100°, and may be obtained pure by distilling several times over solid sodium hydroxide. It has a sweet odour and b. p. 137.8°/750 mm., and D_4^{15} 1.8322. It does not turn brown when exposed to diffused light for several months, and its aqueous or alcoholic solution yields a precipitate with silver nitrate.

Ethyl β -iodoethyl ether (Baumstark, *Ber.*, 1874, 7, 1172; Henry, *Abstr.*, 1885, 882; Demole, *Ber.*, 1876, 9, 743) is best purified by distillation over solid sodium hydroxide. It has b. p. 154.9—155.2°/761 mm. and D_4^{15} 1.6698.

β -Iodoethyl propyl ether, $\text{CH}_3\text{Et}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{I}$, has b. p. 175—175.3°/750 mm. and D_4^{15} 1.5379. J. J. S.

Preparation and Physical Properties of *as*-Tetrachloroethyl Ether. FRED NEHER and WILLIAM FOSTER (*J. Amer. Chem. Soc.*, 1909, 31, 410—412).—A modification of Henry's method (*Abstr.*, 1871, 255) for the preparation of tetrachloroethyl ether,



is described, by means of which the compound can be obtained in a yield of 55—74% of the theoretical. *as*-Tetrachloroethyl ether boils at 189.4°/749.1 mm. (corr.) or 79°/16 mm., and has D_4^{18} 1.4225.

E. G.

***as*-Dichlorovinyl Ethyl Ether: its Preparation from Tetrachloroethyl Ether and its Physical Properties.** FRED NEHER and WILLIAM FOSTER (*J. Amer. Chem. Soc.*, 1909, 31, 412—414).—*as*-Dichlorovinyl ethyl ether, $\text{CCl}_2\text{:CH}\cdot\text{OEt}$ (Godefroy, *Abstr.*, 1886, 607), can be obtained in a yield of 80—90% of the theoretical by the action of zinc on an alcoholic solution of *as*-tetrachloroethyl ether at a temperature below 40°. At higher temperatures the product contains a varying amount of dichloroacetal.

as-Dichlorovinyl ethyl ether boils at 144.2°/765.3 mm. (corr.), and has D_4^{18} 1.2096 and D_4^{20} 1.2081. E. G.

Diffuoroethyl Bromide and Tetrafluorodiethyl Hydrogen Phosphate. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1909, 60—65).—When diffuoroethyl alcohol (1 gram-molecule) is acted on by bromine (1 gram-atom) in the presence of excess of phosphorus, about 25% of the alcohol is recovered unchanged, another 25% is transformed into

difluoroethyl bromide, whilst the remainder is converted into a syrupy liquid, b. p. 253—255°, the analysis and vapour density of which prove it to be *difluoroethyl phosphate*, $\text{PO}(\text{OC}_2\text{H}_5\text{F}_2)_3$. The reaction producing this substance might be represented by either of the two equations: (1) $\text{P} + 5\text{Br} + 4\text{C}_2\text{H}_5\text{F}_2 \cdot \text{OH} = (\text{C}_2\text{H}_5\text{F}_2)_3\text{PO}_4 + \text{C}_2\text{H}_5\text{F}_2\text{Br} + 4\text{HBr}$; (2) $5\text{P} + 25\text{Br} + 20\text{C}_2\text{H}_5\text{F}_2 \cdot \text{OH} = 4(\text{C}_2\text{H}_5\text{F}_2)_3\text{PO}_4 + 8\text{C}_2\text{H}_5\text{F}_2\text{Br} + 17\text{HBr} + \text{H}_3\text{PO}_4$. The amount of hydrogen bromide found experimentally is in favour of the former equation. The difluoroethyl bromide formed is identical with that obtained from tribromoethane (Abstr., 1908, i, 752).

Difluoroethyl phosphate is saponified by ammonia, giving *ammonium tetrafluorodiethyl phosphate*, $\text{NH}_4\text{PO}_4(\text{C}_2\text{H}_5\text{F}_2)_2$, which forms beautiful white, crystalline spangles, and is converted by baryta into the *barium* salt. The salts of silver and lead are both soluble in water, but the *mercurous* salt forms a white, crystalline precipitate insoluble in nitric acid. Tetrafluorodiethyl hydrogen phosphate is remarkably stable towards both acids and alkalis. Heating with excess of nitric acid on a water-bath for thirty-six hours is required in order to obtain the phosphate reaction with ammonium molybdate. E. H.

New Method of Extracting a Phosphated Compound (Phytin) from Plants. ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 64—67).—The author gives the following method for extracting from rice bran the phytin obtained from different sources by several investigators (compare Suzuki and Yoshimura, Abstr., 1908, ii, 124).

The finely-ground rice bran is treated with twice its weight of 0.2—0.3% hydrochloric acid, and the liquid separated by pressing, heated below its boiling point, and neutralised by means of recently-calcined magnesium oxide. The precipitate formed, after washing several times with hot water by decantation, is dissolved in hydrochloric acid, and the solution filtered, decolorised with animal charcoal, and neutralised with magnesium oxide. After re-dissolving and again precipitating, the calcio-magnesium derivative of phytin is obtained. The composition of this compound corresponds with that of the calcio-magnesium derivative of the compound, $\text{O}[\text{CH}_2 \cdot \text{O} \cdot \text{P}(\text{OH})_2]_2$, described by Posternak (Abstr., 1903, ii, 607, 679, 680). The phytin separated in the above manner behaves like an ordinary ester, but is not so readily hydrolysed by alkalis as the latter. T. H. P.

Effect of Neutral Salts on Hydrolysis by Water. DAVID R. KELLOGG (*J. Amer. Chem. Soc.*, 1909, 31, 403—405).—It is well known that ester hydrolysis in the presence of a strong acid is greatly accelerated by the addition of a neutral salt of the acid. Experiments have now been carried out with the object of ascertaining the effect of neutral salts on the rate of hydrolysis in the absence of acids. Ethyl acetate was heated in sealed tubes with water, with potassium chloride solutions of 1%, 10%, and 20% strength, and with a saturated solution of this salt. The results show that the 1% solution produces a considerable acceleration, the 10% solution a much larger acceleration, whilst the 20% solution has but little effect, and a saturated solution exerts a strong inhibiting influence. E. G.

[Preparation of Salts of Iodated Fatty Acids.] **FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co.** (D.R.-P. 202353. Compare Abstr., 1908, i, 122, 123, 310).—*Manganous iodobehenate*, a white, amorphous mass, is obtained by adding an aqueous solution of manganous chloride to potassium iodobehenate in alcoholic solution. The corresponding *manganic*, *ferrous*, and *ferric* salts are prepared similarly. G. T. M.

[Iodination of the Higher Fatty Acids and Esters.] **J. D. RIEDEL** (D.R.-P. 202790).—Ethyl oleate dissolved in alcohol is treated with iodine and mercuric oxide, and, after twenty-four hours, freed from iodine with potassium iodide and thiosulphate. The final residue, after distilling off the solvent, contains 15–26% of iodine. G. T. M.

Elæostearic Acid. **RIKO MAJIMA** (*Ber.*, 1909, 42, 674–680).—The composition $C_{18}H_{32}O_2$, ascribed by Kametaka (*Trans.*, 1903, 83, 1042) to the solid acid, m. p. 48–49°, b. p. 235°/12 mm., in carbon dioxide isolated from oil of *Elæococca Vernicia*, and regarded by Cloez as elæomargaric acid, $C_{17}H_{30}O_2$, and by Maquenne as elæostearic acid, $C_{18}H_{30}O_2$ (Abstr., 1903, i, 62), has been confirmed by the author, who has prepared a *diozonide*, $C_{18}H_{32}O_8$, a yellow, amorphous, semi-solid substance. The products of its decomposition by water include valeraldehyde (thiosemicarbazone, m. p. 65°), valeric acid (anilide, m. p. 60°), azelaic acid, and its semialdehyde (semicarbazone, m. p. 165°). Consequently, elæostearic acid must have its double linkings between the fifth and the sixth and the ninth and the tenth carbon atoms. Succinaldehyde, succinic acid, and its semialdehyde cannot be detected, although the aqueous solution of the decomposition products contains a substance which responds to the pyrrole test. C. S.

Preparation of Ethyl Glyoxylate by the Reduction of Ethyl Oxalate. **FARBENFABRIKEN VORM. FRIEDR. BAYER & Co.** (D.R.-P. 201895).—Ethyl oxalate, when reduced with sodium amalgam and absolute alcohol, yields ethyl glyoxalate, a 30–40% yield of which is obtained in the form of an alcoholate after precipitating the sodium as sodium oxalate and distilling the filtrate from this salt under reduced pressure. The ester itself is obtained by treating the alcoholate with phosphoric oxide. G. T. M.

Syntheses by means of Mixed Organo-metallic Compounds of Zinc. **Preparation of Ketonic Acids and Diketones.** **EDMOND BLAISE and A. KÖHLER** (*Compt. rend.*, 1909, 148, 489–491. Compare Abstr., 1907, i, 749; 1908, i, 248).—The acid esters of the succinic and glutaric series of dibasic acids are readily prepared by the action of acetic anhydride on the acid anhydride. In the case of the higher homologues, it is necessary to mix the normal ester with an alcoholic solution of sodium ethoxide and add the calculated amount of water. Conversion of the acid esters into the corresponding chlorides is best effected by means of thionyl chloride. The following ketonic acids have been prepared by the action of mixed organo-metallic zinc compounds on the chlorides so obtained: *ε-keto-octoic acid*, $COMe \cdot [CH_2]_5 \cdot CO_2H$, m. p. 31–32°; *ε-ketononoic acid*, $C_9H_{16}O_3$, m. p.

52°; η -ketodecoic acid, $C_{10}H_{18}O_3$, m. p. 42°; θ -ketoundecoic acid, $C_{11}H_{20}O_3$, m. p. 64°; δ -keto-octoic acid, $C_8H_{14}O_3$, m. p. 53°.

The corresponding symmetrical diketones are obtained in good yield when the dichlorides of the dibasic acids are treated with the organo-metallic zinc compounds. The reaction, however, is not available in the succinic and glutaric series, since in this instance lactones are obtained. The following diketones are mentioned: *undecane- γ -dione*, $COEt \cdot [CH_2]_5 \cdot COEt$, m. p. 68°; *decane- β -dione*, $C_{10}H_{18}O_2$, m. p. 64°; *dodecane- γ -dione*, $C_{12}H_{22}O_2$, m. p. 72°; *undecane- β -dione*.

W. O. W.

Halogen Derivatives of γ -Hydroxycrotonic Acid. ROBERT LESPIEAU and VIGUIER (*Compt. rend.*, 1909, 148, 419—422. Compare Abstr., 1908, i, 125).—The authors describe further experiments with $\alpha\beta$ -dibromo- γ -hydroxy- Δ^a -butenoic acid which favour the view that this compound belongs to the maleic rather than to the fumaric series. The acid differs from Tönnies' lactone in yielding a *potassium* salt, $OH \cdot CH_2 \cdot CBr \cdot CBr \cdot CO_2K, H_2O$. It appears, therefore, that this lactone, to which Hill ascribed the constitution $\begin{array}{c} CBr-CO \\ || \\ CBr \cdot CH_2 \end{array} > O$ (Abstr., 1894, i, 319), is not a simple derivative of the acid. The acid, however, undergoes conversion into the lactone when its aqueous solution is saturated with hydrogen chloride.

Hydrogen bromide converts γ -hydroxytetrollic acid into a mixture of α -bromo- γ -hydroxy- Δ^a -butenoic acid, $OH \cdot CH_2 \cdot CH \cdot CBr \cdot CO_2H$, m. p. 158—160°, and Hill's lactone, $\begin{array}{c} CH-CO \\ || \\ CBr \cdot CH_2 \end{array} > O$ (*loc. cit.*). Bromine converts the latter into Hill's dibromolactone. The bromo-acid probably belongs to the fumaric series.

Iodine and potassium iodide convert γ -hydroxytetrollic acid into $\alpha\beta$ -di-iodo- γ -hydroxy- Δ^a -butenoic acid, $OH \cdot CH_2 \cdot CI \cdot CI \cdot CO_2H$, m. p. 173—175° (decomp.). Hydrogen bromide converts this into a lactone, m. p. 143—145°, which has not yet been obtained pure.

W. O. W.

Action of Oxalic Acid on Ferric Hydroxide. FRANK K. CAMERON and WILLIAM O. ROBINSON (*J. Physical Chem.*, 1909, 13, 157—158).—The solubility of ferric hydroxide in solutions of oxalic acid of varying strengths has been determined at 25°. The results show that the solubility of the hydroxide is directly proportional to the concentration of the acid, and that no definite basic ferric oxalate is formed from solution at 25°. In all solutions more iron is present than is equivalent to the oxalic acid present, but the solutions have an acid reaction.

G. S.

Conversion of Active α -Bromopropionic Acid into Active Methylsuccinic Acid. EMIL FISCHER and ERICH FLATAU (*Annalen*, 1909, 365, 13—20).—The authors have attempted to increase the number of direct syntheses of optically active substances by replacement of some atom or group attached to the asymmetric carbon atom of an active compound. For this purpose the synthesis of an active

methylsuccinic acid from ethyl sodiocyanoacetate and ethyl *l*-α-bromopropionate was selected, and Bone and Sprankling's method (*Trans.*, 1899, 75, 839) was used.

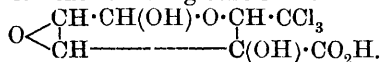
In the condensation care was taken to keep the temperature as low as possible (below 35°) in order to avoid racemisation. The ethyl cyanomethylsuccinate had b. p. 119—153°/10 mm. and α - 17.6° in a 100 mm. tube. It was hydrolysed to propane- $\alpha\alpha\beta$ -tricarboxylic acid by shaking with fuming hydrochloric acid at the ordinary temperature, and the acid isolated as the insoluble barium salt. The acid was crystallised from a mixture of ether and benzene; it had m. p. 150° (decomp.) and $[\alpha]_D^{20}$ - 33.8° in aqueous, or - 57.8° in sodium hydroxide, solution. The acid was decomposed by heating the aqueous solution at 100° for four hours, a levorotatory methylsuccinic acid was obtained, but the rotation varied considerably with different specimens, and was always below the value obtained by Ladenburg (*Abstr.*, 1895, i, 449).

The possibility of the Walden inversion occurring during the synthesis is mentioned. J. J. S.

Chemical Treatment of Bile. Separation of the Bile Acids.

MAURICE PIETTRE (*Compt. rend.*, 1909, 148, 372—374).—After extraction with ether, the bile is desiccated, powdered, and extracted with boiling methyl alcohol. After filtration, the boiling solution is precipitated drop by drop with barium methoxide (compare Étard and Vila, this vol., i, 124), which carries down the pigments. As soon as the solution becomes alkaline, the precipitation is stopped, and the excess of barium is removed by carbon dioxide; the bile salts can now be readily obtained from the clear, colourless solution. The barium methoxide precipitate, after acidification and washing, is extracted with chloroform and yields bilirubin. G. B.

Chloralic Acids. MAURICE HANRIOT (*Compt. rend.*, 1909, 148, 487—489. Compare *Abstr.*, 1893, i, 247; 1894, i, 105; 1895, i, 321; 1896, i, 519).—The compounds of chloral with certain sugars, which the author has termed chloraloses, undergo oxidation when treated with potassium permanganate and sulphuric acid or with nitric acid, giving acids to which the following constitution is ascribed:



In the case of mannochloralose a lactone was obtained on oxidation. α -Glucochloralic acid, $\text{C}_7\text{H}_7\text{O}_6\text{Cl}_3$, forms slender needles, m. p. 212°. β -Glucochloralic acid, $\text{C}_7\text{H}_7\text{O}_6\text{Cl}_3 \cdot 2\text{H}_2\text{O}$, occurs as efflorescent, rhombic tablets, and forms a sparingly soluble sodium salt. The lactone, $\text{C}_7\text{H}_5\text{O}_5\text{Cl}_3$, obtained by the action of acetyl chloride or zinc chloride on the acid, has m. p. 185°. β -Galactochloralic acid, $\text{C}_7\text{H}_7\text{O}_6\text{Cl}_3$, m. p. 307°, forms a lactone, $\text{C}_7\text{H}_5\text{O}_5\text{Cl}_3$, m. p. 130°. Mannochloralic lactone, $\text{C}_8\text{H}_7\text{O}_6\text{Cl}_3$, is sparingly soluble in water, and has m. p. 242°; it dissolves in aqueous ammonia, forming the ammonium salt of the unstable acid. α -Arabinochloralic acid, $\text{C}_7\text{H}_7\text{O}_6\text{Cl}_3$, forms needles, m. p. 320°; the β -acid is identical with β -galactochloralic acid,

β -Xylochloralic acid is identical with β -glucochloralic acid.

W. O. W.

Action of Nitric Anhydride on Mucic Acid. A. CRUM BROWN and G. E. GIBSON (*Proc. Roy. Soc. Edin.*, 1908, 23, 96—97).—Mucic acid and nitric anhydride, both previously cooled in ice, were mixed together and left in a vacuum over sodium hydroxide; on extracting with ether in a Soxhlet tube, and evaporating at the ordinary temperature with a vacuum pump, colourless needles were obtained, which on exposure to air or in a vacuum soon changed to a white powder. The analyses of this substance, although discordant, correspond with a tetranitrate. In the air, the white solid soon begins to decompose with evolution of nitric acid and oxides of nitrogen; on heating, it decomposes violently.

P. H.

The Reduction Products of Sulphurous Acid and their Double Compounds with Aldehydes. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 202825, 202826, and 202827).—The double sodium salt, $\text{HO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SONa}, \text{HO}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{ONa}$, is produced by passing sulphur dioxide into a mixture of zinc dust and aqueous formaldehyde until the metal has dissolved, and then treating the solution with sodium carbonate. A sparingly soluble benzaldehyde zinc hyposulphite can be similarly obtained.

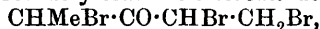
When half the proportions of aldehyde and sulphurous acid are employed, salts of the type $\text{HO}\cdot\text{CHR}\cdot\text{O}\cdot\text{SO}\cdot\text{Zn}\cdot\text{OH}$ are formed; these have twice as much reducing action on indigotin as the foregoing double salts.

Sodium formaldehyde sulphonylate, $\text{HO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SONa}$, is obtained in stable, well defined crystals by evaporating its solutions under greatly reduced pressure and separating the product from the liquid without allowing it to cool.

G. T. M.

Bromo-ketones. J. PASTUREAU (*Bull. Soc. chim.*, 1909, [iv], 5, 226—227. Compare Abstr., 1905, i, 572; 1907, i, 113, 185).—A description of bromo-derivatives of homologues of acetone obtained as already described (*loc. cit.*) from the ketone peroxides.

Diethyl ketone peroxide yields the tribromo-derivative,



b. p. $142^\circ/100$ mm., $D_{20} 1.003$, which on hydrolysis with potassium carbonate gives the keto-alcohol, $\text{OH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$. The latter reduces strongly in the cold, and gives a phenylosazone, m. p. 180 — 181° .

Methyl propyl ketone peroxide, under the same conditions, yields the tetrabromo-derivative, $\text{CHMeBr}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CBr}_3$, m. p. 57° , which separates from boiling alcohol in colourless rhombohedra and hexagonal prisms. On hydrolysis with potassium carbonate, it yields the lactone,

$\begin{array}{c} \text{CO} \text{---} \text{CO} \\ | \qquad \qquad | \\ \text{CH}_2\cdot\text{CHMe} \end{array} > \text{O}$, of which the corresponding hydroxy-acid has only been obtained in the form of the lead salt by hydrolysing the tetrabromo-derivative with litharge in a closed vessel.

T. A. H.

Oxidation of Ketones and Diketones by Hydrogen Peroxide in Presence of Acid. J. PASTUREAU (*Bull. Soc. chim.*, 1909, [iv], 5, 227—229. Compare Baeyer and Villiger, *Abstr.*, 1900, i, 133; Pastureau, *Abstr.*, 1905, i, 572, and 1907, i, 113, 185).—The author has shown already that aliphatic ketones yield, on treatment with hydrogen peroxide in presence of dilute sulphuric acid, the corresponding ketone peroxides and hydroxy-ketones, acetone furnishing acetone peroxide and acetol (acetyl-carbinol). In the present paper this reaction is applied to other products of this class.

Diethyl ketone peroxide, D 1.038, is a liquid insoluble in water (compare Baeyer and Villiger, *loc. cit.*), and with it is formed *propionylmethylcarbinol*, $\text{COEt}\cdot\text{CHMe}\cdot\text{OH}$, which with phenylhydrazine yields acetylpropionyl phenylosazone, m. p. 136°.

Methyl propyl ketone peroxide, D 1.006, is formed along with the keto-alcohol, $\text{CH}_3\text{Ac}\cdot\text{CHMe}\cdot\text{OH}$. Acetophenone yields only hydroxy-acetophenone, $\text{OH}\cdot\text{CH}_2\cdot\text{COPh}$, and benzoic acid.

The diketones, which contain a carbonyl group between two open-chain radicles, yield peroxides, but not those in which the two carbonyl groups are contiguous with closed-chain radicles. These peroxides are highly polymerised, vitreous solids, which are not volatile in steam, but have properties akin to those of the peroxides of the simple ketones (*loc. cit.*). *Acetylacetone peroxide*, $(\text{C}_5\text{H}_{10}\text{O}_4)_n$, is formed along with a *keto-alcohol*, which condenses with phenylhydrazine to form a pyrazole and gives a red coloration with ferric chloride. *Benzoylacetone peroxide*, $(\text{C}_{10}\text{H}_{10}\text{O}_3)_n$, is obtained together with benzoic acid. Dibenzoylmethane and benzil furnish each 2 mols. of benzoic acid, whilst benzoin is decomposed, yielding a little benzoic acid.

T. A. H.

Preparation of Diacetyldioxime [Dimethylglyoxime]. HEINRICH BILTZ (*Zeitsch. anal. Chem.*, 1909, 48, 164—165. Compare Tschugaeff, *Abstr.*, 1905, ii, 613).—Fifty grams of methyl ethyl ketone are dissolved in 100 grams of ether, the solution is cooled in ice, and eighty-two grams of amyl nitrite are added drop by drop while a current of hydrogen chloride is being passed. After a few hours, 150 c.c. of iced water and 50 c.c. of 33% aqueous sodium hydroxide are added, and, after thorough shaking, the alkaline solution is drawn off and the ether is shaken a few times with dilute sodium hydroxide solution. The alkaline solutions are united and shaken with a little ether, and then evaporated on the water-bath to remove the dissolved ether. When cold, the solution is carefully neutralised with dilute sulphuric acid, and a solution of 50 grams of hydroxylamine hydrochloride in 75 c.c. of water is added. After remaining overnight, the crystalline mass is collected, using suction, and then purified by recrystallisation; the yield amounts to 45—50 grams.

L. DE K.

Simple Notation for Indicating the Configuration of the Sugars and Allied Substances. THOMAS S. PATTERSON (*Chem. News*, 1909, 99, 124—126).—The empirical names of the compounds are retained. Attention is confined to the $-\text{OH}$ groups on the right-

hand side of the formula, in which the most highly oxidised end of the chain is always placed uppermost, and the asymmetric carbon atoms are numbered from *below upwards*.

Thus, on the right-hand side of the formula for *d*-arabinose, hydroxyl groups are found on the first and second carbon atoms, and the symbol *d*-arabinose (1 : 2) is applied. Similarly, we have *d*-glucose (1 : 2 : 4) and *l*-ribose (0), there being no hydroxyl group on the right-hand side. For substances having the same group at either end of the molecule, two different symbols are possible; thus *d*-sorbitol is written $\begin{smallmatrix} (1,2,4) \\ (2) \end{smallmatrix}$. In *d*-idosaccharic acid (2 : 4) the two symbols are identical. For inactive substances, for example, dulcitol $\begin{smallmatrix} (1,4) \\ (2,3) \end{smallmatrix}$, the second symbol is entirely different from the first. E. F. A.

Behaviour of Cellobiose and its Osone towards Certain Enzymes. EMIL FISCHER and GÉZA ZEMPLÉN (*Annalen*, 1909, 365, 1—6).—The disaccharide cellobiose (Skraup and König, *Abstr.*, 1901, i, 370; 1902, i, 135) is readily hydrolysed by emulsin, but is not affected by the extract of dry *Frohberg* yeast or yet by the enzymes of *Aspergillus niger* or kephir lactase.

Cellobiososone, obtained from the osazone, is a syrup which sets to a vitreous mass, and in its behaviour towards enzymes resembles cellobiose. The behaviour of the disaccharide is similar to that of gentiobiose (*Abstr.*, 1902, i, 744), isomaltose (*Abstr.*, 1896, i, 119), and to a certain extent milk sugar. In all these compounds it is probable that the two molecules of dextrose are united in the same manner, and that in maltose the condensation is of a different type. J. J. S.

Colloidal Properties of Starch in Relation to its Chemical Constitution. EUGÈNE FOUARD (*Compt. rend.*, 1909, 148, 502—505. Compare this vol., i, 13).—When potassium hydroxide is added in increasing quantities to a perfectly clear starch solution (filtered through collodion), the rotatory power of the latter diminishes, at first rapidly, then more slowly, and finally it approaches asymptotically to the rotatory power for a maltose solution. The change is reversible, so that the rotation increases again on neutralisation; there is a definite rotation for every degree of alkalinity. The rotatory power of the part remaining dissolved when a starch solution gradually gelatinises diminishes while gelatinisation proceeds, and the final portions to be gelatinised have a rotation also approaching asymptotically to that of pure maltose. Starch is therefore to be regarded as being simply a condensation product of maltose of varying degrees of complexity. G. B.

Course of the Oxidation and Hydrolysis of Starch and its Constituents by Hydrogen Peroxide. Z. GATIN GRUZEWSKA (*Compt. rend.*, 1909, 148, 578—580).—Hydrogen peroxide hydrolyses starch and at the same time oxidises it, the final products being maltose and oxalic acid. The constituents of starch, amylopectin, and amylose are acted on in different ways by hydrogen peroxide (as they

are by diastase). In the case of both constituents, dextrans are formed as intermediate products. In the case of amylopectin the attack on the micellæ appears to be simultaneous, in that of amylose successive. G. B.

Cellulose Hydrates. HERMANN OST and F. WESTHOFF (*Chem. Zeit.*, 1909, 33, 197. Compare Abstr., 1907, i, 390).—The name cellulose hydrate has been used by Cross and Bevan (*Trans.*, 1895, 67, 433) to designate substances which contain besides hygroscopic water, also water more firmly retained, such as is present in mercerised cellulose, the composition of which is given as $2C_6H_{10}O_5 \cdot H_2O$. The hydrocelluloses are substances which, in the dry state, contain water in chemical combination; they have the composition $(C_6H_{10}O_5)_n \cdot H_2O$, and it has been shown by Schwalbe (*Abstr.*, 1907, i, 390) that cellulose hydrate is quite different from hydrocellulose.

The present paper records a careful comparison of dried cellulose, cellulose hydrate, and hydrocellulose, and, from the results of the estimation of water driven off at 110—130° and from analyses, the conclusion is drawn that mercerised cellulose contains more hygroscopic water than hydrocellulose; further, that the so-called cellulose hydrates (mercerised cellulose, etc.), when freed from water by drying at 120—125°, have the same composition as ordinary cellulose, namely, $(C_6H_{10}O_5)_n$.

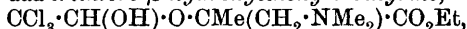
Hydrocellulose, on the other hand, when in the anhydrous state has the composition represented by the formulæ $C_{60}H_{102}O_{51}$, $C_{36}H_{62}O_{31}$, etc., analogous to the hydrolytic decomposition products of starch.

J. V. E.

Putrefaction of Glutamic and Aspartic Acids. L. BORCHARDT (*Zeitsch. physiol. Chem.*, 1909, 59, 96—100).—During putrefaction, glutamic acid yields butyric acid as a result of de-amidation and evolution of carbon dioxide. Aspartic acid also loses NH_2 , and is converted into succinic acid, and finally, by loss of carbon dioxide, into propionic acid. Volatile bases other than ammonia were not detected.

W. D. H.

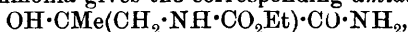
Preparation of Alkyl Dialkylamino- α -trichloro- β -hydroxyethoxyisobutyrate. LES ETABLISSEMENTS POULENC FRÈRES and ERNST FOURNEAU (D.R.-P. 203643).—Esters having pronounced saporific properties with low toxicity are produced by condensing anhydrous chloral with the alkyl dimethylaminohydroxyisobutyrate. *Ethyl dimethylamino- α -trichloro- β -hydroxyethoxyisobutyrate*,



rectangular prisms, m. p. 66—67°, b. p. 140—142°/22 mm., *hydrochloride*, needles, m. p. 181—182°, and *propyl dimethylamino- α -trichloro- β -hydroxyethoxyisobutyrate*, transparent crystals, m. p. 65°, were thus obtained. These esters, when exposed to moist air, undergo hydrolysis to the acid, $CCl_3 \cdot CH(OH) \cdot O \cdot CMe(CH_2 \cdot NMe_2) \cdot CO_2H$. G. T. M.

Aminohydroxy-acids. II. Amino-derivatives of α -Hydroxyisobutyric Acid. ERNEST FOURNEAU (*Bull. Soc. chim.*, 1909, [iv], 5, 229—241. Compare Abstr., 1907, i, 622).—Much of the work now

recorded has been published previously (Abstr., 1908, i, 937), and in this paper fuller experimental details are given and a number of additional derivatives described. The starting point of the investigation was β -chloro- α -hydroxyisobutyronitrile, b. p. 103—104°/16 mm., which was converted into the corresponding acid, of which the *ethyl ester*, b. p. 197°/765 mm. or 106°/30 mm., *propyl ester*, b. p. 217°/765 mm. or 106—107°/16 mm., and *amyl ester*, b. p. 241—242°/765 mm. or 115—116°/12 mm., were prepared. The acid on treatment with ammonia solution in a closed vessel yields β -amino- α -hydroxyisobutyric acid, which is crystalline, decomposes at 281°, and yields a crystalline *hydrochloride* and *sulphate*. The ethyl ester (*loc. cit.*) furnishes an *isovaleryl* derivative, b. p. 194—196°/21 mm., a *urethane*, $\text{OH}\cdot\text{CMe}(\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et})\cdot\text{CO}_2\text{Et}$, b. p. 164—165°/16 mm. (which with alcoholic ammonia gives the corresponding *amide*,



m. p. 125°, silky needles), and a *propylurethane* derivative, b. p. 184°/30 mm. The ethyl ester condenses with potassium *isocyanate*, and on treating the product with hydrochloric acid, 5-hydroxy-5-methyl-dihydrouracil, $\text{NH}\begin{matrix} \text{CO}\cdot\text{CMe}(\text{OH}) \\ \text{CO}\text{---}\text{NH} \end{matrix}\text{CH}_2$, crystallising in colourless tablets from boiling water, is obtained.

The propyl and amyl esters of β -amino- α -hydroxyisobutyric acid were also prepared; their *urethanes* are colourless, syrupy liquids, which are soluble in water, and have b. p. 167—168°/14 mm. and 173—174°/12 mm. respectively.

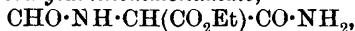
In preparing ethyl β -methylamino- α -hydroxyisobutyrate (*loc. cit.*) by esterifying the acid in the usual manner, some *ethyl methylaminobis-hydroxyisobutyrate*, $\text{NMe}[\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CO}_2\text{Et}]_2$, b. p. 180°/17 mm., is obtained as a thick, oily liquid soluble in water. The *methylamide* of β -methylamino- α -hydroxyisobutyric acid, b. p. 157°/31 mm., is obtained by the action of methylamine on the original ethyl chlorohydroxyisobutyrate in presence of alcohol or benzene.

β -Dimethylamino- α -hydroxyisobutyric acid, m. p. 174°, crystallises in bulky, transparent tablets, and possesses a sweetish, slightly nauseous taste; the *benzoyl* derivative, m. p. 182°, crystallises in spangles, and the *amide*, m. p. 102°, in needles. The ethyl ester (*loc. cit.*) yields the following acyl derivatives: *valeryl*, b. p. 143—145°/20 mm., liquid; *bromovaleryl hydrochloride*, m. p. 142°, colourless prisms; *bromohexoyl hydrochloride*, m. p. 134°, quadrangular tablets; *p-nitrobenzoyl hydrochloride*, m. p. 196°, yellow prisms. The propyl ester (*loc. cit.*) furnishes a *valeryl* derivative, b. p. 148—150°/16 mm., a liquid having a feeble odour of smoked fish; its *hydrobromide*, m. p. 120°, is crystalline, possesses a burning taste, and is employed in medicine under the name "quietol."

T. A. H.

Derivatives of Oximinocyanoacetic Acid. MAX CONRAD and ARNOLD SCHULZE (*Ber.*, 1909, 42, 735—742).—Ethyl oximinocyanoacetate is readily obtained in 87% yield by treating a cold mixture of ethyl cyanoacetate and aqueous sodium nitrite with glacial acetic acid and decomposing the resulting yellow, crystalline sodium derivative

with hydrochloric acid. It is changed by zinc dust and formic acid, D 1·22, into *ethyl formylaminomalonamate*,

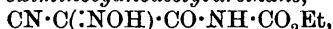


m. p. 142°, the constitution of which is proved by its conversion by concentrated ammonium hydroxide into formylaminomalonamide (this vol., i, 213). Ethyl oximinocyanoacetate is readily oxidised by potassium permanganate to ethyl nitrocyanoacetate, of which the *silver* and the *potassium* derivatives are described. Oximinocyanoacetamide (deoxyfulminuric acid) is readily obtained by treating an aqueous solution of cyanoacetamide and sodium nitrite at 0° with glacial acetic acid and decomposing the resulting sodium derivative with the calculated quantity of hydrochloric acid; by reduction by zinc and formic acid it yields formylaminomalonamide, whilst oxidation by potassium permanganate leads to the formation of nitrocyanoacetamide (fulminuric acid), the potassium salt of which is also obtained by the action of concentrated ammonium hydroxide on the potassium derivative of ethyl nitrocyanoacetate.

Cyanoacetylcarbamide, obtained by heating carbamide, cyanoacetic acid, and acetic anhydride at 60° for three hours, reacts with sodium nitrite in hot water to form yellow crystals of the *sodium* derivative of oximinocyanoacetylcarbamide, $\text{C}_4\text{H}_3\text{O}_3\text{N}_4\text{Na}\cdot\text{H}_2\text{O}$, which develops an intense violet coloration with ferrous sulphate and sodium hydroxide.

Oximinocyanoacetylcarbamide, $\text{CN}\cdot\text{C}(\text{:NOH})\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, m. p. 220° (decomp.), is oxidised by potassium permanganate to the *potassium* derivative of nitrocyanoacetylcarbamide.

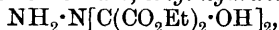
Cyanoacetylurethane, $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, m. p. 167—168°, prepared from urethane, cyanoacetic acid, and acetic anhydride, yields in a similar manner *oximinocyanoacetylurethane*,



m. p. 201° (decomp.), which also gives a violet coloration with ferrous sulphate and sodium hydroxide. C. S.

Action of Hydrazine on Ethyl Mesoxalate. RICHARD S. CURTISS, ALFRED R. KOCH, and E. J. BARTELLS (*J. Amer. Chem. Soc.*, 1909, 31, 416—421).—In earlier papers (Curtiss, *Abstr.*, 1906, i, 339; Curtiss and Tarnowski, *Abstr.*, 1908, i, 760) the action of ammonia and hydrazine on esters of mesoxalic acid has been described.

When ethyl dihydroxymalonate is treated with an aqueous solution of hydrazine hydrate or carbonate, *ethyl hydrazinobistartronate*,



m. p. 58°, is produced, which forms colourless, rhombohedral crystals, and has a bitter taste. It is stable in the air, but if left in a desiccator or carefully heated, water is eliminated and an oily substance is formed. The compound reduces silver nitrate and platinum chloride to the metallic state, and is decomposed by nitrous acid with production of nitrogen, ethyl dihydroxymalonate, and small quantities of a compound, m. p. 253°. Phosphorus pentachloride reacts with ethyl hydrazinobistartronate with evolution of hydrogen chloride, thus proving the presence of hydroxyl groups. When the compound is warmed with mercuric oxide, nitrogen and ethyl dihydroxymalonate are produced.

By the action of benzaldehyde on the hydrazine compound, benzalazine is formed, and by the action of benzoyl chloride or benzoic anhydride, a *dibenzoylhydrazine*, m. p. 241° (corr.), is produced.

When hydrazine hydrate solution is added to an alcoholic solution of ethyl mesoxalate, a *compound*, $C_4H_{18}O_9N_2$, m. p. $125-130^{\circ}$ (decomp.), is obtained which crystallises in colourless needles. E. G.

Reduction of the Esters of *d*-Alanine and of *dl*-Phenyl-alanine. EMIL FISCHER and TOKUHEI KAMETAKA (*Annalen*, 1909, 365, 7—12. Compare Fischer, *Abstr.*, 1908, i, 323; Neuberg, *ibid.*, 322).—A 17% yield of *d*- α -aminopropionacetal, $NH_2 \cdot CHMe \cdot CH(OEt)_2$, is obtained when the *d*-alanine ethyl ester is reduced with sodium amalgam in slightly acid solution and the resulting amino-aldehyde treated with an alcoholic solution of hydrogen chloride at 0° . It is a colourless liquid, b. p. $55-56^{\circ}/11$ mm., has D_{20}^{20} 0.902, and n_D^{20} 1.41955. The solution in hydrochloric acid has $[\alpha]_D^{20} + 14.5^{\circ}$. The *picrate*, $C_{13}H_{20}O_9N_4$, crystallises from benzene in yellow prisms, m. p. 86° (corr.) after sintering at 82° . The *normal oxalate*, $C_{16}H_{26}O_8N_2$, separates as colourless plates when ethereal solutions of the components are mixed; it has m. p. 176° (corr., decomp.). The acetal can be readily hydrolysed, but the hydrochloride of the amino-aldehyde has not been obtained in a crystalline form.

dl- α -Amino- β -phenylpropionacetal, $CH_2Ph \cdot CH(NH_2) \cdot CH(OEt)_2$, has b. p. $103-105^{\circ}$ (corr.)/ 0.25 mm. or $153.5^{\circ}/11$ mm., D_{20}^{20} 0.995, n_D^{20} 1.49383. It is practically insoluble in water, and does not reduce Fehling's solution. The *picrate*, $C_{19}H_{24}O_9N_4$, crystallises from benzene in small, yellow prisms or plates, m. p. $106-107^{\circ}$ (corr.). J. J. S.

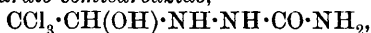
Malonamide Derivatives. MAX CONRAD and ARNOLD SCHULZE (*Ber.*, 1909, 42, 729—735).—Only one of the methylene hydrogen atoms of malonamide can be replaced by an alkyl group by treatment with sodium alkyl oxide and an alkyl halide. Methylmalonamide, $CHMe(CO \cdot NH_2)_2$, has m. p. 212° , and ethylmalonamide, m. p. $212-214^{\circ}$. *o*-Nitrobenzylmalonamide, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH(CO \cdot NH_2)_2$, m. p. 234° (decomp.), is obtained from malonamide, sodium ethoxide, and a cold alcoholic solution of *o*-nitrobenzyl chloride.

The interaction of oximinomalonamide, formic acid, D 1.22, and zinc dust on the water-bath leads to the formation of *formylaminomalonamide*, $HCO \cdot NH \cdot CH(CO \cdot NH_2)_2$, m. p. 206° (decomp.), darkening at $195-200^{\circ}$. Methyl *formylaminomalonate*, $CHO \cdot NH \cdot CH(CO_2Me)_2$, m. p. 85° , b. p. 250° (decomp.), prepared in a similar manner from methyl oximinomalonate, is converted into the preceding compound by an excess of concentrated ammonium hydroxide. Ethyl *formylaminomalonate* has m. p. 48° . The reduction of oximinomalonic esters by zinc dust and 80% acetic acid yields glycine.

Malonyldiurethane, $CH_2(CO \cdot NH \cdot CO_2Et)_2$, obtained by heating malonic acid, urethane, and acetic anhydride for five hours on the water-bath, has m. p. 124° , yields ammonium barbiturate, urethane, and malonamide by treatment with ammonia, and by heating with a solution of sodium nitrite and decomposing the cold product with the calculated amount of hydrochloric acid, forms *nitrosomalonyldiurethane*, $C_9H_{13}O_7N_3$,

m. p. 203—204°, which gives a colourless solution with sodium hydroxide, a yellow solution with ammonium hydroxide, and in aqueous solution yields a deep blue precipitate by careful treatment with sodium hydroxide and ferrous sulphate. C. S.

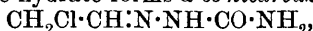
Action of Semicarbazide on Chloroaldehydes. ANDRÉ KLING (*Compt. rend.*, 1909, 148, 568—570).—Chloral hydrate or chloral alcoholate reacts readily with semicarbazide in aqueous solution, forming *chloral hydrate semicarbazide*,



an unstable, crystalline substance decomposing at 90°. When boiled with water or alcohol, it loses hydrogen chloride and forms the semicarbazone of glyoxylic acid.

When an alcoholic solution of dichloroacetaldehyde and semicarbazide is allowed to evaporate in a vacuum, *dichloroacetaldehyde semicarbazide*, $\text{C}_2\text{H}_5\text{OCl}_2\text{N}_3$, remains as a crystalline mass, m. p. 155—156° (decomp.). On boiling with water it is transformed into glyoxalsemicarbazone.

Chloroacetaldehyde hydrate forms a *semicarbazone*,



m. p. 134—135° (decomp.).

W. O. W.

Desmotropy and Merotropy. VI. Constitution of Cyanic Acid. ARTHUR MICHAEL and HAROLD HIBBERT (*Annalen*, 1909, 364, 129—146. Compare this vol., i, 91).—The authors have endeavoured to determine the constitution of cyanic acid by investigating the action of tertiary amines on the substance in the state of vapour and also in solution. The problem is complex on account of the ease of conversion into cyamelide, and the fact that, not only do the primary and secondary amines react in solution to give the corresponding salts, but also the tertiary amines, trimethylamine, triethylamine, and tripropylamine. The salt is mixed, in many cases, with cyamelide, the amount of the latter varying with the nature of the solvent. Triisocamylamine, however, does not give rise to salt formation in any solvent, the precipitate consisting exclusively of cyamelide; the same result is obtained by passing the vapour into the amine at -10° . Since it is possible to prepare the salt indirectly, and it proves to be stable under the conditions just mentioned, the conclusion is drawn that cyanic acid in the state of vapour and in solution is really carbonimide, $\text{CO}:\text{NH}$. The main support of the latter argument lies in the fact that triisocamylamine combines with the weakest acidic substances, such as phenols, to give stable salts, and its power of enolisation is practically non-existent. The salt formation in the case of the other tertiary amines is explained as follows: When a molecule of an amine, NR_3 , comes into the sphere of action of a molecule of carbonimide, $\text{O}:\text{C}:\text{NH}$, there is in every case a tendency towards salt formation. This expresses itself in a primary attraction of the positive nitrogen of the amine for the negative oxygen of the carbonimide, in consequence of which the positive character of the former undergoes a considerable alteration. As

a result, it has a greater affinity for a positive element, for example, hydrogen, which, if pronounced enough, results in the migration to

it of the hydrogen of the carbonimide, as indicated thus : $\begin{array}{c} \text{OC:NH} \\ \swarrow \searrow \\ \text{NR}_3 \end{array}$

If the character of the nitrogen of the amine is rendered strongly positive through the introduction of certain radicles, for example, *isoamyl*, then, in spite of the influencing of the negative oxygen atom, it has not the necessary affinity for hydrogen to enable it to separate the latter from the nitrogen of the carbonimide. *Triisoamylamine*, for this reason, does not yield a salt, but the large amount of free chemical energy in the molecule makes itself felt in the conversion of the carbonimide into cyamelide. From this point of view, salt formation does not presuppose the primary change $\text{-HNCO} \rightarrow \text{NCOH}$, but represents the phenomenon of merotropisation, that is, the formation of a salt directly from a merotropic substance.

The influence of various solvents on the transformation of cyanates into the corresponding carbamides has also been investigated. It is found that there is no simple relation between the specific inductive capacity of the solvent and the rate of conversion (compare Michael and Hibbert, *Abstr.*, 1908, ii, 455).

Alkylammonium cyanates have not been obtained hitherto in a pure state; they may be readily prepared, however, by adding the amine to an ethereal solution of cyanic acid at -10° , except in the case of tripropylamine, *triisobutylamine*, and *triisoamylamine*. The salts of primary and secondary amines change into the corresponding substituted carbamides at the ordinary temperature; the rate of change depends largely on the nature of the amine. The following salts were prepared in the manner just described, and analysed; they are white, crystalline substances, and melt in sealed capillary tubes at the temperatures given. *isoAmylammonium cyanate*, m. p. $49-51^\circ$; *diethylammonium cyanate*, m. p. about $30-32^\circ$; *diisobutylammonium cyanate*, m. p. $53-54^\circ$; *piperidine cyanate* softens at $35-37^\circ$; *trimethylammonium cyanate*, and *triethylammonium cyanate*. *Propylammonium cyanate* and *benzylammonium cyanate* are obtained as white precipitates by adding the amine to a solution of cyanic acid in chloroform. *Triisoamylammonium cyanate* is obtained as a thick oil by adding water to the alcoholic solution of the salt formed by shaking a solution of *triisoamylammonium chloride* in methyl alcohol with silver cyanate at -10° . W. H. G.

Fulminic Acid. II. Two New Methods of Preparation of Fulminic Acid. HEINRICH WIELAND (*Ber.*, 1909, 42, 820-822. Compare *Abstr.*, 1907, i, 196).—(1) Silver fulminate is formed by treating potassium aminomethylnitrosolate with nitric acid in the presence of silver nitrate. The aminomethylnitrosolic acid is undoubtedly decomposed thus: $\text{OH}\cdot\text{C}(\text{NH}_2)\cdot\text{N}\cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{N}_2 + \text{C}\cdot\text{N}\cdot\text{OH}$.

(2) Methenylamino-oxime, when treated with nitric acid, yields fulminic acid, which in the presence of silver nitrate is obtained as its silver salt. Nitrous oxide, undoubtedly derived from ammonium

nitrate formed during the reaction, is evolved; the methenylaminoxime is decomposed thus: $\text{CH}(\text{NH}_2):\text{N}\cdot\text{OH} \rightarrow \text{NH}_3 + \text{C}\cdot\text{N}\cdot\text{OH}$.

W. H. G.

Nitroacetonitrile. IV. WILHELM STEINKOPF (*Ber.*, 1909, 42, 617—621).—The constitution of this compound was fully established (Abstr., 1908, i, 327), but experiments to hydrolyse the nitrile to amide were unsuccessful. It is already known that trichloroacetonitrile may be hydrolysed to the corresponding amide (Abstr., 1907, i, 488), and the hydrolysis of the nitroacetonitrile, D^{18} 1.36, may be accomplished by passing dry hydrogen chloride through an ethereal solution of nitrile (1 mol.) and methyl alcohol (1 mol.) cooled by a freezing mixture: $\text{NO}_2\cdot\text{CH}_2\cdot\text{CN} + \text{MeOH} + \text{HCl} \rightarrow [\text{NO}_2\cdot\text{CH}_2\cdot\text{C}(\text{OMe})\cdot\text{NH}\cdot\text{HCl}] \rightarrow \text{NO}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2 + \text{MeCl}$. The yield is 40%, and the compound so prepared has m. p. 106—107°; it is, however, identical with nitroacetamide prepared by other methods (compare Abstr., 1905, i, 122, m. p. 101—102°; Ratz, Abstr., 1904, i, 858, m. p. 98—99°). This method is recommended as the best method for preparing it.

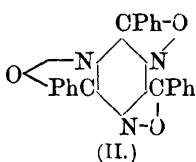
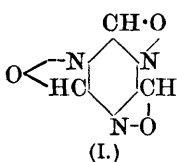
Dichloronitroacetonitrile, $\text{NO}_2\cdot\text{CCl}_2\cdot\text{CN}$, prepared by the action of chlorine on an ice-cold aqueous solution of ammonium acinitroacetonitrile, is a colourless, heavy oil, b. p. 39°/21 mm. It decomposes when boiled under atmospheric pressure, is apt to explode if impure under these conditions, and the vapour excites tears.

When an ice-cold solution of ammonium nitroacetonitrile is treated with a concentrated aqueous solution of sodium nitrite, *cyanomethylnitrolic acid*, $\text{CN}\cdot\text{C}(\text{NOH})\cdot\text{NO}_2$, is formed as a viscous oil solidifying to a mass of hygroscopic crystals. It is unstable, and forms unstable red ammonium and carmine-red silver salts.

W. R.

Nitrile Oxides. II. HEINRICH WIELAND (*Ber.*, 1909, 42, 803—816. Compare Abstr., 1907, i, 527).—It has been shown previously (Abstr., 1907, i, 196) that methylnitrolic acid when warmed with dilute nitric acid decomposes into fulminic and nitrous acids. It is now found that an aqueous solution of methylnitrolic acid when evaporated on a water-bath leaves a residue of carbamide; in this case, nitrous acid is eliminated, and the CNOH residue changes into cyanic acid, which then passes into carbamide. It seemed probable that the substance first formed in these reactions was formonitrile oxide, which then underwent transformation into cyanic acid or fulminic acid. The isolation of formonitrile oxide, although not in the unimolecular form, has shown the correctness of this assumption. When an aqueous solution of methylnitrolic acid is treated with the theoretical quantity of a 16% solution of sodium carbonate at very low temperatures, an orange-red solution is obtained, which almost immediately becomes colourless, and deposits a substance having the empirical composition CHON . This compound has the properties of the hypothetical formonitrile oxide; thus it yields salts of cyanic acid with alkalis, carbamide with ammonia, phenylcarbamide with aniline, formic acid and hydroxylamine with acids, formic acid and ammonia when reduced with zinc dust and acetic acid, hydrogen cyanide when aluminium amalgam is employed as the reducing agent, and

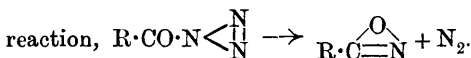
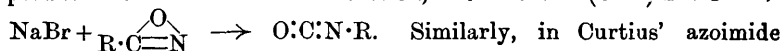
formhydroxamic acid when treated with water at the ordinary temperature. The physical properties of the substance and its close similarity to trioxymethylene, cyamelide, and cyanuric acid suggest



the constitution represented by formula I. It is proposed to name the substance *trifulmin*; it is obtained as a colourless powder, and is almost as explosive as silver fulminate.

Tribenzonitrile oxide (formula II) is prepared from phenylnitrolic acid in the same way as trifulmin. It is a colourless, crystalline substance, m. p. 125—130° (decomp.), and is not so explosive as trifulmin. In its chemical behaviour it is similar to benzonitrile oxide (compare Abstr., 1907, i, 527); thus it is converted by cold alcoholic hydrochloric acid into oxoazoxime hydrochloride to the extent of 80%, whilst the remainder is decomposed into benzoic acid and hydroxylamine. It is converted by aniline into diphenylcarbamide, and when heated in toluene or xylene passes quantitatively into phenylcarbimide.

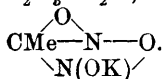
It is suggested that a nitrile oxide is formed as an intermediate product in Hofmann's reaction, thus: $R \cdot C(ONa) \cdot N \cdot Br \rightarrow$



W. H. G.

Nitrile Oxides. III. The Salts of Graul and Hantzsch's Leuconitrolic Acid. HEINRICH WIELAND (*Ber.*, 1909, 42, 816—820. Compare preceding abstract).—Ethynitrolic acid, like the corresponding methyl compound, is decomposed by an aqueous solution of sodium carbonate, yielding *triacetnitrile oxide*, $C_6H_9O_3N_3$, obtained as a brittle, vitreous mass, decomposing at about 95°; it is very similar to trifulmin in its chemical properties.

The remainder of the paper contains confirmation of the work of Graul and Hantzsch (Abstr., 1899, i, 187). It is pointed out that the leuco-salts behave as mixtures of triacetnitrile oxide with a nitrite; thus, aniline hydrochloride in aqueous solution is at once diazotised by potassium leuconitrolate; the latter when heated in xylene yields methyl carbimide, and when treated with aniline yields *s*-phenylmethylcarbamide. It is definitely shown, however, that the leuco-salts are not mixtures; moreover, they have the unimolecular formula $C_2H_5ON_2M$, and it is suggested that they have the constitution



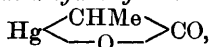
W. H. G.

Hydroxide and Salts of Mercuriethylenediamine. LEONE PESCI (*Gazzetta*, 1909, 39, i, 143—147).—Salts of mercuriethylenediamine, $Hg \cdot C_2H_4(NH_2)_2$, are prepared by the action of ethylenediamine on mercury salts, by boiling ethylenediamine salts with yellow mercuric oxide, or by double decomposition of the acetate. They are

decomposed by hydrogen sulphide, mineral acids, potassium iodide, or sodium thiosulphate.

Mercuriethylenediamine hydroxide, $C_2H_4Hg(NH_2 \cdot OH)_2 \cdot 3 \cdot 5H_2O$, prepared from the sulphate and barium hydroxide, forms a white, amorphous powder, decomp. 128° , soluble in water, decomposed by light. The *chloride* crystallises from boiling water, decomp. 160° ; the *sulphate* forms an insoluble precipitate of microscopic, rectangular tablets, containing H_2O . A preparation known as *sublimina*, containing 43% Hg, appears to contain molecular proportions of this sulphate and of ethylenediamine. The *nitrate* forms microscopic, anhydrous granules, insoluble in water; the *acetate* is also anhydrous, and forms microscopic, hexagonal scales, m. p. 195° . C. H. D.

Synthesis of α -Hydroxymercuri-fatty Acids. II. Methyl Hydroxymercurimethylmalonate and its Product of Hydrolysis, α -Hydroxymercuripropionic Anhydride. WALTER SCHOELLER and WALTER SCHRAUTH (*Ber.*, 1909, 42, 777—785. Compare Abstr., 1908, i, 617).—Whereas methyl mercuridimalonate is formed remarkably easily (*loc. cit.*), alkyl-substituted malonates react sluggishly with mercuric oxide. *Methyl α -hydroxymercurimethylmalonate*, $OH \cdot Hg \cdot CMe(CO_2Me)_2$, results when the ester ($1\frac{1}{4}$ mols.) is shaken with precipitated mercuric oxide (1 mol.) and water for four days at 37° in the dark. Admixed mercuric oxide is removed by careful washing of the product with 1% acetic acid; it decomposes at 235° , and the ester is regenerated by boiling with a halogen acid. *N*-Sodium hydroxide yields *α -hydroxymercuripropionic anhydride*,



in 97% yield; ammonium sulphide causes blackening, a reaction which appears to be a characteristic of α -hydroxymercuri-fatty acids; β -acids do not give this reaction. The blue *copper* salt, $Hg_2C_6H_{10}O_6Cu$, was analysed; the *calcium*, *lead*, and *mercury* salts are white; the *silver*, yellowish-white. Towards mineral acids it behaves similarly to its lower homologue (*loc. cit.*). Sodium α -hydroxymercuripropionate is poisonous, "organotrop"; the β -hydroxy-salt is, on the other hand, a disinfectant, "parasitotrop."

Hydroxymercuripropionic anhydride can be obtained in 93% yield from mercury acetamide and methyl methylmalonate in the presence of alkali. The acetamide formed initially from the condensation of mercury acetamide and methyl methylmalonate is soluble in water, whereas that from methyl malonate is not, and as these regenerate the ester with hydrochloric acid, advantage is taken of these facts for the purification of commercial malonic esters. W. R.

So-called Pure $\Delta^{1,3}$ -Dihydrobenzene and its Molecular Refraction. CARL D. HARRIES and HANS VON SPLAWA-NEYMAN (*Ber.*, 1909, 42, 693—698).—According to Zelinsky and Gorsky (Abstr., 1908, i, 619), $\Delta^{1,3}$ -cyclohexadiene exhibits no optical exaltation, although it contains conjugate double linkings. Brühl (*ibid.*, ii, 1002) has already questioned the constitution of this compound, and the authors bring forward evidence which indicates that the product

obtained by Crossley's (Trans., 1906, 85, 1403) or Zelinsky's (*loc. cit.*) method is a mixture of $\Delta^{1,3}$ -cyclohexadiene and cyclohexene.

This evidence is based on the fact that the ozonide of the hydrocarbon when decomposed with acetic acid yields adipindialdehyde as well as succindialdehyde, and from the former, cyclopentaldehyde (Baeyer and Liebig, Abstr., 1898, i, 638) was readily isolated. J. J. S.

Sodium Derivative of Indene. RUDOLF WEISSGERBER (*Ber.*, 1909, 42, 569—572); GESELLSCHAFT FÜR TEERVERWERTUNG (D.R.-P. 205645. Compare Abstr., 1908, i, 873).—Many unsuccessful attempts have been made to obtain the potassium derivative of indene (compare Thiele, Abstr., 1901, i, 182; Kraemer, *ibid.*, 535). It is now found that the sodium derivative, $C_6H_4 \begin{array}{c} \text{CH} \\ \text{CHNa} \end{array} \text{CH}$, may be prepared by heating indene with sodamide at 110—115°, by treating indene and sodium at 120—130° with ammonia, or by heating indene with sodium at 140—150°; it is obtained as a brown, amorphous mass having the appearance of colophony. The formation of the sodium derivative of indene furnishes a ready means of obtaining this hydrocarbon in a state of purity from the so-called "heavy benzene," b. p. 175—185°, obtained from coal-tar. This fraction is treated in the manner just described, the unattacked hydrocarbon removed by distillation under reduced pressure, and the sodium indene decomposed with water. W. H. G.

Indene in Coal Tar. ADOLF SPILKER and ALFRED DOMBROWSKY (*Ber.*, 1909, 42, 572—573. Compare Kraemer and Spilker, Abstr., 1891, 205).—Pure indene, obtained from coal-tar by the method described in the preceding abstract, has b. p. 182.2—182.4°/761 mm. (corr.), D_{16}^{25} 1.0002, $n_D^{18.5}$ 1.5773, f. p. -2°. Indene dibromide, contrary to the statement of Kraemer and Spilker (*loc. cit.*), is a stable substance crystallising in colourless, thick prisms, m. p. 31.5—32.5°. W. H. G.

Photochemical Reactions of the White and Yellow Diphenyl-octatetrenes. HANS STOBBE (*Ber.*, 1909, 42, 565—568. Compare Abstr., 1908, ii, 339).—From the method of formation, it is probable that the white $\alpha\theta$ -diphenyl- $\Delta^{\gamma\epsilon\eta}$ -octatetrene of Fichter and Hirsch (Abstr., 1901, i, 594) and the yellow $\alpha\theta$ -diphenyl- $\Delta^{\gamma\epsilon\eta}$ -octatetrene of Fittig and Batt (Abstr., 1904, i, 744) are stereoisomerides, in which case it should be possible to convert one into the other by the action of light. It is found that both substances in the presence of air and under the influence of light undergo oxidation, yielding resinous products containing benzaldehyde and benzoic acid. In the absence of oxygen, however, only one substance is acted on, namely, the yellow variety, which passes into the white isomeride. W. H. G.

Photochemical Reactions. IV. Thermodynamic Theory of Photochemical Processes. FRITZ WEIGERT (*Ber.*, 1909, 42, 850—862. Compare Abstr., 1908, ii, 914).—The photopolymerisation of anthracene to dianthracene has been further studied. The proportionality previously found between the amount of light energy

used chemically and the total energy absorbed by the anthracene is confirmed. From experiments made in the dark at 85° and 105°, the conclusion is drawn that the equilibrium $2C_{14}H_{10} \rightleftharpoons C_{28}H_{20}$ is altered in favour of the dianthracene at the higher temperature, and the thermal value of the polymerisation is calculated as -20,000 cal. The relation between the equilibrium constant in the dark and temperature is expressed by the equation $\log K = -4330/T + 10.27$, which has been tested by experiments at different temperatures in toluene solution, and also in benzene and xylene. The high value of 4.5% has been experimentally found to represent that proportion of the energy absorbed by the anthracene which is used chemically.

When a platinum wire heated electrically is made to glow (temperature about 900°) in a boiling solution of anthracene in ether, or light petroleum, which contains solid anthracene, a crust is formed on the wire. This in part consists of dianthracene. E. F. A.

Preparation of Aniline and its Homologues. AKTIENGESSELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 204951).—The halogen of chlorobenzene can be replaced by ammonia by heating the halogenated hydrocarbon with ammonia in presence of copper salts. Chlorobenzene (200 parts), 25% aqueous ammonia (600 parts), and copper sulphate (25 parts), when heated at 180—200° for twenty hours, yield 80% of the calculated amount of aniline. G. T. M.

Preparation of Sulphanilic Acid. AKTIENGESSELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 205150).—Sulphanilic acid in an 80% yield can be obtained by heating chlorobenzene-*p*-sulphonic acid with aqueous ammonia and copper chloride at 170° for twelve hours. G. T. M.

Action of Calcium Hypochlorite on *m*-Nitroaniline. WILHELM KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 93—103. Compare Abstr., 1908, i, 523).—By the action of calcium hypochlorite, in such quantity as to contain $1\frac{1}{2}$ mols. of active chlorine, on 1 mol. of *m* nitroaniline in glacial acetic acid at 40—60°, allowing the solution to remain for twelve hours, a reddish-brown product is obtained when ice-water is added, and a further brownish-yellow precipitate is obtained on partial neutralisation of the filtrate.

The first product consists mainly of 2:6-dichloro-3-nitroaniline, long needles, m. p. 110.8°. The *acetyl* derivative forms glistening crystals, m. p. 128.6°. Together with this is the 2:4:6 trichloro-3-nitroaniline, m. p. 102.5°, the *acetyl* derivative has m. p. 194—195°, and also 2:4-dichloro-3-nitroaniline, m. p. 97.5°, *acetyl* derivative has m. p. 128.9°.

The second fraction contains chiefly 4-chloro-3-nitroaniline, m. p. 97.6°; *acetyl* derivative, m. p. 150°. No trace of 4:6-dichloro-3-nitroaniline could be detected. C. H. D.

[Preparation of the Alkali Derivatives of Aromatic Primary and Secondary Amines.] BASLER CHEMISCHE FABRIK (D.R.-P. 205493).—The aromatic amines do not react readily with the alkali

metals, but it has now been found that when a mixture of alkali metal and an alkali hydroxide is employed, the reaction proceeds smoothly.

A mixture of metallic sodium and potassium hydroxide heated to 200—260° was employed, and at these temperatures aniline, *o*-toluidine, and methylaniline were readily absorbed, forming mixtures of their sodium and potassium derivatives, which were thus obtained as crystalline, dark brown, very reactive products, regenerating the base on treatment with water. G. T. M.

Mercury Double Salts of Tetrahydronaphthylamines. OSKAR GROHMANN and ARJEN BROUWER (*Annalen*, 1909, 365, 50—52. Compare Bamberger, *Abstr.*, 1888, 600, 960).—*ac*- β -Tetrahydronaphthylamine hydrochloride combines with mercuric chloride in two proportions. The one compound, $C_{10}H_{11}\cdot NH_2\cdot HCl\cdot 2HgCl_2$, crystallises from water in long, glistening prisms, m. p. 241·5—242°; the other, $2(C_{10}H_{11}\cdot NH_2\cdot HCl)\cdot HgCl_2$, crystallises in colourless plates, m. p. 221—222°, and is only formed in the presence of an excess of hydrochloric acid. When crystallised from water it yields the less fusible compound.

ar- α -Tetrahydronaphthylamine yields the compound

$C_{10}H_{11}\cdot NH_2\cdot HCl\cdot HgCl_2$, m. p. 179—180°; also a compound, $2(C_{10}H_{11}\cdot NH_2\cdot HCl)\cdot HgCl_2$, which crystallises in doubly refracting plates, m. p. 217·5—219°, and a third compound, $C_{10}H_{11}\cdot NH_2\cdot HCl\cdot 2HgCl_2$, which forms colourless, prismatic needles, m. p. 192·5—193·5°. J. J. S.

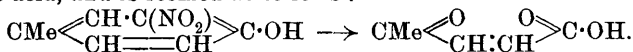
Preparation of 2-*p*-Nitrosoanilinonaphthalene-6 : 8-disulphonic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 205414).—When treated with alcoholic, or concentrated aqueous, hydrochloric acid the nitrosoamines of the 2-arylam'nonaphthalenes are converted into nitroso-derivatives containing the nitroso-group in the contiguous α -position of the naphthalene nucleus. When the nitrosamine of 2-anilinonaphthalene-6 : 8-disulphonic acid is thus treated, the nitroso-group migrates into the phenyl ring in the para-position to the aminic nitrogen, forming 2-*p*-nitrosoanilinonaphthalene-6 : 8-disulphonic acid, $NO_2\cdot C_6H_4\cdot NH\cdot C_{10}H_5(SO_3H)_2$, reddish-brown needles, readily soluble in water. G. T. M.

The Compounds which Cause the Red Colour in Phenol. HARRY D. GIBBS (*Philippine J. Sci.*, 1908, A, 3, 361).—Phenol, which had become red by exposure to sunlight at a temperature of 30°, was treated with a small quantity of sulphurous acid and distilled in steam; the residue in the distillation flask, after filtration from a very small amount of red precipitate, was extracted with ether, and found to contain considerable quantities of catechol and quinone. The red colour is attributed to the solution in phenol of quinone and the highly-coloured condensation product phenoquinone. The presence of oxygen was proved to be necessary for the production of the red colour, since no coloration was produced in moist phenol contained in sealed tubes filled with carbon dioxide on exposure to

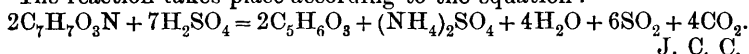
sunlight. This fact, moreover, appears to show that water and carbon dioxide do not react in the presence of sunlight to form hydrogen peroxide and oxygen, as assumed by von Baeyer, since the presence of oxygen in these experiments would have been revealed by the production of a red colour. P. H.

Preparation of *p*-Aminophenol and its *N*-Alkyl Derivatives. AKTIENGESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 205415).—By heating *p*-chlorophenol at 135—140° with ammonia or primary bases (such as methylamine) in the presence of copper salts (copper sulphate, for example), *p*-aminophenol, *p*-methylaminophenol and similar compounds are readily obtained in excellent yield. *p*-Ethylaminophenol, white needles, m. p. 100°, which is thus obtained, gives an oily nitroso-compound. G. T. M.

Behaviour of 3-Nitro-*p*-cresol towards Sulphuric Acid. GUSTAV SCHULTZ and OSKAR LÖW (*Ber.*, 1909, 42, 577—578).—The compound obtained by the action of fuming sulphuric acid on 3-nitro-*p*-cresol, previously thought to have the formula $C_7H_8O_4$ (Schultz, *Abstr.*, 1907, i, 1030), has now been found to be identical with acetyl-acrylic acid, and is formed as follows :



The reaction takes place according to the equation :



Intramolecular Transformations of Acylated Compounds. KARL AUWERS (*Annalen*, 1909, 364, 147—182).—The results obtained in this investigation, together with those published previously on the intramolecular transformations of acylated phenols containing amino- and imino-groups (compare Auwers, *Abstr.*, 1904, i, 581, 736, 1051; Auwers and Bondy, *ibid.*, 1053; Auwers and Bürger, *ibid.*, 1054; Auwers and Dannehl, *Abstr.*, 1908, i, 458), are discussed in detail, and the following conclusions drawn: (1) In ordinary circumstances an acyl group migrates spontaneously from the oxygen to the nitrogen, no matter whether this be the first, second, or third member of a side-chain in the ortho-position, provided the acid character of the acyl group and the basic character of the nitrogen group are sufficiently pronounced. (2) The migration of the acyl group is rendered more difficult by greatly diminishing the basic character of the amino- or imino-group; in many cases a rearrangement is totally prevented. (3) The migration of the acyl group is similarly affected by reducing the acidic character of the acid radicle, but up to the present no case has been observed where the migration has been completely checked. (4) The nitrogen group is able to attract both heavy and light acid radicles, provided its basic character is sufficiently pronounced. The relative weight of the acyl group is, however, a determinative factor in the intramolecular transformation when the compound is a neutral substance, or only slightly basic; as a rule, in such cases, the ease with which the acyl group migrates diminishes greatly with an increase in the weight of the group.

[With KARL MÜLLER.]—*p*-Tolyl methyl ether and chloroacetyl chloride react in equivalent proportions in the presence of aluminium chloride, yielding 3-chloroacetyl-*p*-cresol and 3:5-dichloroacetyl-*p*-cresol (compare Fries and Finck, this vol., i, 42). 3:5-Diacetyl-*p*-cresol, $C_{11}H_{12}O_3$, is obtained when 3 mols. of chloroacetyl chloride are employed; it crystallises in slender needles and long, compact prisms, m. p. 82—83°. 3-Chloroacetyl-*p*-cresol, when reduced with zinc dust and acetic acid, yields 3-acetyl-*p*-cresol, long, glistening, colourless prisms, m. p. 50° (compare Auwers and Betteridge, Abstr., 1900, ii, 262), and when heated with benzoyl chloride yields the *benzoate*, $C_{16}H_{13}O_3Cl$, long, glistening prisms, m. p. 92°. The latter substance, when heated with aniline or *p*-toluidine dissolved in toluene, yields

N-benzoyl-3-phenylglycyl-*p*-cresol, $\begin{array}{c} \text{CH}-\text{CMe}:\text{CH} \\ | \quad | \\ \text{CH}\cdot\text{C}(\text{OH})\cdot\text{C}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NPhBz} \end{array}$, pearly

scales, m. p. 172·5°, and N-benzoyl-3-*p*-tolylglycyl-*p*-cresol, $C_{23}H_{21}O_3N$, silvery leaflets, m. p. 193·5°; the *oxime* of the former, $C_{22}H_{20}O_3N_2$, forms flat, compact needles, m. p. 157—158°. 3-Phenylglycyl-*p*-cresol, $C_{15}H_{15}O_2N$, obtained by boiling 3-chloroacetyl-*p*-cresol with an alcoholic solution of aniline, crystallises in small, slightly yellow needles, m. p. 82—83°; it yields the N-benzoyl derivative, m. p. 172·5°, even when benzoylated in pyridine.

[With HUGO DANNEHL.]—When the acetate of dibromo-*p*-hydroxybenzyl bromide is heated with *p*-nitrophenylhydrazine under pressure at 100°, it yields the α -N-acetate of dibromo-*p*-hydroxybenzyl-*p*-nitrophenylhydrazine, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NAc}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, a chocolate-brown, crystalline substance, m. p. 258—259° (decomp.); the same compound is obtained by condensing *s*-acetyl-*p*-nitrophenylhydrazide with dibromo-*p*-hydroxybenzyl bromide.

[With FRITZ EISENLOHR.]—The phenylurethane of 3-nitro-*p*-cresol, $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$, is obtained by heating the nitrocresol with phenylcarbimide under pressure at 120—130°; it forms pale yellow crystals, m. p. 102°, and when reduced with zinc dust and acetic acid yields O-carbanilido-3-amino-*p*-cresol, $C_{14}H_{14}O_2N_2$, white crystals, m. p. 169°, and N-carbanilido-3-amino-*p*-cresol, $C_{14}H_{14}O_2N_2$; the latter substance may also be prepared by the action of phenylcarbimide on 3-amino-*p*-cresol, or by treating the O-derivative with hot glacial acetic acid; it crystallises in slender, silky needles, m. p. 158—159°.

[With W. HIRT and KARL MÜLLER.]—3-Benzeneazo-*p*-tolyl propionate, $C_{16}H_{16}O_2N_2$, obtained by the action of propionyl chloride on 3-benzene-azo-*p*-cresol, forms small, bright red needles, m. p. 48—49°, and is reduced by sodium amalgam to the corresponding hydrazo-derivative, $C_{16}H_{18}O_2N_2$, a green powder, m. p. 100° (decomp.).

p-Tolueneazo-*p*-tolyl propionate, $C_{17}H_{18}O_2N_2$, can only be obtained by heating the azo-phenol with propionic anhydride; it crystallises in dark red leaflets, m. p. 62°, and when reduced yields the corresponding hydrazo-derivative, $C_{17}H_{20}O_2N_2$, obtained as colourless leaflets, m. p. 105°. Both of the preceding hydrazo-compounds are definitely shown to be O-propionates.

Dibromo-o-propionoxybenzyl bromide, $C_{10}H_9O_2Br_3$, forms white, felted needles, m. p. 89°, and when acted on by phenylhydrazine yields

the α -N-propionyl-3:5-dibromo-2-hydroxybenzylphenylhydrazine, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{N}(\text{COEt})\cdot\text{NHPh}$, pearly leaflets, m. p. 164° ; the same compound is obtained by the action of *s*-propionylphenylhydrazine on dibromo-*o*-hydroxybenzyl bromide. Dibromo-*o*-propionoxybenzyl bromide, when treated with *s*-acetylphenylhydrazine, yields the *o*-propionate of α -N-acetyldibromo-*o*-hydroxybenzylphenylhydrazine, $\text{C}_{18}\text{H}_{18}\text{O}_3\text{N}_2\text{Br}_2$, crystallising in glistening leaflets, m. p. 188 — 189° . The substance is not affected by boiling with glacial acetic acid.

W. H. G.

Crystallography of *p*-Dithymolylamine Dimethyl Ether. A. FERSMANN (*Zeitsch. Kryst. Min.*, 1909, 46, 219; from *Bull. Soc. Nat. Moscou*, 1906, Nos. 1 and 2, 133—138).—The crystals are rhombic [$a:b:c = 1.152:1:0.685$] (compare Decker and Solonina, *Abstr.*, 1905, i, 197).

L. J. S.

Separation of *o*- and *p*-Phenolsulphonic Acids. JULIUS OBERMILLER (D.R.-P. 202168).—A solution of *o*- and *p*-phenolsulphonic acids is treated with barium carbonate and evaporated until granular aggregates of barium *o*-phenolsulphonate separate, accompanied by needles of the para-salt. The latter is dissolved by the cautious addition of water, and the less soluble ortho-salt thus separated. The mother liquor is treated with magnesium sulphate and evaporated until magnesium *p*-phenolsulphonate separates. The final mother liquor contains a little of the meta-isomeride and more of the ortho-salt.

When the free acids are converted into magnesium salts and their solutions evaporated, the major portion of the para-salt separates first. Further addition of magnesia to the mother liquor leads to separation of the dimagnesium salt of the ortho-acid.

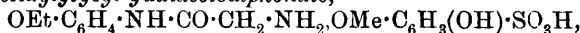
G. T. M.

Preparation of *p*-Aminophenol-2 sulphonic Acid. AKTIENGESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 202566).—*p*-Aminophenol-2-sulphonic acid is prepared by heating 4-chlorophenol-2-sulphonic acid with aqueous ammonia and copper chloride at 165° .

G. T. M.

New Salts of Guaiacolsulphonic Acid. ACHILLE TAGLIAVINI (*Boll. chim. farm.*, 1909, 48, 6—9).—Potassium guaiacolsulphonate is used as a drug; salts have now been prepared with antipyretic and analgesic bases.

p-Phenetidylglycyl guaiacolsulphonate,



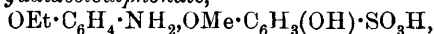
prepared by adding an ethereal solution of the base to a concentrated alcoholic solution of the acid, forms small crystals, m. p. 183° .

Euquinine guaiacolsulphonate,



prepared by mixing hot solutions of basic euquinine sulphate and barium guaiacolsulphonate, forms a powder, m. p. 84° .

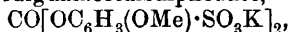
p-Phenetidine guaiacolsulphonate,



prepared similarly to the first salt mentioned, forms microscopic crystals, m. p. 186—188°. C. H. D.

Preparation of Salts of Carbonatoguaiacol-mono- and -disulphonic Acids. ALFRED EINHORN (D.R.-P. 203754).—It has been found that carbonyl chloride will condense with alkali guaiacolsulphonates in alkaline solution, giving derivatives in which the carbonyl group becomes attached to two phenolic oxygens.

Potassium carbonatodiguiacoldisulphorate,



needles from water, is produced by passing carbonyl chloride into an alkaline solution of potassium guaiacolsulphonate (thiocol). Potassium carbonatodiguiacolsulphonate, $\text{C}_6\text{H}_4(\text{OMe})\cdot\text{O}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{SO}_3\text{K}$, is similarly obtained from a mixture of guaiacol and its sulphonate.

G. T. M.

2-Hydroxystilbene. STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1909, 42, 825—827).—2-Hydroxystilbene, prepared from 2-methoxystilbene by heating with alcoholic potassium hydroxide at 160°, crystallises in colourless needles, m. p. 147°, which dissolve in dilute sodium hydroxide with a green fluorescence; 2-acetoxystilbene forms colourless needles, m. p. 54—55°.

2-Acetoxystilbene dibromide, $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CHPhBr}$, prepared by the addition of bromine in carbon disulphide solution, separates in long, glistening needles, m. p. 150°. When heated with sodium ethoxide, it is converted into the 1-phenylcoumarone, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{O} \\ \text{CH} \end{smallmatrix}\rangle\text{CPh}$, m. p. 120—121°, described by Stoermer (*Abstr.*, 1904, i, 181).

2-Stilbenyloxyacetic acid, $\text{CHPh}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, crystallises in long needles, m. p. 136°; the dibromide forms colourless needles, m. p. 188° (decomp.).

Ethylene di-2-stilbenyl ether, $\text{C}_2\text{H}_4(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CHPh})_2$, formed by the action of ethylene bromide on an alcoholic solution of sodium-*o*-hydroxystilbene, crystallises in colourless needles, m. p. 110°.

E. F. A.

Preparation of Anthranol and its Derivatives from the Corresponding Anthraquinones by Reduction with Metals and Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 201542).—Anthranol is readily obtained by adding copper or aluminium powder to a solution of anthraquinone in concentrated sulphuric acid at 30—40°, and pouring the decolorised solution into water; it is recrystallised from glacial acetic acid containing a trace of aluminium and a little hydrochloric acid.

α -Aminoanthranol can be similarly prepared from α -aminoanthraquinone by reduction with aluminium bronze in cold concentrated sulphuric acid.

G. T. M.

Disoeugenol. ERNESTO PUXEDDU (*Gazzetta*, 1909, 39, i, 131—137).—Whilst isoeugenol and similar compounds containing the allyl group readily polymerise, the isomerides containing the propenyl group do not yield polymerides. isoeugenol is best etherified by treatment

with sodium hydroxide and ethyl sulphate; the ethyl ether forms brilliant scales, m. p. 64° (compare Eykman, Abstr., 1890, 748). The molecular weight in acetic acid solution is normal. Dry hydrogen chloride in ethereal solution converts it into a polymeride crystallising from aqueous alcohol in white prisms, m. p. 130° . The polymeride obtained by Wassermann (Abstr., 1879, 790) had a lower m. p. and was insoluble in ether, whereas the new compound dissolves readily in ether. It is insoluble in water, dilute acids, or aqueous alkalis.

Diisoeugenol is best prepared by heating an alcoholic solution of isoeugenol with fuming hydrochloric acid on the water-bath. It forms white needles, m. p. 180° . Ethyl sulphate or iodide converts its sodium derivative into an ethyl ether identical with that obtained by the direct polymerisation of isoeugenol ethyl ether.

The nature of the isomerism of the two diethyl ethers is not yet certain. The products of bromination and oxidation are under investigation. C. H. D.

Polymerisation of Aromatic Ethylenic Compounds. LUIGI FRANCESCONI and ERNESTO PUXEDDU (*Gazzetta*, 1909, 39, i, 202—211).—Although compounds in which the side-chain contains a pair of doubly-linked carbon atoms, one of which is directly joined to the benzene ring, generally polymerise, there are great differences in the readiness with which polymerisation takes place in related compounds. The authors have studied the influence of constitution in the case of eugenol and isoeugenol and their ethers, and of safrole and isosafrole.

Diisoeugenol is obtained when light acts on an alcoholic solution of isoeugenol in presence of hydrochloric acid, or by the action of hydrogen chloride on the dry ethereal solution (compare Puxeddu, preceding abstract). The product is in all cases identical with that obtained by Tiemann (Abstr., 1892, 45) by the hydrolysis of the acetyl derivative.

Eugenol and safrole do not polymerise when treated by either method. isosafrole yields a viscous product.

Diisoeugenol dimethyl ether crystallises from aqueous alcohol in long, white needles, m. p. 106° .

Bromine reacts with diisoeugenol in chloroform solution, yielding a dibromo-derivative, m. p. 168° , which on analysis did not give figures corresponding with any simple formula.

Bromine converts diisoeugenol dimethyl ether in ethereal solution into a monobromo-derivative, $C_{22}H_{27}O_4Br$, crystallising from alcohol, m. p. 125° . C. H. D.

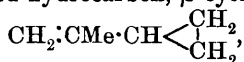
Cyclic Trimethylene Compounds of the Type $RHC \begin{smallmatrix} \diagup CH_2 \\ \diagdown CH_2 \end{smallmatrix}$.

PIERRE BRUYLANTS (*Bull. Acad. roy. Belg.*, 1908, 1011—1084).—The author has prepared a series of compounds containing the cyclopropyl group, and has recorded in a series of tables the relations obtaining between the boiling points and densities of these compounds and the corresponding isopropyl and allyl derivatives. The compounds examined include: (1) ketones of the type $R \cdot CO \cdot CH \begin{smallmatrix} \diagup CH_2 \\ \diagdown CH_2 \end{smallmatrix}$, obtained by

the action of organomagnesium derivatives on ethylenoacetonitrile (*cyclopropanecarboxylonitrile*), $\text{NC}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2 \\ | \\ \text{CH}_2\end{smallmatrix}\right\rangle$; (2) the secondary alcohols, $\text{OH}\cdot\text{CHR}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2 \\ | \\ \text{CH}_2\end{smallmatrix}\right\rangle$, prepared from the ketones by reduction; (3) the tertiary alcohols, $\text{OH}\cdot\text{CRR}'\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2 \\ | \\ \text{CH}_2\end{smallmatrix}\right\rangle$, prepared by applying the Grignard reaction to the ketones; (4) the chlorides, bromides, iodides, and acetates of the tertiary alcohols; (5) the ethers and unsaturated hydrocarbons obtained from these salts.

cycloPropyl methyl ketone, $\text{COMe}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2 \\ | \\ \text{CH}_2\end{smallmatrix}\right\rangle$ (Perkin, *Trans.*, 1885, 835; Lipp, *Abstr.*, 1889, 843), prepared by the action of magnesium methyl bromide on *cyclopropanecarboxylonitrile*, has b. p. $114^\circ/772$ mm. *cycloPropyl ethyl ketone*, $\text{COEt}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2 \\ | \\ \text{CH}_2\end{smallmatrix}\right\rangle$, b. p. $132\text{--}133^\circ$ (corr.)/767 mm., D^{20} 0.9152, n_D^{20} 1.42931, on reduction with sodium and alcohol yields *cyclopropylethylcarbinol*, $\text{OH}\cdot\text{CHEt}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2 \\ | \\ \text{CH}_2\end{smallmatrix}\right\rangle$, b. p. $140^\circ/767$ mm., D^{20} 0.8901, n_D^{20} 1.4326; the *acetate* has b. p. $159^\circ/765$ mm., D^{20} 0.8175. *cycloPropyl isopropyl ketone*, $\text{COPr}^\beta\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2 \\ | \\ \text{CH}_2\end{smallmatrix}\right\rangle$, b. p. $139\text{--}141^\circ/769$ mm., D^{20} 0.9006, n_D^{20} 1.42731, yields on reduction *cyclopropylisopropylcarbinol*, $\text{OH}\cdot\text{CHPr}^\beta\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2 \\ | \\ \text{CH}_2\end{smallmatrix}\right\rangle$, b. p. $151\text{--}152^\circ/769$ mm., n_D 1.43643; the *acetate* has b. p. $171\text{--}173^\circ$.

cycloPropyldimethylcarbinol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2 \\ | \\ \text{CH}_2\end{smallmatrix}\right\rangle$ (Zelinsky, *Abstr.*, 1901, i, 661; 1902, i, 70), prepared by the action of magnesium methyl bromide on ethyl *cyclopropanecarboxylate*, has b. p. $124^\circ/776$ mm., D^{20} 0.9335, n_D^{20} 1.43232; the *chloride* has b. p. $132\text{--}133^\circ$, D^{20} 0.9441; the *bromide* has b. p. $152\text{--}153^\circ/766$ mm., D^{20} 1.218; the *iodide* has b. p. $113\text{--}114^\circ/55$ mm., D^{20} 1.338; the *acetate* has b. p. $159\text{--}160^\circ$, D^{20} 0.9167. The unsaturated hydrocarbon, β -*cyclopropylpropylene*,



b. p. $77^\circ/758$ mm., D^{20} 0.7375, n_D^{20} 1.45037, is obtained advantageously by the action of dry potassium hydroxide on the preceding bromide at 170° ; it is also produced by the action of alcoholic potassium hydroxide on the chloride, bromide, or iodide, or by the direct dehydration of the alcohol by means of phosphoric oxide, and combines with bromine to form the *tribromo*-derivative, $\text{CH}_2\text{Br}\cdot\text{CMeBr}\cdot\text{CBr}\left\langle\begin{smallmatrix}\text{CH}_2 \\ | \\ \text{CH}_2\end{smallmatrix}\right\rangle$. 1-Ethoxy-

1-isopropylcyclopropane, $\left\langle\begin{smallmatrix}\text{CH}_2 \\ | \\ \text{CH}_2\end{smallmatrix}\right\rangle\text{CPr}^\beta\cdot\text{OEt}$, b. p. $140\text{--}145^\circ$, D^{20} 0.82493, n_D^{20} 1.42481, is formed together with the preceding hydrocarbon when *cyclopropyldimethylcarbinol* is heated with alcohol at 100° , or by the action of alcoholic potassium hydroxide on its bromide, chloride, or

iodide; it reacts with hydrobromic acid to form 1-bromo-1-isopropyl-cyclopropane, $\begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix} > \text{CPr}^\beta \text{Br}$, b. p. 174° or $108\text{--}110^\circ/55$ mm., D^{20} 1.1597, which is isomeric with the bromide of the original alcohol.

cycloPropyldiethylcarbinol, $\text{OH} \cdot \text{CEt}_2 \cdot \text{CH} < \begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix}$, has b. p. $158\text{--}159^\circ/759$ mm., D^{20} 0.9055, n_D^{20} 1.44638; the *chloride* has b. p. $160\text{--}166^\circ$, D^{20} 0.9407; the *bromide* has b. p. $186\text{--}187^\circ/756$ mm., D^{20} 1.1479; the *iodide* has b. p. $152^\circ/55$ mm., D^{20} 1.3357; when the bromide is heated with alcoholic potassium hydroxide, a mixture of the ethylenic *hydrocarbon*, $\text{CHMe} \cdot \text{CEt} \cdot \text{CH} < \begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix}$, γ -cyclopropyl- Δ^β -amylene, and the *ether*, $\text{CHEt}_2 \cdot \text{C}(\text{OEt}) < \begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix}$ (β -ethyl- α -ethyleno- α -ethoxybutane), is produced; the hydrocarbon has b. p. $129\text{--}130^\circ$, D^{20} 0.7644, n_D^{20} 1.45841, and the ether has b. p. $176\text{--}178^\circ$, D^{20} 0.8130.

cycloPropylmethylethylcarbinol, $\text{OH} \cdot \text{CMeEt} \cdot \text{CH} < \begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix}$, has b. p. $141\text{--}142^\circ/761$ mm., D^{20} 0.90119, n_D^{20} 1.44135; the *chloride* has b. p. $150\text{--}153^\circ$, D^{20} 0.9391; the *bromide* has b. p. $167\text{--}168^\circ/766$ mm., D^{20} 1.1938; the *iodide* has b. p. $128\text{--}130^\circ/55$ mm., D^{20} 1.3499. The ethylenic *hydrocarbon*, $\text{CHMe} \cdot \text{CMe} \cdot \text{CH} < \begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix}$ (β -cyclopropyl- Δ^β -butylene), is obtained from the preceding bromide by the action of potassium hydroxide at 170° , and has b. p. $107\text{--}109^\circ/764$ mm., D^{20} 0.7743, n_D^{20} 1.44476. M. A. W.

Action of Sodium and Amyl Alcohol on Cholesterol. G. G. WILENKO and SIGMUND MOTYLEWSKI (*Bull. Acad. Sci. Cracow*, 1908, 837—841. Compare Diels and Abderhalden, *Abstr.*, 1906, i, 272; Neuberg, *ibid.*, 356; Windaus, *ibid.*, 1907, i, 610).—In addition to dihydrocholesterol two new products have been obtained by reducing cholesterol with sodium and boiling amyl alcohol. One of these resembles coprosterol, and is termed 1-coprosterol. Of the three compounds it is the one most readily soluble in ethyl alcohol, and crystallises in long needles, m. p. $86\text{--}87^\circ$. It has $[\alpha]_D -14.3^\circ$, and gives most of the colour reactions characteristic of ordinary coprosterol. The third product, termed γ -cholesterol, $\text{C}_{27}\text{H}_{46}\text{O}$, is sparingly soluble in ethyl alcohol, and crystallises in glistening, rhombic plates, m. p. $135\text{--}137^\circ$. Some specimens were dextro-rotatory, others inactive. It yields an *acetate*, m. p. $100\text{--}102^\circ$, but does not form an additive compound with bromine. The best yields of γ -cholesterol are obtained when the reduction is carried out at $110\text{--}115^\circ$. Higher temperatures favour the formation of 1-coprosterol. J. J. S.

Phytosterol from Rape Seed Oil. ADOLF WINDAUS and A. WELSCH (*Ber.*, 1909, 42, 612—616. Compare Windaus and Hauth, *Abstr.*, 1907, i, 129, 921).—The phytosterol from rape seed oil, like

phytosterols from other sources, is a mixture of a stigmasterol and a sitosterol, which may be separated by the action of bromine on the mixture of acetyl derivatives. The stigmasterol yields a compound, $C_{30}H_{48}O_2Br_4$, analogous to stigmasteryl acetate tetrabromide. This is termed *brassicasteryl acetate tetrabromide*, and crystallises from a mixture of chloroform and alcohol in well-developed, rhombic plates, which decompose at 209° .

Brassicasteryl acetate, $C_{30}H_{48}O_2$, obtained by the action of zinc dust and acetic acid on the tetrabromide, crystallises from alcohol in thin, six-sided plates, m. p. $157-158^\circ$. When hydrolysed with alcoholic potash it yields *brassicasterol*, $C_{28}H_{46}O, H_2O$, which also crystallises from alcohol in six-sided plates, m. p. 148° . It loses the water of hydration at 100° , and has $[\alpha]_D^{18} - 64^\circ 25'$ in chloroform and $-63^\circ 31'$ in ether; the *propionate*, $C_{31}H_{50}O_2$, has m. p. 132° , and yields a *tetrabromide* which decomposes at 206° . The *benzoate* crystallises from alcohol in long, glistening needles, m. p. 167° .

The sitosterol can be obtained from the mother liquors of the stigmasterol tetrabromide in the form of its dibromide. The sitosterol has m. p. 142° and $[\alpha]_D^{20} - 34^\circ 20'$ in ether. The acetate has m. p. 134° ; propionate, 116° ; cinnamate, 151° , and benzoate, 143° .

J. J. S.

Preparation of Crystalline Salts of *o*-Dihydroxyphenylethanolmethylamine. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 202169. Compare Abstr., 1908, i, 418).—*o*-Dihydroxyphenylethanolmethylamine hydrochloride, colourless crystals, m. p. 157° , was prepared by adding alcoholic hydrochloric acid to synthetically prepared *o*-dihydroxyphenylethanolmethylamine moistened with absolute alcohol.

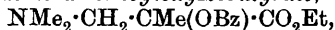
G. T. M.

Crystallography of 2-Methylcyclohexyl Benzoate. MISS E. D. REVUTZKY (*Zeitsch. Kryst. Min.*, 1909, 46, 218; from *Bull. Soc. Nat. Moscou*, 1906, Nos. 1 and 2, 139—141).—The crystals are rhombic [$a:b:c = 0.9460:1:0.7811$].

L. J. S.

Preparation of Acyl Derivatives of the Esters of the Aminohydroxy-acids. LES ÉTABLISSEMENTS POULENC FRÈRES (D.R.-P. 202167. Compare Abstr., 1908, i, 937).—The acylation of the alkyl esters of the aminohydroxy-acids must be effected in the absence of strong alkalis in order to avoid hydrolysis of the ester group.

Ethyl β -dimethylamino- α -benzoyloxyisobutyrate,



was obtained in the form of its *hydrochloride*, needles, m. p. 137° , by mixing cold benzene solutions of benzoyl chloride and ethyl dimethylaminohydroxyisobutyrate; the *base* is a syrup, b. p. $210^\circ/42$ mm. The *methyl* and *amyl* esters are prepared similarly; their hydrochlorides melt at $149-150^\circ$ and 134° respectively; the corresponding bases boil at $220^\circ/75$ mm. and $213^\circ/27$ mm. The patent contains descriptions of six other similar esters.

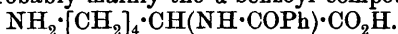
G. T. M.

Synthesis of Inactive Lysine from Piperidine. JULIUS VON BRAUN (*Ber.*, 1909, 42, 839—846).—The opening of the piperidine

ring by means of phosphorus chloride has been made use of for the synthesis of cadaverine, pimelic acid, and ϵ -leucine (Abstr., 1904, i, 918, 970, 1019; 1907, i, 524). Amongst the products of this reaction are two, namely, ϵ -phenoxyhexonitrile, $C_6H_5O \cdot [CH_2]_5 \cdot CN$, and benzoyl- ϵ -leucinonitrile, $COPh \cdot NH \cdot [CH_2]_5 \cdot CN$, which contain the skeleton of lysine. The corresponding phenoxyhexoic acid forms a compound, $C_6H_4Br \cdot O \cdot [CH_2]_4 \cdot CHBr \cdot CO_2H$, m. p. 105° , in which the α -bromine atom can be replaced by NH_2 , but the elimination of the brominated phenyl group by bromine could not be carried out. On the other hand, ϵ -benzoylaminohezoic acid can be brominated in the α -position, the bromine replaced by NH_2 , and the benzoyl group eliminated, giving inactive lysine.

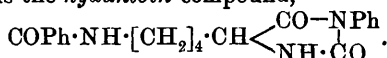
ϵ -Benzoylaminohezoic acid, $COPh \cdot NH \cdot [CH_2]_5 \cdot CO_2H$, is obtained, on hydrolysing the nitrile with potassium hydroxide under special precautions, in long, colourless needles, m. p. 79° . It decomposes when distilled, even in a vacuum, forming benzoic acid and the ϵ -lactam, $NH \cdot [CH_2]_5 \cdot CO$. When brominated in presence of phosphorus a con-

siderable excess of bromine is required. Apparently the imide bromide complex, $C_6H_5 \cdot CBr \cdot NX$, is formed at the same time as the α -carbon is brominated, but the complex is destroyed on adding water. α -Bromo- ϵ -benzoylaminohezoic acid, $COPh \cdot NH \cdot [CH_2]_4 \cdot CHBr \cdot CO_2H$, forms a mass of colourless needles, m. p. 166° . It reacts with aqueous ammonia at 0° , forming α -amino- ϵ -benzoylaminohezoic acid, m. p. 268° when heated quickly, m. p. 263° when slowly heated. The monobenzoyllysine described by Fischer and Weigert (Ber., 1902, 35, 3772) was probably mainly the α -benzoyl compound,



Inactive lysine, obtained by heating benzoyllysine with excess of hydrochloric acid for several hours under pressure at 115° , is in all respects identical with the product obtained by Fischer and Weigert (*loc. cit.*).

Characteristic is the *hydantoin* compound,



By the action of phenylcarbimide on ϵ -benzoyllysine the *hydantoic acid*, $COPh \cdot NH \cdot [CH_2]_4 \cdot CH(NH \cdot CO \cdot NHPh) \cdot CO_2H$, is first formed as a grey mass. This is warmed with concentrated hydrochloric acid and converted into the *hydantoin*, crystallising in matted needles, m. p. 156° . E. F. A.

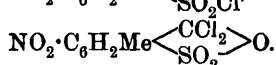
Preparation of *o*-Nitrobenzonitrile and *o*-Nitrobenzamide. KALLE & Co. (D.R.-P. 204477).—When *o*-nitrobenzaldoxime is warmed with dilute aqueous sodium carbonate for nine hours, it yields *o*-nitrobenzamide together with a small amount of *o*-nitrobenzoic acid. When heated with a weak solution of potassium cyanide for nine hours, this oxime furnishes *o*-nitrobenzonitrile with small quantities of *o*-nitrobenzamide and *o*-nitrobenzoic acid. G. T. M.

Preparation of 2-Nitro-4-aminobenzoic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 204884).—2-Nitro-4-amino-

benzoic acid, yellowish-brown crystals, m. p. 234—235°, has now been obtained by reducing 2 : 4-dinitrobenzoic acid with sodium sulphide at 90° in the absence of alkalis. G. T. M.

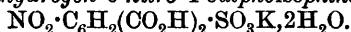
Oxidation Products of 6-Nitro-1 : 3-dimethylbenzene-4-sulphonic Acid. WILLIAM J. KARSLAKE and P. A. BOND (*J. Amer. Chem. Soc.*, 1909, 31, 405—410).—Potassium 6-nitro-1 : 3-xylene-4-sulphonate has been prepared by a modification of Claus and Schmidt's method (Abstr., 1886, 708). When this salt is oxidised with cold alkaline solution of potassium permanganate, the following three products are obtained.

(1) *Potassium 4-nitro-2-sulpho-5-toluate*. The corresponding *barium*, *barium hydrogen*, and *silver* salts are described. By the action of phosphorus pentachloride on the potassium salt, a mixture of two *chlorides* is obtained, which melt at 133° and 93°; it is probable that the compound of higher m. p. is the symmetrical chloride, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me} \begin{smallmatrix} \text{COCl} \\ \text{SO}_2\text{Cl} \end{smallmatrix}$, whilst the other is the unsymmetrical chloride,



(2) *Potassium 6-nitro-4-sulpho-3-toluate*. The *potassium hydrogen* and *silver* salts are also described. The *acid* crystallises in prismatic plates. The *chloride*, m. p. 90° (corr.), when treated with concentrated ammonia, yields a *compound*, m. p. 274°, which is probably the diamide.

(3) *Potassium dihydrogen 6-nitro-4-sulphoisophthalate*,



The *acid chloride* is obtained in two forms, one, m. p. 147°, crystallising in needles, and the other, an oily liquid; when treated with ammonia, the former gives a *compound*, m. p. 277°, and the latter a *compound*, crystallising in coarse needles. E. G.

Methyl Salicylate. II. Solubility in Water at 30°. HARRY D. GIBBS (*Philippine J. Sci.*, 1908, A, 3, 357—359. Compare Abstr., 1908, ii, 906).—The solubilities of methyl salicylate at 30° in water and N/10 sulphuric acid are shown to be 0.014 and 0.077 gram in 100 grams of solvent respectively. Slight improvements are described in the colorimetric method for determining methyl salicylate (*loc. cit.*). P. H.

Preparation of o-Alkylthiolbenzoic Acids and their Alkyl Esters. FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 203882).—*Methyl o-methylthiolbenzoic acid*, $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$, colourless needles, m. p. 66—67°, obtained by adding methyl sulphate to thiosalicylic acid dissolved in aqueous sodium hydroxide, is hydrolysed into *o-methylthiolbenzoic acid*, m. p. 168—170°, this acid being also produced from thiosalicylic acid and sodium methyl sulphate in aqueous sodium hydroxide.

Ethyl o-ethylthiolbenzoate, $\text{SEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$, crystals, m. p. 27—28°, b. p. 152—153°/10 mm., is obtained by treating sodium thiosalicylate with ethyl sulphate; the use of sodium ethyl sulphate in this reaction leads to *o-ethylthiolbenzoic acid*, yellow crystals, m. p. 134—135°.

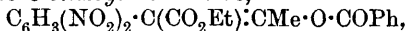
G. T. M.

Preparation of Alkylthiosalicylic [*o*-Alkylthiolbenzoic] Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 203388).—The *o*-alkylthiolbenzoic acids can be produced in one operation from the *o*-aminobenzoic acids by diazotising the latter, neutralising the diazo-solution, and then treating with sodium sulphide and sodium methyl sulphate, gradually heating to 60° or 70°. *o*-Methylthiolbenzoic and ethylthiolbenzoic acids, m. p. 168—169° and 134—135° respectively, were obtained in this way. G. T. M.

Ethyl α -Dinitrophenylacetoacetate and Related Compounds. I. WALTHER BORSCHKE (*Ber.*, 1909, 42, 601—612. Compare Heckmann, *Abstr.*, 1884, 178).—A 75% yield of ethyl α -2:4-dinitrophenylacetoacetate can be obtained by heating an ethereal solution of chloro-(or bromo)-2:4-dinitrobenzene with a suspension of ethyl sodio-acetoacetate in ether for one hour on the water-bath. The corresponding *methyl* ester, $C_6H_3(NO_2)_2 \cdot CHAc \cdot CO_2Me$, crystallises from methyl alcohol in compact, yellow needles, m. p. 114°, and is not so readily soluble as the ethyl ester. The ester forms a stable sodium derivative when its ethereal solution is treated with sodium or sodium ethoxide, but it has not been found possible to replace the sodium by alkyl groups. α -Alkylated acetoacetic esters do not condense with chloro-2:4-dinitrobenzene.

Dry ammonia reacts with an ethereal solution of the ester, yielding acetamide and ethyl 2:4-dinitrophenylacetate. Phenylhydrazine reacts in a similar manner, yielding ethyl 2:4-dinitrophenylacetate and *s*-acetylphenylhydrazine; with a hot ethereal or alcoholic solution of aniline, 2:4-dinitrophenylacetanilide, $C_6H_3(NO_2)_2 \cdot CH_2 \cdot CO \cdot NHPh$, m. p. 181°, is formed.

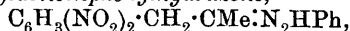
Benzoyl chloride reacts with the sodium derivative of the dinitro-ester, yielding the *O*-benzoyl derivative,



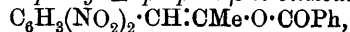
which crystallises from boiling alcohol in rhombic, yellow plates, m. p. 142—143°. When hydrolysed it yields benzoic acid and dinitrophenylacetone. It has not been found possible to transform this *O*-benzoyl into an isomeric *C*-benzoyl derivative.

2:4-Dinitrophenylacetone, $C_6H_3(NO_2)_2 \cdot CH_2 \cdot CO \cdot CH_3$, is readily obtained by hydrolysing the original ester with concentrated sulphuric acid, and crystallises from dilute alcohol in brilliant, pale yellow needles, m. p. 75°. The ketone dissolves in dilute alkali hydroxides, yielding blood-red solutions, from which the ketone cannot be recovered. It does not react with aniline even in the presence of formic acid, and with an alcoholic solution of *p*-nitrosodimethylaniline in the presence of sodium hydrogen carbonate yields a small amount of a dark green, crystalline compound, probably the *p*-dimethylaminoanil of 2:4-dinitrobenzaldehyde (*Abstr.*, 1902, i, 682).

2:4-Dinitrophenylacetonephenylhydrazone,

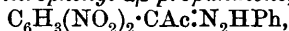


crystallises from hot alcohol in orange-red needles, m. p. 124—125°. The ketone reacts with benzoyl chloride in the presence of pyridine, yielding α -2:4-dinitrophenyl- Δ^{α} -propene- β -ol benzoate,



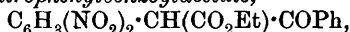
which crystallises from dilute alcohol in pale yellow needles, m. p. 90°.

An alcoholic solution of the ketone reacts with a solution of diazobenzene chloride and sodium acetate, yielding the *α*-phenylhydrazone of *α*-2 : 4-dinitrophenyl-*αβ*-propanedione,

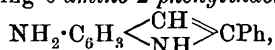


which crystallises from a mixture of alcohol and ethyl acetate in brilliant, orange-red needles, m. p. 201—202° (decomp.). With phenylhydrazone it yields the *bisphenylhydrazone*, $\text{C}_{21}\text{H}_{18}\text{O}_7\text{N}_6$, in the form of glistening, black needles, which decompose at 206°. Sodium hydroxide produces a black coloration with an alcoholic solution of the monohydrazone, but this gradually changes to a pale red colour, and the addition of water precipitates a compound, $\text{C}_{15}\text{H}_{11}\text{O}_3\text{N}_3$, which crystallises from a mixture of chloroform and alcohol in pale green, glistening prisms, m. p. 183—184°. This compound is probably 6-nitro-3-acetyl-1-phenylisindazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{C}(\text{Ac})\text{NPh} \cdot \text{N}$ (compare Meyer, Abstr., 1889, 516).

Ethyl α-2 : 4-dinitrophenylbenzoylacetate,



is obtained by the action of an alcoholic solution of bromo-2 : 4-dinitrobenzene (1 mol.) on ethyl sodiobenzoylacetate (2 mols.). It forms a yellow oil, and when hydrolysed with concentrated sulphuric acid yields *ω*-2 : 4-dinitrophenylacetophenone, $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{CH}_2 \cdot \text{COPh}$, which crystallises from a mixture of chloroform and alcohol in slender, colourless needles, m. p. 136—137°. The ketone reacts with stannous chloride solution, yielding 6-amino-2-phenylindole,

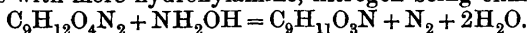


m. p. 240°. The base readily turns dark-coloured on exposure to the air; the *hydrochloride* forms colourless plates, which turn green on exposure to the air.

J. J. S.

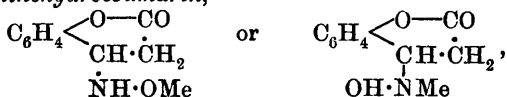
Action of Free Hydroxylamine on Lactones. LUIGI FRANCESCONI and GUIDO CUSMANO (*Gazzetta*, 1909, 39, i, 189—202).—Whilst *santonin* reacts with 3 mols. of hydroxylamine, one of which unites with the lactone group, *desmotroposantonin*, which contains the same lactone grouping but no ethylenic linkings, is not attacked by hydroxylamine (compare Abstr., 1908, i, 272). *Phthalide* is indifferent towards hydroxylamine, whilst *coumarin*, which contains a double linking in the *β*-position with respect to the carbonyl, takes up 2 mols. of the base. The reaction with *coumarin* has been studied in detail.

Although Tiemann found (Abstr., 1886, 880) that *coumarin* did not react with hydroxylamine, the combination readily takes place if a methyl-alcoholic solution of the free base is used and the reacting substances are allowed to remain together for six days. The product is a mixture of *dihydroxylaminohydrocoumarin*, $\text{C}_9\text{H}_{12}\text{O}_4\text{N}_2$, white crystals, m. p. 130—131°, and *aminohydrocoumaric* [*aminomelilotic*] acid, $\text{C}_9\text{H}_{11}\text{O}_3\text{N}$, m. p. 208°. Low temperature and high concentration favour the formation of the former compound, which at higher temperatures reacts with more hydroxylamine, nitrogen being eliminated :



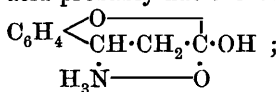
Dihydroxylaminohydrocoumarin dissolves slowly in water to a neutral solution, reduces Fehling's solution, and gives an intense reddish-violet coloration with ferric chloride. It probably contains the lactone ring, and has the constitution $C_6H_4 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CH(NH \cdot OH) \cdot CH_2 \end{smallmatrix} \begin{smallmatrix} C(OH) \cdot NH \cdot OH \\ \diagup \quad \diagdown \\ CH_2 \end{smallmatrix}$. It is readily hydrolysed by dilute acids. Acetone forms with it a condensation product, $C_{12}H_{13}O_3$, crystallising from alcohol in transparent, rectangular tablets. This product does not reduce Fehling's solution until after hydrolysis.

On attempting to methylate with methyl sulphate, the alkali causes the removal of hydroxylamine from the carbonyl group, and *methylhydroxylaminohydrocoumarin*,



is obtained in large, clear prisms, m. p. 167–168°. The methyl derivative does not reduce Fehling's solution or give a coloration with ferric chloride.

Aminohydrocoumaric acid probably has the constitution



it does not reduce Fehling's solution.

C. H. D.

Preparation of Substituted *o*-Carboxyphenylthioglycollic Acids. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P., 202243).—The homologues of anthranilic acid, when diazotised and treated successively with a metallic sulphide and sodium chloroacetate, are converted into the corresponding *o*-carboxyphenylthioglycollic acids in one operation.

6-Carboxy-3-methylphenylthiolacetic acid (annexed formula) is thus produced from homoanthranilic acid. G. T. M.

Exception to the General Method for Preparation of Aldehydes by means of Glycidic Acids. RENÉ POINTET (*Compt. rend.*, 1909, 148, 417–419).—The following substituted glycidic acids, prepared by condensing ethyl chloroacetate with ketones of the type $R \cdot CO \cdot R'$, do not lose carbon dioxide when heated, and are therefore not available for the preparation of the corresponding aldehydes of the type $CHRR' \cdot CHO$ by Darzen's method (Abstr., 1905, i, 117).

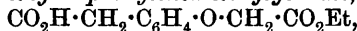
Diphenylglycidic acid, $O \begin{smallmatrix} CPh_2 \\ | \\ CH \cdot CO_2H \end{smallmatrix}$, m. p. 146°. The *ethyl* ester has m. p. 47° and b. p. 202–204°/12 mm.

Phenyl-p-tolylglycidic acid, $O \begin{smallmatrix} CPh \cdot C_6H_4Me \\ | \\ CH \cdot CO_2H \end{smallmatrix}$, m. p. 134°. The *ethyl* ester has b. p. 225°/18 mm.

Phenyl-p-anisylglycidic acid, $O \begin{smallmatrix} CPh \cdot C_6H_4 \cdot OMe \\ | \\ CH \cdot CO_2H \end{smallmatrix}$, m. p. 110°. The *ethyl* ester, has b. p. 240°/20 mm.

When heated, this acid loses carbon monoxide and forms *phenyl-p-anisylacetic acid*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, m. p. 100° . W. O. W.

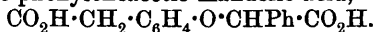
Attempts to Synthesise Chromenol and its Derivatives. S. CZAPLICKI, STANISLAUS VON KOSTANECKI, and VICTOR LAMPE (*Ber.*, 1909, 42, 827—838).—Since the direct addition of hydrogen cyanide to salicylaldehyde methyl ether does not give satisfactory results, to prepare *o*-hydroxyphenylacetic acid, the sodium hydrogen sulphite compound of the aldehyde is converted into *o*-methoxymandelonitrile, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CN}$, and this is heated with eight times its weight of hydrogen iodide. If a smaller proportion is taken, *o*-methoxyphenylacetic acid, m. p. 124° , described by Pschorr (*Abstr.*, 1900, i, 232), is obtained. The hydroxyphenylacetic acid so obtained forms colourless, glistening prisms, m. p. 147° ; the lactone, *isocoumaranone*, has m. p. $28\cdot5^\circ$. It reacts with ethylbromoaacetic acid in presence of sodium, forming *ethyl 2-phenyleneacetic-glycollate*,



which was converted directly into *o-phenyleneacetic-glycollic acid* by heating with alcoholic potassium hydroxide. This forms colourless needles, m. p. $158\text{—}159^\circ$, and shows no coloration with ferric chloride; the *diethyl* ester separates in colourless needles, m. p. $48\text{—}49^\circ$. *p*- and *m*-Hydroxyphenylacetic acids may be prepared in a similar manner, but the yield is much less satisfactory.

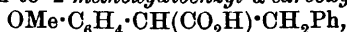
p-Methoxymandelonitrile, m. p. 63° (Tiemann and Köhler, *Abstr.*, 1882, 57), is obtained by the action of potassium cyanide on the sodium hydrogen sulphite compound of anisaldehyde, and is converted into *p*-hydroxyphenylacetic acid when boiled with hydriodic acid. *m*-Methoxymandelonitrile is obtained as a yellow oil from *m*-methoxybenzaldehyde in a similar manner, and is converted by hydrogen iodide into *m*-hydroxyphenylacetic acid, m. p. 129° (Salkowski, *Abstr.*, 1884, 1176).

The lactone of *o*-hydroxyphenylacetic acid and ethyl α -bromophenylacetate interact in presence of sodium in alcoholic solution, forming the *ethyl* ester of *o*-phenyleneacetic-mandelic acid,

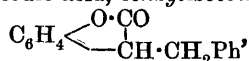


The acid is obtained as a thick oil, which crystallises in short, wide needles, m. p. 178° . The *diethyl* ester forms short, wide needles, m. p. 61° .

2-Methoxystilbene- α -carboxylic acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CHPh}$, is obtained in colourless, short needles, m. p. $145\text{—}146^\circ$. It is reduced by sodium amalgam to *2-methoxydibenzyl- α -carboxylic acid*,



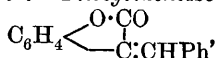
which separates in thick prisms united in masses, m. p. $93\text{—}94^\circ$. When heated with hydriodic acid, *benzylisocoumaranone*,



is obtained as an oil, which crystallises from alcohol in colourless plates, m. p. 61° . This lactone is converted into *2-hydroxydibenzyl- α -carboxylic acid* when heated with alcoholic potassium hydroxide, but this passes back into the lactone when recrystallised from water.

2 : 3' : 4'-Trimethoxystilbene- α -carboxylic acid, prepared by the interaction of veratraldehyde on 2-methoxyphenylacetic acid, crystallises in colourless needles, m. p. 185—186°. 2 : 3' : 4'-Trimethoxydibenzyl- α -carboxylic acid forms granular crystals, m. p. 125—126°.

2-Hydroxystilbene- α -carboxylic acid, prepared by the interaction of *o*-hydroxyphenylacetic acid and benzaldehyde, crystallises in long, colourless plates, m. p. 155°. Benzylidenesisocoumaranone,



formed at the same time as the above, separates in yellow prisms or concentrically-grouped needles. The crystals are coloured orange by concentrated sulphuric acid.

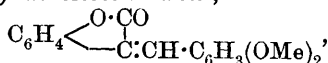
Benzylidenesisocoumaranone is the chromogen of a new class of dyes which contain the same complex chromophore ($\text{CO} \cdot \text{C} : \text{C}$) as the oxindogenides, $\begin{array}{c} \text{O} \cdot \text{C} : \text{CH}^- \\ \diagdown \text{CO} \end{array}$, and are therefore termed isooxindogenides.

The three isomeric methoxy-2-hydroxystilbene- α -carboxylic acids have been prepared in a similar manner. They all yield sodium salts sparingly soluble in cold sodium hydroxide, and are converted into the corresponding lactones when melted.

The 2'-methoxy-compound crystallises in needles from benzene or plates from dilute alcohol, m. p. 152°; the 3'-methoxy-derivative forms thick crystals, m. p. 148°; the 4'-methoxy-acid yields broad needles, m. p. 140°.

2'-Methoxybenzylidenesisocoumaranone forms broad, prismatic, yellow needles, m. p. 126—127°; the 3'-isomeride forms yellow prisms, m. p. 118—119°; the 4'-lactone separates in yellow needles, m. p. 132°.

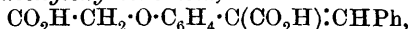
3' : 4'-Dimethoxybenzylidenesisocoumaranone,



forms orange-yellow, prismatic needles, m. p. 99—100°.

2-Hydroxy-3' : 4'-dimethoxystilbene- α -carboxylic acid, prepared by hydrolysis of the above lactone, crystallises in needles, m. p. 187°.

α -Carboxy-2-stilbenyloxyacetic acid,

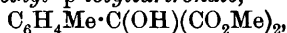


formed by the interaction of hydroxystilbenecarboxylic acid and ethyl bromoacetate, crystallises in plates, m. p. 204—205°. α -Carboxy-2-dibenzoyloxyacetic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2\text{Ph}$, separates in rosettes of colourless needles, m. p. 165°. It is obtained either by reduction of the foregoing compound or by the interaction of ethyl-bromoacetate or 2-hydroxydibenzyl- α -carboxylic acid. E. F. A.

Condensation of Mesoxalic Esters with Aromatic Hydrocarbons. ALFRED GUYOT and G. ESTEVA (*Compt. rend.*, 1909, 148, 564—566. Compare this vol., i, 158).—When a mesoxalic ester is treated with an aromatic hydrocarbon in presence of concentrated sulphuric acid, condensation occurs with formation of a substituted tartronic ester of the type $\text{OH} \cdot \text{CPh}(\text{CO}_2\text{R})_2$. A portion of this ester undergoes condensation with a second molecule of the hydrocarbon,

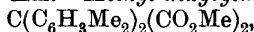
giving a substituted malonic ester of the type $CPh_2(CO_2R)_2$. The two esters are separated by distillation in a vacuum.

The following compounds have been prepared in this way: *Methyl phenyltartronate*, $OH \cdot CPh(CO_2Me)_2$, silky needles, m. p. 67° , b. p. $165^\circ/11$ mm. The *ethyl* ester occurs as a crystalline mass, m. p. 28° , b. p. $170^\circ/10$ mm. *Methyl p-tolyltartronate*,



m. p. 72° , b. p. $175^\circ/11$ mm. The *ethyl* ester forms prisms, m. p. 41° , b. p. $180^\circ/9$ mm. *Methyl ditolylmalonate*, $C(C_6H_4Me)_2(CO_2Me)_2$, needles, m. p. 126.5° . The *ethyl* ester forms prisms, m. p. 93.5° .

Methyl o-xyllyltartronate, $C_6H_3Me_2 \cdot C(OH)(CO_2Me)_2$, needles, m. p. 94.5° , b. p. $185^\circ/11$ mm. The *ethyl* ester forms a crystalline mass, m. p. 35° , b. p. $193^\circ/13$ mm. *Methyl dixyllylmalonate*,



m. p. 135° . The *ethyl* ester forms prisms, m. p. 67° . *Ethyl phenyltolylmalonate*, $C_6H_4Me \cdot CPh(CO_2Et)_2$, has m. p. 55.5° .

These compounds are also obtained when ethyl oximinomalonate is substituted for ethyl mesoxalate in the above preparation; the yields, however, are poor. W. O. W.

Compounds from Lichens. XVII. Substances Present in Lobulated Lichens (Peltigeraceæ). WILHELM ZOPF (*Annalen*, 1909, 364, 273—313. Compare Abstr., 1907, i, 218).—Twelve members of the family *Peltigera* have been investigated, and a hitherto unknown derivative of orcinol, named peltigerin, has been isolated to the extent of 2 to 3% from eight of them, namely, *P. aphthosa*, *P. malacea*, *P. horizontalis*, *P. venosa*, *P. polydactyla*, *P. scabrosa*, *P. propagulifera*, and *P. lepidophora*. Peltigerin is not present in *P. prætextata*, *P. canina*, *P. rufescens*, *P. spuria*, *Nephroma arcticum*, *N. antarcticum*, *N. resupinatum*, *N. lævigatum*, *N. parile*, *Solorina crocea* or *S. saccata*.

Peltigerin, $C_{21}H_{20}O_8$ or $C_{16}H_{16}O_6$, crystallises from acetone or ether in thin, colourless leaflets with a silvery lustre, and from glacial acetic acid in long, slender, curved needles; it sinters at about 160° and changes into a turbid liquid at 170 — 180° , which becomes transparent at about 220° . When peltigerin is heated carefully, it yields a sublimate consisting of *peltigeric acid*, $C_{10}H_{12}O_4$, and *peltigronic acid*. The former acid crystallises in large, compact plates and prisms, m. p. about 127° ; it is coloured red by calcium hypochlorite and gives a violet coloration with ferric chloride. Peltigronic acid crystallises in rosettes of long needles, m. p. 144 — 145° (decomp.).

Zeorin has been detected in *P. malacea*, *P. horizontalis*, *P. propagulifera*, *N. arcticum*, *N. antarcticum*, *N. lævigatum*, and *N. parile*. It is not present in the other representatives of these genera which have been investigated.

d-Uscic acid was isolated from *Nephroma arcticum* and *N. antarcticum*.

Mannitol has hitherto been obtained from only two lichens; it has now been separated from *P. malacea*, *P. horizontalis*, *P. aphthosa*, *P. polydactyla*, *P. canina*, *P. rufescens*, *P. spuria*, *P. prætextata*,

Nephroma resupinatum, *N. lævigatum*, *N. parile*, *Solorina crocea*, and *S. seccata*.

Acids, namely, one from each, have been isolated from *P. scabrosa*, *P. polydactyla*, *P. venosa*, *P. horizontalis*, and *Solorina saccata*; they become red when treated with calcium hypochlorite, but have not been investigated further, owing to the small quantities obtained.

Peltigera malacea contains an *acid* which crystallises in small, white needles, m. p. 220°.

P. aphthosa contains two *acids*, both of which are turned red by calcium hypochlorite; one crystallises in slender needles, softens at 120°, m. p. 125—130°; the other crystallises in small aggregates of slender needles, sinters at 200°, m. p. about 220°.

In addition to soloric acid (compare Zopf, Abstr., 1895, i, 297), *Solorina crocea* contains an acidic substance, which it is proposed to designate *solorinin*; it crystallises in small, thin, colourless leaflets, begins to decompose at about 170°, and forms a reddish-brown liquid at 230°.

Peltigera canina contains a neutral substance, *caninin*, crystallising in colourless, rhombic plates.

Two indifferent substances have been isolated from *P. polydactyla*, namely, *polydactylin*, crystallising in silky, white needles, m. p. about 178—180°, and *peltidactylin*, which crystallises in glistening, colourless, rectangular plates, m. p. about 237—240°.

Nephtrin was detected in *Nephroma arcticum* and *N. lævigatum*, but not in *N. resupinatum* or *N. antarcticum* (compare Hesse, Abstr., 1898, i, 679).
W. H. G.

The Oxidation of Organic Compounds by means of the Compounds of Nitric Acid with Aldehydes or Ketones. ALEXIS A. SHUKOFF (D.R.-P. 206695).—The aldehydes and ketones readily form nitrates when added to concentrated nitric acid, the product usually crystallising out. *Benzaldehyde nitrate*, m. p. -1°, is obtained by adding the aldehyde to fuming nitric acid and cooling to -10°. Camphor nitrate, m. p. 180°, produced by adding 152 parts of camphor to 70 parts of fuming nitric acid, separates on cooling with ice. These substances are convenient oxidising agents for organic compounds which may be dissolved in these very fusible nitrates and left to oxidise at the ordinary temperature. Anthracene dissolves in benzaldehyde nitrate on gently warming, and anthraquinone separates forthwith. Borneol and isoborneol are similarly oxidised to camphor.
G. T. M.

Condensation of Aminohydroxy-acids with Aromatic Aldehydes. ERNESTO PUXEDDU (*Gazzetta*, 1909, 39, i, 121—131. Compare Abstr., 1908, i, 286).—In continuation of former work on the influence of substituents on the condensation of aminohydroxy-acids with aldehydes, it has been found that *o*- and *p*-nitrobenzaldehyde readily condense with 5-amino-*o*- or -*m*-cresotic acid. Unlike salicylaldehyde, *p*-hydroxybenzaldehyde does not condense with either acid. Anisaldehyde, *p*-tolualdehyde, and catechualdehyde are also without action, whilst vanillaldehyde condenses with 5-amino-*o*-cresotic acid,

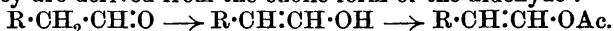
although slowly, but not with its meta-isomeride. In the latter case, the methyl group is in the ortho-position relatively to the nitrogen atom.

The products are coloured, crystalline substances, insoluble in water and in most organic solvents, except alcohol and acetic acid. They are acid in character. Their constitution is under investigation.

The compound from 5-amino-*m*-cresotic acid and *p*-nitrobenzaldehyde forms a *hydrochloride*, m. p. 96°.

C. H. D.

Constituents of Ethereal Oils: Further Decomposition of Eksantalal; Enolisation of Aldehydes by Conversion into the Corresponding Unsaturated Esters; enol-Phenylacet-aldehyde-monoacetate. FRIEDRICH W. SEMMLER (*Ber.*, 1909, 42, 584—591).—In the work on essential oils, it has been frequently noticed that although secondary alcohols give good yields of ketones when oxidised with an acetic acid solution of chromic anhydride, only poor yields of aldehydes can be obtained from primary alcohols under similar conditions, appreciable amounts of less volatile products being formed at the same time. This is now shown to be due to the enolising action of the acetic acid and the formation of an acetate of the unsaturated alcohol. These acetates are termed monoacetates in order to distinguish between them and the diacyl derivatives to which aldehydes give rise; the prefix enol is also used in order to indicate that they are derived from the enolic form of the aldehyde:



It is only aldehydes which contain hydrogen attached to the α -carbon atom which can react in this manner.

enol-Phenylacetaldehyde monoacetate (*phenylvinyl acetate*),
 $CHPh : CH \cdot OAc$,

is readily formed when the aldehyde is boiled for an hour with twice its weight of acetic anhydride; it has b. p. 119—121°/10 mm., D^{20}_D 1.065, n_D 1.5483. When reduced it yields phenylethyl alcohol and ethyl alcohol, and when oxidised with ozone the products are benzaldehyde and benzoic acid. Hydrolysis with dilute mineral acids at 100—110° yields phenylacetaldehyde and acetic acid. Phenylacet-aldehyde has b. p. 85—86°/10 mm., D^{20}_D 1.0252, and n_D 1.53191. Heptaldehyde, citral, citronellal, and various other aldehydes react in a similar manner.

The formation of these esters of the enolised aldehydes affords the basis of a simple method by means of which the aldehyde group CHO can be removed and an aldehyde or ketone containing one less carbon atom obtained.

The readiness with which aldehydes form acetates must be borne in mind when estimating the amount of alcohol present in an essential oil.

Tricyclic enol-*eksantalal* monoacetate, $C_{10}H_{14} : CH \cdot OAc$, has b. p. 132—135°/10 mm., D^{20}_D 1.023, and n_D 1.4881, and is laevorotatory. It is usually accompanied by a small amount of a diacetate, $C_{15}H_{22}O_4$, which has a higher b. p.

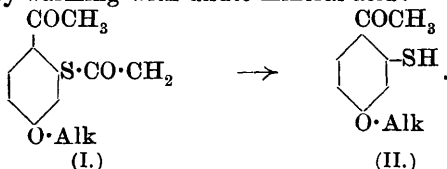
When reduced, the monoacetate yields eksantalol, $C_{11}H_{18}O$, and when oxidised with ozone in benzene solution yields tricyclic *nor-eksantalone*, $C_{10}H_{14}O$, which has b. p. 101—102°/10 mm., D^{20}_D 0.988,

and n_D 1.485. It yields a *semicarbazone*, $C_{10}H_{14}:N:NH \cdot CO \cdot NH_2$, m. p. 216° , and an *oxime*, $C_{10}H_{14}:N \cdot OH$, b. p. $142-144^\circ/10$ mm.

The behaviour of eksantalal indicates that it contains a hydrogen atom attached to the carbon atom which is in the α -position with respect to the aldehyde group. J. J. S.

Constitution of Dichloropiperonal. GEORGE BARGER (*Ber.*, 1909, 42, 763—765. Compare *Trans.*, 1908, 93, 563, 735).—Polemical. A reply to Pauly (this vol., i, 165). W. R.

Preparation of 5-Alkyloxy-2-acetylphenyl Mercaptan. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 202632).—When treated with acetyl chloride in the presence of aluminium chloride, the 3-alkyloxyphenyl mercaptans give rise to diacetyl derivatives (I), from which the alkyloxyacetylphenyl mercaptans (II) are produced by warming with dilute mineral acid:



5-Methoxy-2-acetylphenyl mercaptan, colourless plates, m. p. $94-96^\circ$, and 5-ethoxy-2-acetylphenyl mercaptan, colourless crystals, m. p. 68° , which are thus produced, yield sulphur colouring matters on oxidation. G. T. M.

Organic Syntheses by means of Sunlight. EMMANUEL PATERNÒ (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 104—105 *).—A solution of benzophenone in amylene, exposed to sunlight, deposits in a few days large crystals of a compound, m. p. 109° , which may be converted into a hydrocarbon containing 18 atoms of carbon; it therefore probably has the amylene chain attached to the carbonyl carbon, the oxygen forming a bridge. Oxidation regenerates benzophenone. Acetophenone and amylene yield a liquid compound, boiling at $235-237^\circ$. The compound from benzaldehyde and amylene boils at $229-231^\circ$.

Octane and decane react with benzophenone in sunlight, being partly converted into benzopinacene and unsaturated hydrocarbons, the latter then reacting with benzophenone to form compounds analogous to that from amylene. Some of these compounds are found by analysis and cryoscopic measurements to be formed from 1 mol. of benzophenone and 1 mol. of unsaturated hydrocarbon, but their properties are similar to those of the resins, which may also have a simple constitution.

Benzene does not react with benzophenone, whilst its homologues undergo complex reactions. With ethylbenzene the principal product is a crystalline compound, m. p. $88-89^\circ$, which has the properties of a tertiary alcohol, and yields a hydrocarbon, m. p. $124-126^\circ$, and a resin.

Certain alcohols, ethers, and esters react in similar manner to the hydrocarbons. C. H. D.

* and *Gazzetta*, 1909, 31, i, 237—250.

Crystallography of Nitrodesmotroposantonin and β -Naphthyl Propyl Ketone. ARISTIDE ROSATI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 129—132).—Nitrodesmotroposantonin (Bargellini and Daconto, *Abstr.*, 1908, i, 819) forms rhombic crystals, $a:b:c = 0.4133:1:2.2646$. It is dextrorotatory in solution.

β -Naphthyl propyl ketone forms triclinic crystals, sometimes several centimetres in length, $a:b:c = 0.6774:1:0.6029$, $\alpha = 94^\circ 31'$, $\beta = 140^\circ 3.5'$, $\gamma = 90^\circ 27'$. C. H. D.

9-Formylfluorene. I. WILHELM WISLICENUS and MARTIN WALDMÜLLER (*Ber.*, 1909, 42, 785—789. Compare Wislicenus and Densch, *Abstr.*, 1902, i, 291).—9-Formylfluorene, obtained by the condensation of fluorene and ethyl formate, using dry potassium ethoxide as the condensing agent, exists in two tautomeric forms.

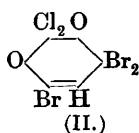
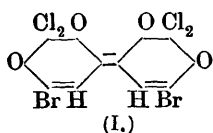
α -Formylfluorene, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C}:\text{CH}\cdot\text{OH}$, is a yellow, viscid oil, b. p. 196—197°/14 mm., 193—193.5°/12 mm., which slowly changes into a solid, transparent, yellow, resinous mass. Mol.-wt. determinations of the latter substance show that it is *bimolecular* formylfluorene, $(\text{C}_{14}\text{H}_{10}\text{O})_2$; it yields the unimolecular variety when distilled under reduced pressure. α -Formylfluorene, when treated with phenylcarbimide, yields the *additive* product, $\text{C}_{13}\text{H}_8:\text{CH}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$, which crystallises in colourless needles, m. p. 145—146°; the *benzoate*, $\text{C}_{13}\text{H}_8:\text{CH}\cdot\text{OBz}$, forms small, slender, colourless needles, m. p. 158—159°; the *acetate*, $\text{C}_{13}\text{H}_8:\text{CH}\cdot\text{OAc}$, crystallises in small, colourless plates, m. p. 132—134°.

β -Formylfluorene, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CH}\cdot\text{CHO}$, obtained by treating a solution of the α -modification in aqueous alkali with dilute sulphuric acid, crystallises in colourless, glistening leaflets; it turns yellow and sinters at 70°, and is completely converted into the α -form at about 90°. The *phenylhydrazone*, $\text{C}_{20}\text{H}_{16}\text{N}_2$, crystallises in almost colourless leaflets, m. p. 126—127°; the *anilino-derivative*, $\text{C}_{20}\text{H}_{15}\text{N}$, forms small, glistening, yellow needles, m. p. 155°. W. H. G.

Tribromoresoquinone. THEODOR ZINCKE and F. SCHWABE (*Ber.*, 1909, 42, 797—802).—The statement of Meyer and Desamari (*Abstr.*, 1908, i, 658) that tribromoresoquinone is a tribromo-*m*-benzoquinone is refuted; it is either a derivative of *p*-dibenzoquinone or *o*-dibenzoquinone, although the latter is very improbable.

This statement is supported by (1) mol.-wt. determinations; (2) reduction of the substance to tetrabromodiresorcinol; (3) conversion of the reduction product by bromine and water at the ordinary temperature into tribromoresoquinone, and by chlorine under similar conditions into a chlorodibromoresoquinone.

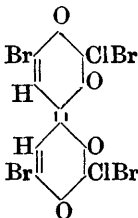
Dichlorotribromoresorcinol, when heated, loses bromine and passes



into dichlorobromoresoquinone (compare Benedikt, *Abstr.*, 1879, 55, 464, 717). It is very probable that the latter substance is analogous with tribromoresoquinone, and has the formula (I),

whilst the substance from which it is prepared is a ketochloride having the constitution (II).

Chlorodibromoresoquinone, obtained by the action of chlorine on a solution of tetrabromodiresorcinol in dilute acetic acid, crystallises in nodules of small, yellow needles, m. p. 212° (decomp.). It is reduced to *dichlorodibromodiresorcinol*, $C_{12}H_6Cl_2Br_2O_4$, crystallising in long, slender needles, m. p. 271° ; the same substance is apparently produced by the reduction of dichlorobromoresoquinone.



W. H. G.

Preparation of Anthraquinone- $\alpha\beta$ -sulphonic Acids. R. WEDEKIND & Co. (D.R.-P. 202398).—The β -anthraquinone mono- and di-sulphonic acids undergo sulphonation with fuming sulphuric acid in the presence of mercury or mercuric salts, and give rise to new polysulphonic acids containing sulphonic groups in α -positions. Anthraquinone-3-sulphonic acid sulphonated at 160° with fuming acid (40% SO_3), and a small amount of mercuric sulphate furnishes chiefly anthraquinone-1:6- and -1:7-disulphonic acids. These acids are also obtained by starting with anthraquinone itself and sulphonating as before in the presence of mercuric sulphate, employed in a coarse, granular form.

G. T. M.

Preparation of Halogenated Anthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 205913. Compare following Abstract).—The replacement of the sulphonic group by halogen in the anthraquinonedisulphonic acids may be effected in two stages by employing moderate amounts of halogenating agent. *Potassium 1-chloroanthraquinone-5-sulphonate*, pale yellow needles, is obtained by treating sodium anthraquinonedisulphonate with sodium chlorate and hydrochloric acid and salting out the product with potassium chloride so soon as appreciable amounts of the original disulphonate are no longer apparent. *Potassium 1-bromoanthraquinone-5-sulphonate*, yellow needles, is produced in a similar manner by employing bromine instead of chlorate and hydrochloric acid.

Similar results are obtained with anthraquinone-1:8- and -2:7-disulphonic acids, the sulphonic groups being replaced by chlorine in two stages.

G. T. M.

Replacement of Halogen by Hydroxyl in Substituted Anthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 203083).—When the halogenated anthraquinones are heated with fuming sulphuric acid, either with or without boric acid, the halogen atoms are more or less replaced by hydroxyl. 1:4-Dichloroanthraquinone and 4-chloro-1-hydroxyanthraquinone give rise to quinzarin (1:4-dihydroxyanthraquinone), and 2:4-dibromo-1-aminoanthraquinone furnishes 2-bromo-4-amino-1-hydroxyanthraquinone, m. p. 243° .

G. T. M.

[Preparation of Alkylaminoanthraquinone Derivatives.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 205096).—Potassium 1:4-diethylaminoanthraquinone-5-sulphonate, blue needles with bronzy lustre, is obtained by heating at 100—120° aqueous ethylamine and the leuco-derivative of potassium quinizarin-5-sulphonate; by using methylamine, the corresponding dimethylaminoanthraquinone-5-sulphonate was produced. G. T. M.

Preparation of Derivatives of 1:3-Diaminoanthraquinone. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 205036).—*o*-Benzoylbenzoic acid on treatment with concentrated nitric and sulphuric acids furnishes among other products 3:5-dinitro-*o*-benzoylbenzoic acid, which on reduction gives rise to 3:5-diamino-*o*-benzoylbenzoic acid, $C_6H_3(NH_2)_2 \cdot CO \cdot C_6H_4 \cdot CO_2H$, this substance having the property of condensing with great readiness to form 1:3-diaminoanthraquinone.

Trinitro-2-*p*-toluoylbenzoic acid, m. p. 217—218.5°, from the nitration of 2-*p*-toluoylbenzoic acid, is reduced by iron and acetic acid to triamino-2-*p*-toluoylbenzoic acid, which on warming with dilute ammonia gives 1:3:(?)-triamino-2-methylantraquinone, yellowish-red needles, m. p. above 300°.

1:3-Diamino-2-methylantraquinone, yellowish-red needles, m. p. 273—276°, is obtained by reducing 1:3-dinitro-2-*p*-toluoylbenzoic acid with iron and dilute acetic acid; the intermediate 1:3-diamino-2-*p*-toluoylbenzoic acid having largely condensed during reduction, the remainder is condensed by warming with acetic acid.

1:3-Diamino-2-methoxyanthraquinone, reddish-yellow needles, m. p. 225—230°, is obtained by a similar set of operations from *p*-anisoylbenzoic acid. G. T. M.

[Preparation of Leuco-derivatives of Diaminoanthraquinones from the Corresponding Hydroxylic Compounds.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 205149).—The leuco-derivative of quinizarin when heated with alcoholic ammonia (25%) at 100° gives rise to the leuco-derivative of 1:4-diaminoanthraquinone, leaflets with green metallic reflex, m. p. 272° (decomp.). The leuco-derivative of 1:4:5:8-tetrahydroxyanthraquinone, obtained by reducing the tetrahydroxy-compound with alkali hyposulphite, when treated with alcoholic ammonia gives rise to the leuco-derivative of 1:4-diamino-5:8-dihydroxyanthraquinone, needles, decomposing at 284°. Other leuco-derivatives of the hydroxyanthraquinones undergo this change on treatment with ammonia. G. T. M.

Preparation of Arylaminoanthraquinones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 201905).—4-Amino-1-*p*-tolylamino-8-methoxyanthraquinone, lustrous, coppery leaflets, m. p. 226°, is prepared by heating 4-nitro-1:8-dimethoxyanthraquinone with *p*-toluidine and stannous chloride at 60—90°; its sulphonic acids are wool dyes giving fast shades of blue. G. T. M.

Preparation of 4-Chloro-1-hydroxyanthraquinone. R. WEDEKIND & Co. (D.R.-P. 202770).—4-Chloro-1-hydroxyanthraquinone is

readily obtained by adding simultaneously to 1-hydroxyanthraquinone, suspended in strong sulphuric acid at 110—115°, solutions of potassium chlorate and hydrochloric acid.

G. T. M.

Preparation of Thiocyanogen Derivatives of Anthraquinone.

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 206054).—The replacement of the diazonium group by thiocyanogen occurs readily in the benzene and naphthalene series only in the presence of cuprous thiocyanate. In the anthraquinone series this replacement takes place merely on boiling the diazonium thiocyanate with water.

α-Thiocyanoanthraquinone, $\text{CNS} \cdot \text{C}_{24}\text{H}_7\text{O}_2$, yellow needles, m. p. 231°, was obtained by diazotising *α*-aminoanthraquinone in concentrated sulphuric acid and boiling the aqueous solution of the diazo-salt with potassium thiocyanate. Other thiocyano-derivatives with this group in positions 2 and 1 : 5 are similarly produced.

G. T. M.

Preparation of Benzanthrone and its Derivatives.

BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 204354. Compare Abstr., 1907, i, 324, 943; 1908, i, 193, 661).—The aminoanthraquinones and their derivatives condense with glycerol and concentrated sulphuric acid to yield benzanthrone derivatives; it has now been found that this condensation can be effectively carried out by using instead of glycerol such of its derivatives as mono- and di-chlorohydrin and acetin (glyceryl acetate).

G. T. M.

Preparation of Halogen Derivatives of Benzanthrone.

BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 205294).—*β*-Chloro-benzanthrone, dark green powder or yellow needles, is obtained by condensing *β*-chloroanthraquinone with glycerol, aniline sulphate, and concentrated sulphuric acid at 140°. In this condensation acetin may be employed instead of glycerol.

More highly halogenated benzanthrone derivatives can be similarly prepared from dichloro- and dibromo-anthraquinone.

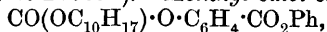
G. T. M.

Crystallography of the Anhydride of Menthyl Xanthate.

N. SURGUNOFF (*Zeitsch. Kryst. Min.*, 1909, 46, 219—220; from *Bull. Soc. Nat. Moscou*, 1906, Nos. 1 and 2, 142—152).—The crystals are hemihedral-rhombic [$a : b : c = 1.4478 : 1 : 2.3533$].

L. J. S.

The Preparation of Mixed Carbonates from Hydroaromatic Alcohols and Ethyl Salicylate. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 206055).—*Menthyl salol carbonate*,



colourless crystals, m. p. 57—58, is produced by condensing salol and menthyl chlorocarbonate in benzene containing pyridine; it is also formed by the interaction of salol chlorocarbonate and menthol in the presence of quinoline.

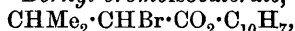
Menthyl salicylacetol carbonate, $\text{CO}(\text{OC}_{10}\text{H}_{17}) \cdot \text{OC}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{COMe}$, colourless, tasteless crystals, m. p. 87°, is prepared from menthyl chlorocarbonate and acetonyl salicylate, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{COMe}$.

Thymyl salol carbonate from salol chlorocarbonate and thymol, forms colourless and odourless needles, m. p. 78—79°.

Santalyl salacetol carbonate, a yellow, syrupy liquid, is produced from santalol and salacetol chlorocarbonate, the latter reagent being obtained by the interaction of carbonyl chloride and salacetol in the presence of dimethylaniline. The patent refers to several other mixed carbonates of a similar type. G. T. M.

[Preparation of Bornyl Acetate.] OTTO ZEITSCHEL (D.R.-P. 204163).—The existing process for the production of bornyl acetate from pinene is expensive, owing to the large proportion of glacial acetic acid employed. It has now been found that this ester can be produced from its generators, French turpentine and glacial acetic acid, when interacting in molecular proportions at 200° for about five hours. In this way 30—40% of bornyl acetate, 30—40% of limonene, and 10—15% of camphene are obtained. G. T. M.

Preparation of Bornyl and *iso*Bornyl Bromoisovalerates. CHEMISCHE FABRIK AUF ACTIEN VORM. E. SCHERING (D.R.-P. 205263 and 205264).—*Bornyl bromoisovalerate*,



oil, b. p. 163°/10 mm., is obtained by heating in chloroform solution equivalent quantities of borneol and bromoisovaleryl chloride or bromide; it may also be obtained from borneol and bromoisovaleric anhydride at 100°, bromoisovaleric acid and concentrated sulphuric acid at 80°, or from camphene and bromoisovaleric acid in the presence of zinc chloride.

*iso*Bornyl bromoisovalerate, oil, b. p. 160°/3 mm., is similarly prepared, and can also be produced by mixing *isobornyl isovalerate* with bromine at 100°; a bromine carrier accelerates this action, which takes a similar course with bornyl *isovalerate*. G. T. M.

Crystallography of Two Xanthogenamides (Thio-urethanes). EVGRAF S. FEDOROFF and D. N. ARTEMÉEFF (*Zeitsch. Kryst. Min.*, 1909, 46, 215—218; from *Bull. Soc. Nat. Moscou*, 1906, Nos. 1 and 2, 110—132. Compare Tschugaeff, *Abstr.*, 1902, i, 604).—1-Phenyl-3-*l*-bornyl-2-ethyl-iminoxanthide, monoclinic [$a:b:c = 0.5785:1.0:5.008$; $\beta = 100^\circ 59'$]. 1:2-Diphenyl-3-fenchyl-iminoxanthide, rhombic [$a:b:c = 0.9484:1.0:0.9512$]. L. J. S.

Optically Active Menthones. ERNST BECKMANN (*Ber.*, 1909, 42, 846—850).—*l*-Menthone, obtained from *l*-menthol by oxidation with chromic acid, has $[\alpha]_D - 28.5^\circ$; when inverted with 90% sulphuric acid in the cold, it has $[\alpha]_D + 28.1^\circ$. This product is a mixture of *l*-menthone with a highly dextrorotatory *d*-isomenthone. The mixture of oximes from the product can be separated by dissolving in ether and passing in dry hydrogen chloride. A crystalline precipitate, m. p. 132°, $[\alpha]_D + 35.9^\circ$, is obtained, whilst the mother liquors yield a compound having m. p. 117—118°, $[\alpha]_D - 62.6^\circ$. These are identical with the oxime hydrochlorides of *d*-isomenthone and *l*-menthone. The corresponding oximes have the following constants: *d*-isomenthone-oxime, $[\alpha]_D + 41^\circ$, syrup; *l*-menthoneoxime, $[\alpha]_D - 42.5^\circ$ m. p. 59°.

d-isoMenthone gives the same product on inversion as *l*-menthone. *d*-isoMenthone semicarbazone crystallises in colourless needles, m. p. 154°, $[\alpha]_D + 46.5^\circ$. *l*-Menthone semicarbazone has m. p. 184°, $[\alpha]_D - 64^\circ$. From "inverted" menthone a semicarbazone, m. p. 116°, $[\alpha]_D + 26.6^\circ$, has been obtained (compare Barrowcliff, Trans., 1907, 91, 863).

E. F. A.

Preparation of Camphor. SCHMITZ & Co. (D.R.-P. 203791).—The metallic derivatives of borneol and isoborneol are readily oxidised to camphor and metallic hydroxide. A current of air passed through a cold toluene solution of sodium isobornyl-oxide or calcium bornyl-oxide leads to the production of camphor and sodium hydroxide or calcium hydroxide respectively. A similar result is obtained by warming together (in xylene) mercuric oxide and sodium isobornyl-oxide.

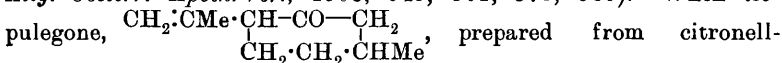
G. T. M.

[The Interaction of Hydroaromatic Ketones and Magnesium Aryl Halides.] BRUNO SZELINSKI (D.R.-P. 202720).—Carvone and pulegone, when submitted to the Grignard reaction with magnesium aryl halides, furnish the following compounds: *benzyl-dihydrocarvone*, m. p. 69°, b. p. 204—206°/26 mm., *oxime*, m. p. 138°; *α -naphthyl-dihydrocarvone*, viscid oil, m. p. 150°, b. p. 230—233°/34 mm., *oxime*, oily; *benzyl-dihdropulegone*, b. p. 210—215°/35 mm., *oxime*, oily.

These products, when mixed with collodion, wool, or cellulose acetate, give rise to transparent, flexible celluloid, which is more resistant to heat than camphor-celluloid, and has a much higher decomposition point.

G. T. M.

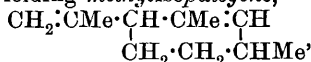
isoPulegone. ALFRED EBERT (*Chem Zentr.*, 1909, i, 21; from *Zeitsch Allg. Oesterr. Apoth.-Ver.*, 1908, 545, 561, 573, 589).—When *iso*-pulegone,



aldehyde (Tiemann and Schmidt, Abstr., 1897, i, 198), is dissolved in ether and submitted to the action of magnesium methyl iodide, *methylisopulegyl alcohol*, $\text{CH}_2:\text{CMe}\cdot\text{CH}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2$, is obtained.



It is a pale yellow liquid, having a geranium-like odour, b. p. 93—94°/12 mm., $D^{20}_D 0.91085$, $[\alpha]^{20}_D 19.54^\circ$, $n^{20}_D 1.46992$. In cold ethereal solution this substance reacts with phosphorus trichloride, forming *methylisopulegyl chloride*, $\text{C}_{11}\text{H}_{19}\text{Cl}$, a colourless liquid, b. p. 92—93°/10 mm., which loses HCl when boiled for three hours with alcohol and potassium acetate, yielding *methylisopulegene*,



a colourless liquid, b. p. 95—97°/12 mm., 182—184°/750 mm., $D^{20}_D 0.84$, $[\alpha]^{20}_D + 46.27^\circ$, $n^{20}_D 1.4724$.

Methylisopulegene is also obtained by distilling, under ordinary pressure, the crude product of acetylating methylisopulegyl alcohol.

J. V. E.

Preparation of Santalol Ethers. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 202352).—*Santalyl methyl ether*, colourless liquid, b. p. 149—156°/16 mm., was obtained by the following processes: (1) boiling together santalyl chloride and methyl-alcoholic sodium methoxide; (2) adding methyl sulphate to sodium santalol suspended in ether; (3) heating together sodium santalol and methyl iodide in toluene.

Santalyl ethyl ether, colourless liquid, b. p. 169—174°/22 mm., was prepared from santalyl bromide and alcoholic sodium ethoxide.

Santalyl phenyl ether, viscid oil, b. p. 232°/20 mm., and *santalyl menthyl ether*, colourless syrup, b. p. 201—210°/5 mm., were obtained by heating santalyl chloride in xylene solution with sodium phenoxide and sodium menthoxide respectively.

G. T. M.

Preparation of Santalyl Halides. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 203849).—*Santalyl chloride*, oil, b. p. 162—167°/15 mm., is readily prepared by heating under reduced pressure *santalyl chlorocarbonate*, obtained by the interaction of carbonyl chloride and santalol or sandal oil in the presence of dimethylaniline in benzene solution; it may also be produced by the action of phosphorus pentachloride or thionyl chloride. Santalyl bromide is similarly obtained from phosphorus pentabromide.

G. T. M.

Preparation of Santalyl Allophanate. VEREINIGTE CHININ-FABRIKEN ZIMMER & Co. (D.R.-P. 204922).—*Santalyl allophanate*, $C_{15}H_{23}O \cdot CO \cdot NH \cdot CO \cdot NH_2$, white needles, m. p. 162°, may be prepared in a variety of ways: (1) Cyanic acid is added to santalol dissolved in light petroleum; (2) santalol is added to a benzene solution of carbamide chloride, either alone or in presence of dimethylaniline; (3) santalol and phenyl carbamate or allophanate are heated under reduced pressure.

G. T. M.

An Aldehyde from Pinene. CARL D. HARRIES and HANS VON SPLAWA-NEYMAN (*Ber.*, 1909, 42, 879—880).—By boiling pinene ozonide with water, Harries and Neresheimer (*Abstr.*, 1908, i, 194) were unable to characterise the aldehydic substance formed, but the present authors find that the decomposition proceeds more smoothly in glacial acetic acid solution at 90°. After evaporating the acetic acid in a vacuum at 35°, the residue is fractionated under 12 mm. pressure. The fraction distilling at 115—125° gives with semicarbazide the *disemicarbazone* of *pinonaldehyde*, $C_{12}H_{22}O_2N_6$, which crystallises in small, round aggregates, m. p. 214—215°.

J. C. C.

Preparation of Camphene. CHEMISCHE FABRIK VORM. SANDOZ (D.R.-P. 204921).—It was already known that the velocity of hydrolysis of pinene hydrochloride by alkali hydroxide is increased by the presence of feebly acidic substances, such as phenols and naphthols. It is now found that this result is effected by neutral compounds, such as sodium or calcium toluene-*p*-sulphonate, sodium naphthalene- β -sulphonate, and sodium naphthalene-2 : 7-disulphonate.

G. T. M.

Elaterin and Some of its Derivatives. ARMAND BERG (*Compt. rend.*, 1909, 148, 566—568. Compare Abstr., 1898, ii, 447; 1906, i, 596; 1907, i, 146; Pollak, Abstr., 1906, i, 973).—Polemical against Hemmelmayr (Abstr., 1907, i, 230). The author maintains the accuracy of his formula for elaterin, $C_{28}H_{38}O_7$, which he has confirmed by determinations of the molecular weight of diacetyelaterin and other derivatives.

Hemmelmayr's "elateridin," obtained in the hydrolysis of elaterin by sulphuric acid, is stated to have the formula $C_{26}H_{36}O_6$. The author proposes to call this compound *anhydroelateridin* and to reserve the name elateridin for the substance obtained when the hydrolysis is effected by alcoholic potassium hydroxide. Analysis and molecular-weight determinations by the cryoscopic method show that elateridin has the formula $C_{26}H_{38}O_7$.

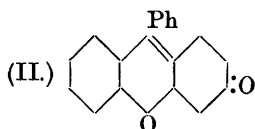
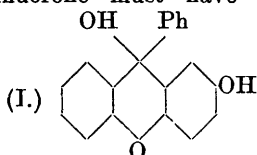
On treatment of elaterin with bromine, a mixture of amorphous bromo-derivatives is obtained; since these cannot be separated by crystallisation, Hemmelmayr's determination of the molecular weight of the product cannot be regarded as establishing his formula for elaterin. W. O. W.

The Phosphorus Content of Chlorophyll. JULIUS STOKLASA, VLADIMIR BRDLIK, and ADOLF ERNEST (*Ber. deut. bot. Ges.*, 1907, 27, 10—20. Compare Abstr., 1908, i, 279).—Polemical against Tsvett (Abstr., 1908, i, 440) and Willstätter (Abstr., 1907, i, 71). Chlorophyll contains phosphorus as glycerophosphoric acid. Tsvett's partial agreement with Willstätter (who denies that chlorophyll contains phosphorus) is not based on experimental results. The authors show by Tsvett's own "chromatographic" method (adsorption of the pigments by calcium carbonate) that phosphorus always accompanies the chlorophyll in adsorption, and that in autumn when the green colour disappears from the leaves, the phosphorus also disappears. G. B.

Completely Methylated Flavonol Derivatives. NICOLAI WALIASCHKO (*Ber.*, 1909, 42, 726—728).—In reply to Herzig and Hofmann (this vol., i, 165) the author states that trimethyl- and pentamethyl-quercetin are readily obtained from quercetin, methyl sulphate, and potassium hydroxide under his conditions (Abstr., 1904, i, 760). The ready formation of the pentamethylated derivative necessitates an alteration of Kostanecki and Dreher's generalisation (Abstr., 1893, i, 217), the revised version of which should read: the alkylation of the hydroxyl group ortho to the carbonyl group, whilst not accomplished, or to only slight extent, by an alkyl halide, is readily effected by methyl sulphate and an alkali hydroxide. C. S.

Constitution of the Fluorescein and Quinolophthalein Dyes. WALTER KROPP and HERMAN DECKER (*Ber.*, 1909, 42, 578—584).—Kehrmann and Dengler have recently (Abstr., 1908, i, 1002) prepared phenylfluorone, the chromogen of fluorescein, to which they assigned an ortho-quinonoid constitution, and the present authors have endeavoured to prepare the corresponding chromogen of quinolphthalein by the hydrolysis of 2-methoxy-9-phenylxanthonium bromide (compare

Decker and von Fellenberg, Abstr., 1907, i, 1065) and subsequent neutralisation, but they find the only product to be a colourless carbinol base, namely, 2-hydroxy-9-phenylxanthen-9-ol (formula I). There is thus a fundamental difference between the two series of compounds, and the conclusion is drawn that Kehrmann and Dengler's phenylfluorone must have a para-quinonoid structure (II), and



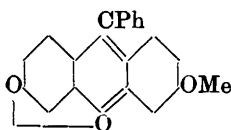
consequently fluorescein must also possess the older para-quinonoid constitution, whilst the ortho-quinonoid formula for the alkali salts of quinolphthalein, which is the only one that explains their colour, cannot be upheld.

2-Hydroxy-9-phenylxanthonium bromide, $C_6H_4 \begin{matrix} \text{CPh} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{OH} \\ \text{OBr} \cdot \text{C} \cdot \text{CH} \cdot \text{CH} \end{matrix}$, prepared by heating 2-methoxy-9-phenylxanthen-9-ol with hydrobromic acid, crystallises in dark red plates, which darken on warming, and melt and decompose at about 300° . On hydrolysis it yields 2-hydroxy-9-phenylxanthen-9-ol, crystallising in colourless, rhombic prisms, m. p. $158-160^\circ$ (decomp.). The *chloride*, red rosettes of plates; *iodide*, long, blackish-red plates; *platinichloride*, dark red needles, and *ferrichloride*, dark red crystals, m. p. $193-194^\circ$ (corr.), are described.

When 3-methoxy-9-phenylxanthonium chloride is heated with hydrochloric acid under pressure, the corresponding hydroxy-compound is formed, which with sodium hydroxide furnishes phenylfluorone. The properties of this compound are not those of a phenolbetaine, which should be soluble in water and not extractable from its solutions by ether or benzene. Moreover, it should (were it a betaine) be at least as strongly coloured as the oxonium salts, but it is only orange-yellow, whilst the corresponding salts are red. It is therefore to be regarded as the chromogen of fuchsone, a conclusion which is confirmed by R. Meyer's observation of the correspondence between the spectrum curves of the fluoresceins and phthaleins.

J. C. C.

Carboxonium Dyes. II. Strongly Basic, Neutral, Salt-forming, Nitrogen-free Oxonium Compounds and the Constitution of Fluorescein. FRIEDRICH KEHRMANN and O. DENGLE [with KARL SCHEUNERT] (*Ber.*, 1909, 42, 870-879).—By the interaction of methyl sulphate and resorcinolbenzein, and of methyl sulphate and fluorescein methyl ester, the authors have been able



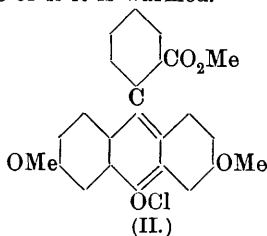
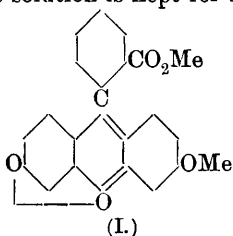
to obtain, on hydrolysis of the resulting methosulphate, oxonium bases which are strongly basic and give neutral salts.

3-Methoxy-9-phenylfluorone (annexed formula), prepared by the action of methyl sulphate on resorcinolbenzein in nitrobenzene solution at 150°

and subsequent hydrolysis of the product, forms clusters of chrome-red needles, m. p. 202°. It is more strongly basic than the parent base.

The *chloride* forms reddish-yellow prisms with a blue reflex, and the *platinichloride* is an orange-red, crystalline powder. On methylation under the same conditions as above, 3-methoxy-9-phenylfluorone yields the *carbinol base* of 3:6-dimethoxy-9-phenylxanthylium (annexed formula: as *methosulphate*). The *chloride* forms yellow prisms or plates with a blue reflex. The *nitrate*, *iodide*, *dichromate*, *platinichloride*, *methyl ether*, m. p. 112°, and *ethyl ether*, colourless prisms, m. p. 158°, are described.

By the interaction of methyl sulphate and fluorescein methyl ester a mixture of two compounds is formed. The first, 3:6-dimethoxyfluoran, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{C} \diagdown \\ \text{CO}\cdot\text{O} \end{smallmatrix} \begin{smallmatrix} \diagdown \text{C} \diagup \\ \text{C}_6\text{H}_3(\text{OMe}) \end{smallmatrix} \text{O}$, crystallises in colourless tablets, m. p. 197°, and the second, the *phenolbetaine* of *methoxyfluorescein methyl ester* (formula I) forms brick-red needles, m. p. 176—177°. The *chloride* forms orange-red grains, and undergoes hydrolysis only when the aqueous solution is kept for a long time or if it is warmed.



Treatment of the above compound with methyl sulphate as before furnishes the *methosulphate* of *methyl 3:6-dimethoxy-9-phenylxanthylium-2'-carboxylate*, from which the *chloride* (formula II), amber-yellow prisms with a bluish-violet reflex, the *nitrate*, yellow leaflets, the *dichromate*, *iodide*, and *platinichloride* were prepared. J. C. C.

Syntheses in the Brazan Group. A. GRAFMANN and STANISLAUS VON KOSTANECKI (*Ber.*, 1909, 42, 822—824).—Liebermann's method for the preparation of hydroxybrazanquinones from dichloro-*a*-naphthaquinone and phenols only holds for resorcinol and, as is now found, for orcinol.

3-Hydroxy-1-methylbrazanquinone, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me} \begin{smallmatrix} \diagup \text{O}\cdot\text{C}\cdot\text{CO} \\ \diagdown \text{C} \diagup \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$, is obtained in red needles, m. p. 315°, which dissolve both in dilute sodium hydroxide and in concentrated sulphuric acid with a blue coloration. The 3-acetoxy-derivative crystallises in lustrous, golden plates, m. p. 278°. If the acetylation is carried out in presence of zinc dust, the acetylated leuco-compound, 3:1':4'-triacetoxy-1-methylbrazan, is obtained; this crystallises in colourless needles, m. p. 243—244°, and is dissolved in concentrated sulphuric acid with a

green coloration and intense dark green fluorescence. *3-Methoxy-1-methylbrazanquinone*, obtained on methylation with methyl sulphate, forms orange-yellow needles, m. p. 240° , which can be distilled without decomposition and dissolve in concentrated sulphuric acid with a blue coloration. When acetylated in presence of zinc dust, *3-methoxy-1-methyl-1':4'-diacetoxybrazan* is formed; this separates in colourless, glistening crystals or needles, m. p. $221-222^{\circ}$.

The above compounds are formulated as 3-hydroxy-1-methyl derivatives, but they may with equal right be represented as 1-hydroxy-3-methylbrazanquinones.

E. F. A.

Reduction of the Thiophen Nucleus. VICTOR THOMAS (*Bull. Soc. chim.*, 1909, [iv], 5, 182).—In connexion with the publication of a note by Padoa and Ponti (*Abstr.*, 1907, i, 146) on the reduction of the furan nucleus by hot nickel, the author points out that he is studying the reduction of the thiophen nucleus by this method, and the results so far obtained show that the reaction takes a different course from that found for furan by the Italian chemists, the ring being ruptured and benzene formed.

T. A. H.

Preparation of Leuco-derivatives. Substituted "Thioindigotin." FARBERWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 204763).—*2-Methylthiol-4-methylbenzoic acid*, $C_6H_3Me(SMe) \cdot CO_2H$, is prepared by diazotising 4-methylanthranilic acid and treating the diazo-solution successively with potassium xanthate and sodium methyl sulphate. *Methylthiolcarboxymethylbenzoic acid* [*4-carboxy-methylthiolacetic acid*], $CO_2H \cdot CH_2 \cdot S \cdot C_6H_3Me \cdot CO_2H$, yellow crystals, m. p. $194-195^{\circ}$, is obtained by replacing sodium methyl sulphate by sodium chloroacetate in the preceding reaction. The former of these two substances yields *3-oxy-6-methylthionaphthen*, m. p. 84° , and *3-oxy-6-methylthionaphthencarboxylic acid* on treatment with sodium-lead in the presence of alkali hydroxide at 210° ; the latter gives the same products when heated at $180-190^{\circ}$ with aqueous alkali hydroxide.

These thionaphthen derivatives when heated with sodium thio-sulphate and glycerol at $120-130^{\circ}$ furnish the leuco-derivative of "dimethylthioindigotin," from which on oxidation the red colouring matter is produced.

The patent contains reference to other substituted "thioindigotins."

G. T. M.

[Preparation of a Thioindigoid Dye from Acenaphthenequinone.] BASLER CHEMISCHE FABRIK (D.R.-P. 205377).—Acenaphthenequinone when heated with carbomethoxy-*o*-thiobenzoic acid or 2-hydroxythionaphthen, either alone or with a condensing agent, such as anhydrous sodium carbonate or sodium acetate and acetic anhydride, yields a colouring matter which crystallises from hot glacial acetic acid or benzene as a yellow or brownish-red powder. This compound probably has the following constitution:

$C_{10}H_6 \begin{matrix} & CO & CO \cdot C_6H_4 \\ & \diagdown & \diagup \\ & C = C - S \end{matrix}$

G. T. M.

(compare *Abstr.*, 1908, i, 979).

Preparation of a Substituted α -Oxythionaphthen. KALLE & Co. (D.R.-P. 202696. Compare Abstr., 1908, i, 953).—4-Chloro-2-nitrothiophenol, when reduced with iron and hydrochloric acid and the product treated with sodium chloroacetate, gives rise to 4-chloro-2-aminophenylthiolacetic acid. The latter substance, when successively diazotised and treated with cuprous cyanide, furnishes *p*-chloro-*o*-cyanophenylthiolacetic acid, white needles, m. p. 164—165°.

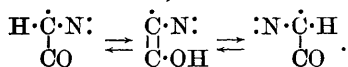
4-Chloro-2-aminothionaphthencarboxylic acid, which results from the alkaline hydrolysis of the cyano-compound, yields *chloro- α -oxythionaphthen*, white needles, m. p. 106°, when heated with dilute sulphuric acid, ammonia and carbon dioxide being simultaneously eliminated.

G. T. M.

Partial Racemism. ALBERT LADENBURG (*Annalen*, 1909, 364, 227—271).—A résumé of the author's publications on this subject, abstracts of which have already appeared (compare Ladenburg and Herz, Abstr., 1898, i, 296, 405; Ladenburg and Doctor, Abstr., 1898, i, 707; 1899, i, 310; Ladenburg and Bobertag, Abstr., 1903, i, 575; Ladenburg and Fischl, Abstr., 1907, i, 586; Ladenburg and Herrmann, Abstr., 1908, i, 364).

W. H. G.

Cinchona Alkaloids. IX. Oxidation of Cinchona Alkaloids to Ketones. PAUL RABE [with WILHELM NAUMANN and ERICH KULIGA] (*Annalen*, 1909, 364, 330—352).—It has been shown previously (Abstr., 1908, i, 100) that cinchonine contains a secondary hydroxyl group, since on oxidation it yields a ketone, namely, cinchoninone. It is now found that cinchonidine, quinine, quinidine, and hydrocinchonine, when oxidised with chromic acid, also yield ketones, and are consequently to be regarded as secondary alcohols. The ketone derived from cinchonidine is definitely proved to be identical with that obtained from cinchonine; at first sight it would appear that two stereoisomeric ketones should be formed, but it has been shown that cinchoninone is a tautomeric substance (Abstr., 1908, i, 100, 361); consequently, the stereoisomeric ketones derived from the two alkaloids are able to pass one into the other, thus:



The ketone derived from cinchonine and cinchonidine is the less soluble of these isomeric forms which crystallises from the equilibrium mixture. The fact that cinchoninone exhibits mutarotation is in agreement with this statement.

Only one ketone, namely, quininone, is obtained when quinine and quinidine are oxidised. Hydrocinchonine gives rise to hydrocinchoninone. Both these ketones exhibit mutarotation.

The final optical rotatory power of an alcoholic solution of cinchoninone from cinchonine is $[\alpha]_D^{13} + 76.25^\circ$ ($c = 3.279$), $[\alpha]_D^{10} + 75.52^\circ$ ($c = 3.270$), and from cinchonidine is $[\alpha]_D^{13} + 72.31^\circ$ ($c = 3.305$) and $[\alpha]_D^{13} + 71.61^\circ$ ($c = 3.3025$). The difference in the optical behaviour of the two specimens is due to the presence of impurity, since the methiodide of the compound from cinchonine has $[\alpha]_D^{11} + 65.39^\circ$

($c = 2.0645$ in chloroform) and from cinchonidine, $[\alpha]_D^{12} + 65.35^\circ$ ($c = 2.058$ in chloroform).

Quininone, $C_{20}H_{22}O_2N_2$, prepared by oxidising quinine or quinidine with chromic acid in strong sulphuric acid, crystallises in almost colourless needles or leaflets, m. p. 101° (heated slowly) or 108° (heated quickly), $[\alpha]_D^{23} + 73.79^\circ$ (final value; $c = 2.141$ in alcohol). It is an amphoteric substance; the *hydrochloride*, $C_{20}H_{22}O_2N_2 \cdot HCl$, obtained as a hygroscopic, yellow, crystalline powder, has m. p. $210-212^\circ$, $[\alpha]_D^{14} + 58.67^\circ$ (final value; $c = 1.926$ in alcohol); the *sulphate* is an amorphous substance, m. p. about $106-108^\circ$; the *picrate*, $C_{26}H_{25}O_9N_5$, forms canary-yellow crystals, m. p. $232-233^\circ$; the *picrolonate*, $C_{30}H_{30}O_7N_6$, crystallises in small, yellow, prismatic needles, m. p. $197-198^\circ$; the *methiodide*, $C_{20}H_{22}O_2N_2 \cdot MeI$, forms almost colourless, feathery crystals, m. p. $213-214^\circ$; the *oxime*, $C_{20}H_{23}O_2N_3$, is a vitreous substance, m. p. about 113° .

Hydrocinchoninone, $C_{19}H_{22}ON_2$, prepared from hydrocinchonine, forms pale yellow crystals, m. p. 138° , $[\alpha]_D^{15} + 76.06^\circ$ (final value; $c = 3.300$), $[\alpha]_D^{19} + 76.22^\circ$ (final value; $c = 2.296$). The *methiodide*, $C_{19}H_{22}ON_2 \cdot MeI$, forms small, pale yellow crystals, m. p. $234-235^\circ$; the *hydrochloride*, $C_{19}H_{22}ON_2 \cdot HCl$, is white and sinters at 256° , m. p. 265° ; the *dihydrochloride* is very deliquescent, and could not be crystallised; the *picrate*, $C_{25}H_{25}O_8N_5$, forms yellow crystals, m. p. 186° ; the *picrolonate*, $C_{29}H_{30}O_6N_6$, is an orange, crystalline substance, m. p. about 90° (decomp.); the *oxime*, $C_{19}H_{23}ON_3$, is an amorphous, yellow powder, m. p. $88-100^\circ$ (decomp.).

W. H. G.

Preparation of Quinine and Cinchonine *p*-Aminophenylarsinates. VEREINIGTE CHEMISCHE WERKE AKTIENGESellschaft (D.R.-P. 203081).—*Quinine p-aminophenylarsinate*, white needles, m. p. 202° , is obtained by double decomposition from quinine hydrochloride and sodium *p*-aminophenylarsinate. *Cinchonine p-aminophenylarsinate*, small prisms, m. p. 180° , is obtained similarly.

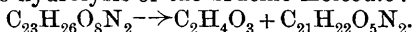
G. T. M.

Preparation of Cotarnine Cholate. F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 206696).—*Cotarnine cholate*, yellow powder, m. p. $118-120^\circ$ (decomp.), readily soluble in water and alcohol, is produced by mixing cholic acid and cotarnine in water or some other suitable solvent and evaporating the solution to dryness in a vacuum at 45° . This compound is employed in gynaecology.

G. T. M.

Strychnos Alkaloids. III. Reactions of Brucinonic Acid and Fission of the Brucine Molecule. HERMANN LEUCHS and LOTHAR E. WEBER (*Ber.*, 1909, 42, 770—777. Compare *Abstr.*, 1908, i, 563; this vol., i, 120).—It has already been shown that the dibasic brucinonic acid contains two methoxyl groups and the $>N \cdot CO$ radicle, groupings which are contained in brucine itself. The remaining oxygen atom is now shown to be ketonic, as the acid gives *brucinonic acid oxime*, $C_{23}H_{25}O_8N_3$, a crystalline powder, m. p. 293° (corr., decomp.), $[\alpha]_D^{20} + 128.2^\circ$, and a *semicarbazone*, $C_{24}H_{27}O_8N_5 \cdot 3H_2O$, which forms colourless needles, m. p. $250-251^\circ$ (corr., decomp.), $[\alpha]_D^{20} + 252^\circ$. On

reduction with sodium amalgam, the semicarbazone is converted into the isomeric compound, $C_{24}H_{27}O_8N_5$, which forms crystals, m. p. 237—238°, $[\alpha]_D^{20} + 128.4^\circ$; the nature of this derivative has not yet been elucidated. Brucinonic acid yields on reduction with sodium amalgam *brucinolic acid*, $C_{23}H_{26}O_8N_2$, which separates from chloroform in crystals, m. p. 250—251° (corr., decomp.), $[\alpha]_D^{20} - 22^\circ$; its *acetyl* derivative has m. p. 295° (decomp.). The solution of this acid in normal sodium hydroxide ($1\frac{1}{2}$ mols.) gradually deposits *brucinolone*, $C_{21}H_{22}O_5N_2$, which crystallises from glacial acetic acid in massive prisms, m. p. 289° (corr.), $[\alpha]_D^{20} - 32.12^\circ$; a molecular-weight determination in acetic acid gave 354, calc. 382; this substance is neutral. The alkaline mother liquor contains glycollic acid, and these compounds have been derived from the hydrolysis of the brucine molecule:



W. R.

Crystallography of Pyridine Derivatives. EVGRAF S. FEDOROFF (*Zeitsch. Kryst. Min.*, 1909, 46, 210—213; from *Verh. russ. Min. Ges.*, 1905, 43, 207—236).—2-Oximinobenzoylpyridine (two modifications: colourless, rhombic crystals and pale yellow, monoclinic crystals); 4-oximinobenzoylpyridine (monoclinic); 4-benzoylpyridine picrate (monoclinic); phenyl-2-pyridylcarbinol (rhombic); 2-benzylpyridine picrate (monoclinic); 4-benzylpiperidine platinichloride (rhombic ?); 4-benzylpyridine picrate (triclinic). L. J. S.

Resolution of the Racemic Cincholeuponic Acids into their Active Forms. ALFRED WOHL and RUDOLF MAAG (*Ber.*, 1909, 42, 627—633. Compare Wohl and Losanitsch, *Abstr.*, 1908, i, 47).— α - and β -Cincholeuponic acids have been resolved by the aid of brucine; the β -*d*-acid is identical with the acid obtained from quinine or cinchonine; a further step in the synthesis of quinine has therefore been accomplished.

Fractional crystallisation of the brucine salt of α -*r*-cincholeuponic acid does not give a pure salt, but a mixture of the *r*-salt with the salt of the *l*-acid. The *l*-acid can, however, be obtained from the acid derived from this salt by crystallisation from water. α -*l*-Cincholeuponic acid is anhydrous and forms prisms, m. p. 253° (corr.), $[\alpha]_D^{20} - 35.0^\circ$ in a 4.42% solution. The *d*-acid from the syrupy filtrate of the brucine salt gave m. p. 253° and $[\alpha]_D^{20} + 34.90^\circ$. α -*r*-Acetylcincholeuponic anhydride, prepared by boiling acetic anhydride and the hydrobromide for half an hour, crystallises from a mixture of alcohol and ether in rosettes of needles, m. p. 121°, and is converted by hot water into α -*r*-acetylcincholeuponic acid, $C_{10}H_{15}O_8N$, which forms needles, m. p. 175° (corr.).

The β -acid was resolved by using the acetyl compound instead of the acid itself. β -*r*-Acetylcincholeuponic anhydride forms rosettes, m. p. 135—136° (corr.), and the *acid*, from anhydride and water, has m. p. 184—185° (corr.). Resolution of this acid by brucine gave the β -*d*-acetylcincholeuponic acid, m. p. 167—168°, $[\alpha]_D^{20} + 19.86^\circ$, which is identical with the compound from quinine. Hydrolysis by 20% hydrochloric acid gave β -*d*-cincholeuponic acid hydrochloride, $[\alpha]_D^{20} 38.04^\circ$, m. p. 192—194°; a crystallographic examination, showing that the

compound was identical in all respects with that obtained from cinchonine by Skraup. The *l*-hydrochloride has m. p. 192—194° and $[\alpha]_D^{20} - 36.51^\circ$. W. R.

New Quinoline Derivatives and Examples of Steric Hindrance. OTTO STARK [with FELIX HOFFMANN] (*Ber.*, 1909, 42, 715—719. Compare Abstr., 1907, i, 973).—Benzoylacetone condenses with an alcoholic solution of *o*-aminobenzaldehyde in the presence of a little piperidine, yielding 3-benzoyl-2-methylquinoline, $C_{17}H_{13}ON$, and not 3-acetyl-2-phenylquinoline. The compound crystallises from light petroleum in well-developed prisms, m. p. 61—62°. The oxime, $C_{17}H_{14}ON_2$, forms colourless needles from alcohol, and has m. p. 230—231°. When distilled with potassium hydroxide and a little water, the ketone yields α -quinaldine.

Dibenzoylmethane reacts with *o*-aminobenzaldehyde at 200—210°, yielding 3-benzoyl-2-phenylquinoline, $C_{22}H_{15}ON$, which crystallises from methyl alcohol in needles, m. p. 134—135°. It does not yield an oxime under ordinary conditions, but a 7% yield of oxime, $C_{22}H_{16}ON_2$, can be obtained when a large excess of hydroxylamine hydrochloride (6 mols.) and sodium hydroxide (18 mols.) are used in alcoholic solution. It has m. p. 210—211°. When decomposed by distillation with potassium hydroxide, the ketone yields 2-phenylquinoline and benzoic acid.

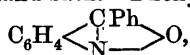
Examples of steric hindrance were noticed in the formation of the ketones, and also in the formation of the oximes. J. J. S.

Tetrahydroacridone. H. TIEDTKE (*Ber.*, 1909, 42, 621—626).—In analogous manner to the preparation of tetrahydroacridine from *o*-aminobenzaldehyde (Abstr., 1908, i, 682), tetrahydroacridone is obtained by the condensation of anthranilic acid and cyclohexanone. In this case, however, the intermediate product can be isolated, cyclohexanone-anil-o-carboxylic acid, $CO_2H \cdot C_6H_4 \cdot N \cdot C_6H_{10}$. It is obtained by heating the acid and the hydroaromatic ketone at 120° during one to two hours, and separates from benzene as a crystalline compound, m. p. 148°. It decomposes spontaneously on keeping, is hydrolysed by boiling water into its components, and has basic as well as acidic properties.

To prepare the tetrahydroacridone, $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \text{N} \end{smallmatrix} C_6H_5$, the anthranilic acid and cyclohexanone are heated first at 120° and afterwards at 220°. The yield is 40%, the remainder forming aniline and carbon dioxide. It crystallises from alcohol in small, colourless needles, m. p. 358°, and is easily soluble in dilute sulphuric acid, a property which can be utilised for the separation of acridone and tetrahydroacridone. It is oxidised by dry air at 280° into acridone, and distillation with zinc dust results in the formation of acridine. W. R.

New Method of Formation of Acridone. ALFRED KLIEGL (*Ber.*, 1909, 42, 591—594. Compare Graebe and Lagodzinski, Abstr., 1892, 1086).—When 10—20 grams of *o*-nitrodiphenylmethane are carefully heated in a tubulated retort, a vigorous reaction begins at 300°. This reaction can be controlled by immersing the retort in cold sand so that the mass boils regularly; water and some *o*-nitrodiphenyl-

methane pass over, and a residue is left, which sets to a crystalline mass. When this is distilled (without thermometer), a small amount of *o*-aminobenzophenone passes over and then acridone. The reaction is less vigorous when the nitrohydrocarbon is mixed with liquid paraffin and heated on a sand-bath. Phenylantranil,

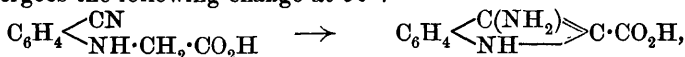


appears to be formed as an intermediate product (compare Bamberger and Elger, Abstr., 1903, i, 560), and can be isolated by means of an alcoholic mercuric chloride solution.

p-Tolylantranil when heated yields 3-methyl-9-acridone, $\text{C}_{14}\text{H}_{11}\text{ON}$, which crystallises from glacial acetic acid in microscopic needles resembling acridone. Both compounds yield *hydrochlorides* when hydrochloric acid is added to the suspension of the compound in hot glacial acetic acid.

J. J. S.

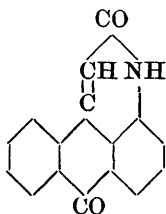
Preparation of Indoxylcarboxylic Acid and Indoxyl. KALLE & Co. (D.R.-P. 206903).—*o*-Nitrobenzonitrile, when reduced at low temperatures with iron and acetic or hydrochloric acid, gives a good yield of *o*-aminobenzonitrile, from which *o*-cyanophenylglycine is readily obtained. The latter, on heating with 35% sodium hydroxide, undergoes the following change at 90° :



and this intermediate product, when further heated with alkali at 150 – 220° , loses ammonia and passes into indoxylcarboxylic acid and indoxyl, from which indigotin can be produced in the usual way.

G. T. M.

[Preparation of Pyridones of the Anthracene Series.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 203752. Compare Abstr., 1908, i, 456).—1-Acetylamino-anthraquinone, like its methyl derivative, undergoes



condensation to form a pyridone when heated in nitrobenzene solution with finely-divided potassium hydroxide at 140° . The product, *anthrapyridone* (annexed formula), is sparingly soluble in organic media, and dissolves in concentrated sulphuric acid to a yellow, fluorescent solution. Four other compounds of this type are described in the patent. G. T. M.

Preparation of *p*-Phenylenediamine. AKTIENGESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 202170).—*p*-Phenylenediamine is readily obtained by heating *p*-dichlorobenzene, ammonia (25%), and copper sulphate for twenty hours at 170 – 180° , and finally at 200° .

G. T. M.

Preparation of *p*-Phenylenediaminesulphonic Acid. AKTIENGESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 202564 and 202565).—*p*-Phenylenediaminesulphonic acid is readily obtained by heating together *p*-dichlorobenzenesulphonic acid, copper chloride, and

ammonia (25%) at 170°. This acid is also produced in the foregoing manner when the dichloro-acid is replaced by *p*-chloroaniline-2-sulphonic acid.

G. T. M.

Preparation of *p*-Phenylenediaminesulphonic Acid. AKTIENGESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 202564, 204972).—*p*-Phenylenediaminesulphonic acid is obtained by heating 4-chloroaniline-3-sulphonic acid with aqueous ammonia in presence of copper salts.

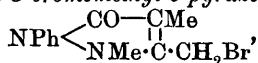
G. T. M.

Preparation of 4-Amino-4'-hydroxydiphenylamine. AKTIENGESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 204596).—The oxidation of *p*-phenylenediamine and phenol to indophenol is readily effected by hypochlorite solution in the presence of copper salts. When reduced with sodium sulphide, the indophenol gives rise to 4-amino-4'-hydroxydiphenylamine.

G. T. M.

Preparation of 1-Aryl-2:4-dialkyl-3-halogenmethyl-5-pyrazolones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 206637).—It has been found that the 1-aryl-3-methyl-2:4-dialkyl-5-pyrazolones yield halogen additive products, which, after removal of hydrogen halide, furnish monohalogenated derivatives in which the halogen is situated in the methyl group.

1-Phenyl-2:4-dimethyl-3-bromomethyl-5-pyrazolone,



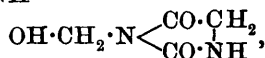
leaflets or prisms, m. p. 113°, produced from 1-phenyl-2:3:4-trimethyl-5-pyrazolone by the successive action of bromine and sodium carbonate, yields, on boiling with water, 3-hydroxy-1-phenyl-2:3:4-trimethylpyrazolone, colourless prisms, m. p. 170°.

1-Phenyl-2:4-dimethyl-3-chloromethyl-5-pyrazolone, colourless crystals, m. p. 110—112°, is similarly obtained, and from 1-phenyl-2:3-dimethyl-4-ethyl-5-pyrazolone a similar series of operations leads to 1-phenyl-2-methyl-3-bromomethyl-4-ethyl-5-pyrazolone, colourless crystals, m. p. 112—113°, and 1-phenyl-2-methyl-3-hydroxymethyl-4-ethyl-5-pyrazolone, needles, m. p. 122—123°.

G. T. M.

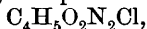
Condensation of Hydantoin with Formaldehyde. ROBERT BEHREND and RUDOLF NIEMEYER (*Annalen*, 1909, 365, 38—49).—

Hydroxymethylhydantoin, $\text{OH} \cdot \text{CH}_2 \cdot \text{N} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ | \\ \text{CO}-\text{NH} \end{array}$ or



is readily prepared by heating hydantoin with 40% formaldehyde solution (1.3 mols.). It crystallises from alcohol in felted needles, m. p. 125—135°. When heated at 120—130° for several hours, it forms a clear, fused mass, which yields the compound $\text{C}_7\text{H}_8\text{O}_4\text{N}_4$ when crystallised from hot water. The hydroxymethyl derivative is completely hydrolysed when boiled with water for an hour.

Phosphorus pentachloride, or, even better, concentrated hydrochloric acid, transforms the hydroxy-compound into *chloromethylhydantoin*,

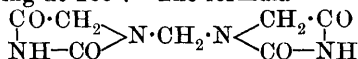


which crystallises from benzene or chloroform in well-developed prisms, m. p. 150—157°. It has not been found possible to reduce the hydroxy- or chloro-derivative to methylhydantoin.

When hydantion is warmed with formaldehyde in the presence of hydrochloric acid, complex condensation products are formed.

The compound, $\text{C}_8\text{H}_{10}\text{O}_5\text{N}_4$, is obtained when a few drops of concentrated hydrochloric acid are used. It crystallises from hot water in the absence of hydrochloric acid as compact, colourless prisms, m. p. 203—212°. In the presence of hydrochloric acid it yields the compound, $\text{C}_7\text{H}_8\text{O}_4\text{N}_4$.

This latter compound is also formed when hydantoin and formaldehyde are condensed in a strongly acid liquid. It crystallises from hot water, in which it is sparingly soluble, in lancet-shaped needles, m. p. 295°, after sintering at 285°. The formula



is suggested.

A compound, $\text{C}_{14}\text{H}_{18}\text{O}_9\text{N}_6$, is produced when equal volumes of concentrated hydrochloric acid and 40% formaldehyde solution are used in the condensation. It crystallises from hot water in slender prisms, m. p. 183—188°. When boiled for some time with water or alcohol it loses formaldehyde, and ultimately yields the compound $\text{C}_7\text{H}_8\text{O}_4\text{N}_4$. In the preparation of the compound $\text{C}_{14}\text{H}_{18}\text{O}_9\text{N}_6$, considerable amounts of amorphous compounds are formed. When washed with alcohol, these form a hard cake, m. p. 83—85°, and readily absorb water.

J. J. S.

Synthetical Experiments in the Iminazole [Glyoxaline] Group. ADOLF WINDAUS (*Ber.*, 1909, 42, 758—763).—4-Methylglyoxaline condenses with formaldehyde when heated for eight hours in a closed tube at 120° to form a crumbly, hygroscopic mass, not of glyoxaline-4-ethanol, as might have been expected, but of 4-methylglyoxaline-5-carbinol. Picrolonic and phosphotungstic acids give precipitates with its aqueous solution; the platinichloride is difficultly soluble. Reduction of this substance with hydriodic acid gives 4:5-dimethylglyoxaline (oxalate, m. p. 261°; *picrate*, $\text{C}_{11}\text{H}_{11}\text{O}_7\text{N}_5$, m. p. 195°; aurichloride, m. p. 179—180°; nitrate, m. p. 175—176°: compare Künne, *Abstr.*, 1895, i, 685), a result which shows that the above conclusion is correct, as otherwise ethylglyoxaline would be formed. The methyl group in position 4 is not therefore reactive; it is the methylene group in the ring which gives the derivative, and this reaction, which is a general one for aldehydes, is not a possible method for the production of histidine derivatives. In the light of this result, doubt is thrown on the correctness of the constitution assigned by Gerngross to the product obtained from methylglyoxaline and chloral (this vol., i, 189). *Dibenzoylbutylenediamine*, $\text{C}_8\text{H}_{18}\text{O}_2\text{N}_2$, from dimethylglyoxaline, benzoyl chloride, and sodium hydroxide, crystallises in long needles, m. p. 241°.

Methylglyoxaline, when heated with nitric acid (D 1.5) at 80° for thirty minutes, gives a 60% yield of a *nitromethylglyoxaline*, $C_4H_5O_2N_3$, which crystallises from water in long prisms, decomp. 248°; solutions in ammonia or potassium hydroxide are intensely yellow, and bromine gives a *bromonitromethylglyoxaline*, $C_4H_4O_2N_3Br$, which forms prisms, m. p. 228° (decomp.).

1:4-Dimethylglyoxaline gives a *nitro-derivative*, $C_5H_7O_2N_3$, which separates from water in long needles, m. p. 160—161°, and which does not yield alkali salts. The 2:5-dimethylglyoxaline on nitration gives 4-nitro-2:5-dimethylglyoxaline, $CMe \begin{smallmatrix} \text{NH} \text{---} CMe \\ \diagdown \quad \diagup \\ C(NO_2) \cdot N \end{smallmatrix}$; this forms long needles from water, m. p. 252°; its aqueous solution is neutral, but its *potassium* salt is intensely yellow, and is supposed to have the *isoiminazole* constitution: $CMe \begin{smallmatrix} N \text{---} CMe \\ \diagdown \quad \diagup \\ C(:NO_2K) \cdot N \end{smallmatrix}$, a conclusion which is in harmony with the experimental fact that the 1-methyl nitro-derivative does not give a salt.

W. R.

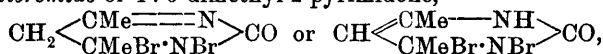
Preparation of Pyridazine. SIEGMUND GABRIEL (*Ber.*, 1909, 42, 654—658).—The disadvantages attending the preparation of pyridazine by the three methods already known (Täuber, *Abstr.*, 1895, i, 301; Gabriel and Colman, *ibid.*, 1899, i, 390; Marquis, *ibid.*, 1903, i, 370) are avoided by the author, who obtains the substance in quantity by the following method. An aqueous solution of α -ketoglutaric acid (Blaise and Gault, *Abstr.*, 1908, i, 713) is treated with hydrazine sulphate dissolved in *N*-sodium hydroxide, and the mixture evaporated to dryness; the residue by crystallisation from hot water yields the *sodium* salt, $C_5H_5O_3N_2Na \cdot C_5H_5O_3N_2 \cdot 2H_2O$, from which, by boiling 10% hydrochloric acid, hydrated *pyridazinone-3-carboxylic acid*, $CO \begin{smallmatrix} \text{NH} \text{---} N \\ \diagdown \quad \diagup \\ CH_2 \cdot CH_2 \end{smallmatrix} C \cdot CO_2H \cdot H_2O$, is obtained; this, when anhydrous, has m. p. 198°, and by treatment with bromine in glacial acetic acid yields *pyridazone-3-carboxylic acid*, $CO \begin{smallmatrix} \text{NH} \text{---} N \\ \diagdown \quad \diagup \\ CH \cdot CH \end{smallmatrix} C \cdot CO_2H$, m. p. 259—260° (decomp.), which is changed quantitatively by fusion into 6-pyridazone, $CO \begin{smallmatrix} \text{NH} \text{---} N \\ \diagdown \quad \diagup \\ CH \cdot CH \end{smallmatrix} CH$, m. p. 103—104°. The latter, by warming with phosphoryl chloride, yields 3-chloropyridazine, m. p. 35°, from which pyridazine is obtained by means of hydriodic acid and red phosphorus.

C. S.

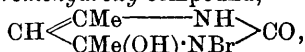
Constitution of Acetylacetonecarbamide [4:6-Dimethyl-2-pyrimidone]. II. Action of Bromine on Acetylacetonecarbamide and on its Benzylidene Derivatives. OTTO STARK (*Ber.*, 1909, 42, 708—714. Compare Evans, *Abstr.*, 1893, i, 129).—The dibenzylidene derivative of 4:6-dimethyl-2-pyrimidone (following abstract) readily combines with bromine in acetic acid solution, yielding a red dibromide. 4:6-Dimethyl-2-pyrimidone yields a similar yellow dibromide in chloroform solution provided that all traces of moisture are absent. In both compounds the bromine has added

itself on to a double linking in the ring. The bromides react readily with alcohol or water, yielding bromo-hydroxy- or bromo-ethoxy-derivatives. It has not been found possible to obtain tetrabromides.

The *dibromide* of 4 : 6-dimethyl-2-pyrimidone,

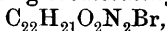


is insoluble in most organic solvents; it turns dark grey at 160°, but is not molten at 360°. When rubbed with water, the yellow colour disappears, and the *bromohydroxy*-compound,



is obtained. This crystallises from alcohol in slender needles, which darken at 250°, sinter at about 330°, and decompose at 345°. The same product is obtained by the action of bromine on an acetic acid solution of the pyrimidone, and, when shaken with concentrated hydrobromic acid in the cold, yields Evans's dibromodihydroxy-derivative, $\text{CH}_2 \begin{array}{c} \text{CMe(OH)} \cdot \text{NBr} \\ \text{CMe(OH)} \cdot \text{NBr} \end{array} \text{CO}$. The corresponding *bromoethoxy*-derivative, $\text{C}_8\text{H}_{13}\text{O}_2\text{N}_2\text{Br}$, obtained by the action of ethyl alcohol on the dibromide, decomposes at 340—350°, after sintering at 330°.

The *dibromide* of the dibenzylidene derivative, $\text{C}_{20}\text{H}_{16}\text{ON}_2\text{Br}_2$, decomposes at 322—325°, after turning brown at 240° and sintering at 318°. The *bromohydroxy*-derivative, $\text{C}_{20}\text{H}_{17}\text{O}_2\text{N}_2\text{Br}$, crystallises from alcohol in orange-yellow needles, sinters at 304°, and decomposes at 310—312°. The corresponding *bromoethoxy*-derivative,



crystallises from alcohol in orange-yellow needles, which decompose at 308°, after sintering at 303—305°. J. J. S.

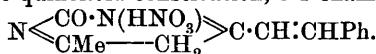
Constitution of Acetylacetonecarbamide (4 : 6-Dimethyl-2-pyrimidone). Condensation with Aromatic Aldehydes. I. ORTO STARK (*Ber.*, 1909, 42, 699—708. Compare Evans, *Abstr.*, 1893, i, 129; Combes, *ibid.*, i, 454; de Haan, *Abstr.*, 1908, i, 454).—Evans's compound condenses with alcoholic solutions of aromatic aldehydes in the presence of small amounts of piperidine. When benzaldehyde is used, a mono- and a di-benzylidene derivative are formed, and it is thus probable that it is the methyl and not the methylene hydrogen atoms which condense with the aldehydic oxygen. With *p*-hydroxybenzaldehyde and vanillin, only one molecule of aldehyde reacts. It is suggested that the condensation products are formed from the tautomeric form of the carbamide, namely, 4 : 6-dimethyl-2-pyrimidone; thus the monobenzylidene derivative is represented as



this is practically colourless, but the corresponding *p*-hydroxy- and hydroxymethoxy-compounds are respectively dark yellow and yellowish-brown in colour.

The salts derived from these condensation products have a much

deeper colour, namely, yellowish-red to dark red, and it is suggested that they have the quinonoid constitution, for example :



A mixture of the mono- and di-benzylidene derivatives is formed even when less than 1 gram-molecule of benzaldehyde is used for each gram-molecule of the pyrimidone, but with an excess of the aldehyde the dibenzylidene compound alone is formed. The two can be fairly readily separated, as the di-compound is only sparingly soluble in alcohol.

4-Benzylidenemethyl-6-methyl-2-pyrimidone, $\text{C}_{13}\text{H}_{12}\text{ON}_2$, crystallises from aqueous alcohol to which a few drops of ammonia solution have been added in slender, colourless needles, m. p. 188—189°, after sintering at 184°. The presence of the least trace of acid produces a yellow coloration.

It yields a colourless sodium salt, a yellow sulphate, an orange-yellow hydrochloride, and an orange-coloured nitrate.

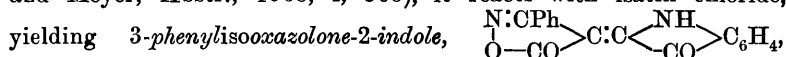
The dibenzylidene derivative, $\text{C}_{20}\text{H}_{16}\text{ON}_2$, crystallises from boiling methyl alcohol in glistening, golden-yellow needles, which turn brown at 230°, sinter at 270°, and melt and decompose at 275°. The salts have a red colour and are sparingly soluble. The p-hydroxybenzylidene derivative, $\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_2$, separates from methyl alcohol as a dark yellow, crystalline powder, m. p. 278—280° (decomp.); it dissolves in mineral acids, yielding solutions with a blood-red colour, and in sodium hydroxide to a yellow solution.

J. J. S.

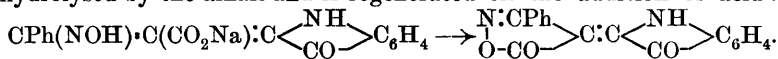
New Synthesis of Pyrazine Derivatives by the Action of Aromatic Nitroso-o-hydroxy-compounds on Acetaldehyde in the Presence of Ammonia or Primary Aliphatic Amines. MARTIN LANGE (*Ber.*, 1909, 42, 574—577).—An account of this work has already appeared in D.R.-P. 196563 (*Abstr.*, 1908, i, 839).

W. H. G.

Indigoid Dyes Derived from Phenylisooxazolone. ANDRÉ WAHL (*Compt. rend.*, 1909, 148, 352—354).—Since phenylisooxazolone behaves as though it contains the grouping $\cdot\text{CH}_2\cdot\text{CO}$ (compare Wahl and Meyer, *Abstr.*, 1908, i, 368), it reacts with isatin chloride,



crystallising in garnet-red needles with a bronzy reflex. The corresponding indigoid dyes derived from the three methoxyphenylisooxazolones form reddish-brown crystals with a coppery reflex. The solutions of the compounds in aqueous sodium hydroxide or carbonate are almost colourless, and yield the parent coloured compounds on the addition of acid. It is probable that the isooxazolone nucleus is hydrolysed by the alkali and is regenerated on the addition of acid :



The yellow solutions obtained by treating the substances with

sodium hyposulphite do not yield the parent compounds when treated with acids or oxidising agents, for example, hydrogen peroxide. The *leuco*-derivatives apparently do not combine with animal or vegetable fibres.

Ethyl anisoylacetate has b. p. 189—190°/10—12 mm. (decomp.) (compare Schoonjans, Abstr., 1898, i, 425).

The following compounds were prepared: *o*-methoxyphenylisooxazolone crystallises in white needles, m. p. 106°; *m*-methoxyphenylisooxazolone forms white plates, m. p. 115°; the *p*-derivative forms white needles, m. p. 143° (compare Schoonjans, *loc. cit.*). W. H. G.

The Antique Purple Dye from Murex brandaris. PAUL FRIEDLÄNDER (*Ber.*, 1909, 42, 765—770. Compare Abstr., 1907, i, 867).—This dye, obtained from the above mollusc, is now shown to be 6 : 6'-dibromindigotin, $C_{16}H_8O_2N_2Br_2$, by a direct comparison with the synthetic dye as regards its spectroscopic behaviour, colour reactions, and solubility. The influence on the colour of indigotins where positions 6 and 6' are occupied is emphasised. W. R.

Preparation of Indazyl Derivatives by means of Ortho-ketonic Hydrazines. PAUL CARRÉ (*Compt. rend.*, 1909, 148, 491—494.* Compare Freundler, Abstr., 1904, i, 108).—The following compounds are obtained when *o*-nitrobenzophenone is reduced by zinc dust and alcoholic sodium hydroxide: (1) benzaldehyde; (2) *o*-aminobenzophenone, m. p. 110—111° (compare Geigy, Abstr., 1885, 1236); this reacts with phenylthiocarbimide giving *o*-phenylbenzophenone-thiocarbamide, $NHPh \cdot CS \cdot NH \cdot C_6H_4 \cdot CPh$, m. p. 156—157°; (3) 4 : 4'-diamino-2 : 2'-dibenzylidiphenyl; (4) 4 : 4'-diamino-2-benzylidiphenyl, $NH_2 \cdot C_6H_4 \cdot C_6H_3(NH_2) \cdot CH_2Ph$, white prisms, m. p. 209°; the hydrochloride decomposes at 200°; (5) a minute quantity of a white substance having the characteristic properties of an indazyl derivative.

o-Azobenzophenone, $CPh \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot CPh$, orange-red crystals, m. p. 201—202°, has been prepared by oxidising *o*-azodiphenylmethane (this vol., i, 121) with chromic acid. When treated successively with ammonium hydrosulphide and mercuric oxide it forms 2-*o*-benzophenone-3-phenylindazole, $C_6H_4 \cdot \begin{smallmatrix} CPh \\ | \\ N \end{smallmatrix} \cdot C_6H_4 \cdot CPh$, white crystals, m. p. 134—135°. W. O. W.

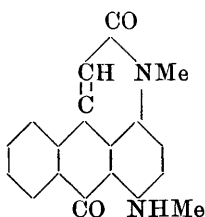
[**Anthrapyridone Derivatives.**] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 205095).—Those anthrapyridones containing a halogen atom in the para-position to the imino-group readily yield *p*-arylaminoanthrapyridones on heating with aromatic bases. These products on sulphonation yield fast wool dyes.

6-*p*-Tolylamino-4-methylantrapyridone, reddish-brown crystals, is produced by heating together 6-chloro-4-methylantrapyridone, *p*-toluidine, and anhydrous sodium acetate.

4 : 6-Di-*p*-tolylaminoanthrapyridone is similarly obtained from 4 : 6-dichloroanthrapyridone. G. T. M.

* and *Bull. Soc. chim.*, 1909, [iv], 5, 283—285.

Preparation of Amino-, Alkylamino-, or Arylamino-anthrapyridones. FARBEFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 201904. Compare Abstr., 1908, i, 456).—The anthrapyridones which contain negative substituents in the benzene rings are readily acted on by primary or secondary bases, giving rise to amino-derivatives which are either dyes or may be employed in the production of colouring matters.

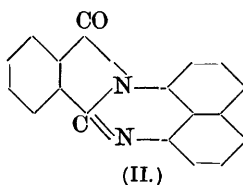
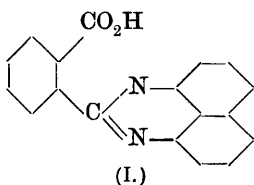


6-Methylamino-3-methylanthrapyridone (annexed formula) separates in red crystals from a pyridine solution of methylamine and *p*-bromo-anthrapyridone after heating at 120° for five hours.

6-*p*-Tolylamino-3-methylanthrapyridone is produced by heating at 160—170° *p*-toluidine with either *p*-methoxyanthrapyridone or *p*-bromo-anthrapyridone; its sulphonic acid dyes wool in violet-red shades which are very fast to light.

G. T. M.

[Production of Iminazoles from 1:8-Naphthylenediamine.] FARBEFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 202354).—By condensing 1:8-naphthylenediamine with the polybasic acids or their anhydrides, a series of coloured condensation products of the iminazole series are obtained. Phthalic anhydride gives rise successively to the products $C_{18}H_{12}O_2N_2$ and $C_{18}H_{10}ON_2$, represented respectively by formulæ I and II.



The former is a yellow compound, m. p. 185°; the latter separates from glacial acetic acid in red needles with a golden reflex, m. p. 227—228°. Similar condensation products are obtained by the use of citric acid, maleic anhydride, succinic anhydride, and *o*-benzoic sulphinide.

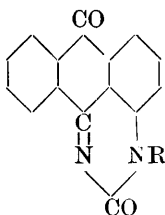
G. T. M.

Preparation of Anthrapyrimidones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 205038).—A new class of anthracene derivatives, the anthrapyrimidones (formula I), are produced by condensing the α -aminoanthraquinones or the α -alkylamino-anthraquinones with urethane, alcohol and water being eliminated. The reaction is a general one.

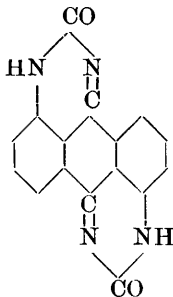
1-Anthrapyrimidone (with H replacing R in the formula), golden-yellow needles, m. p. above 280°, is obtained by heating together α -aminoanthraquinone, urethane, and zinc chloride at 170—180°.

1:5-Anthradipyrimidone (II), a brownish-red powder, is similarly

produced by heating together in nitrobenzene, 1:5-diaminoanthraquinone, urethane, and zinc chloride.



(I.)



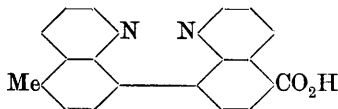
(II.)

G. T. M.

Preparation of Anthrapyrimidones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 205914. Compare preceding abstract).—1-Anthrapyrimidone has now been prepared by condensing the α -halogenated anthraquinones with carbamide in the presence of metallic salts; thus 1-bromoanthraquinone, carbamide, and copper chloride when condensed give this product together with water and hydrogen bromide.

G. T. M.

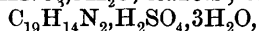
8:8'-Diquinolylcarboxylic Acids. ZYG. VON JAKUBOWSKI and STEFAN VON NIEMENTOWSKI (*Ber.*, 1909, 42, 634—654).—Previous to this investigation no quinolylcarboxylic acids were known, and the first to be examined are those derived from 5:5'-dimethyl-8:8'-diquinolyl (Abstr., 1905, i, 300). The oxidation of this compound is a matter of considerable difficulty; acid or alkaline potassium permanganate, nitric acid, chromic acid in acetic acid solution, fusion with potassium hydroxide and lead peroxide were ineffective. Chromic anhydride in sulphuric acid was found to be suitable, and the mono-



or di-carboxylic acid could be obtained by altering the conditions. **5-Methyl-8:8'-diquinolyl-5'-carboxylic acid** (annexed formula) was prepared by concentrating a mixture of dimethylquinolyl (1 part), 50% sulphuric acid (10 parts), and chromic anhydride (1.4 parts) at 100° until the chromic acid disappears. The purification is carried out by neutralising first with ammonia, then repeatedly crystallising the barium salt, and afterwards converting into potassium salt and recrystallising this. The acid forms a fine white, microcrystalline powder, m. p. 331—332° (decomp.), and is amphoteric in character. The following salts have been prepared: *ammonium*, $C_{20}H_{18}O_2N_2(NH_4) \cdot 3H_2O$, rhombic plates which decompose at 120° into water, ammonia, and acid; *potassium*, $C_{20}H_{13}O_2N_2K \cdot 5H_2O$, leaflets; *barium*, $C_{40}H_{26}O_4N_4Ba \cdot 12H_2O$, leaflets, and a *silver* salt. Also the following: the *hydrochloride*, $C_{20}H_{14}O_2N_2 \cdot 2HCl \cdot H_2O$; *nitrate*, $C_{20}H_{14}O_2N_2 \cdot 2HNO_3$,

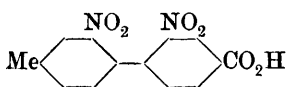
and *sulphate*, all of which crystallise in leaflets. 8:8'-*Diquinolyl-5:5'-dicarboxylic acid*, $C_{20}H_{12}O_4N_2$, is obtained from the reaction mixture of the base, chromic anhydride, and sulphuric acid after twenty-four hours at the ordinary temperature, and is purified first by conversion into the barium salt. The acid is next separated from small quantities of the monocarboxylic acid by treatment with hydrochloric acid, the monocarboxylic acid being soluble in dilute acid, whereas the dicarboxylic acid has no basic properties, and is insoluble in this menstrum. It is a microcrystalline powder, m. p. 415° (decomp.), and has been characterised by the *ammonium*, $C_{20}H_{10}O_4N_2(NH_4)_2, H_2O$, *potassium*, $C_{20}H_{10}O_4N_2K_2, 5H_2O$, *barium*, $C_{20}H_{10}O_4N_2Ba, 7\frac{1}{2}H_2O$, and *silver* salts, all of which crystallise in leaflets and are more easily soluble than the corresponding monocarboxylates.

Distillation of the monocarboxylic acid under diminished pressure leads to the formation of carbon dioxide and 5-methyl-8:8'-*diquinolyl*, $C_{19}H_{14}N_2$, which crystallises in colourless, diagonal plates, m. p. $211.5-212^\circ$; the *hydrochloride*, $C_{19}H_{14}N_2, 2HCl, 5H_2O$, forms needles; the *nitrate*, $C_{19}H_{14}N_2, 2HNO_3, 3H_2O$, leaflets; *sulphate*,



leaflets, and the *platinichloride*, $C_{19}H_{14}N_2, H_2PtCl_6$, orange crystals. Dry distillation of the dicarboxylic acid yields an acid and a base. The acid, 8:8'-*diquinolyl-5-carboxylic acid*, $C_{19}H_{12}O_2N_2$, is a white, microcrystalline powder, m. p. $310-312^\circ$, is amphoteric in character, and is identical with the acid obtained by the oxidation of 5-methyl-8:8'-*diquinolyl* with chromic anhydride and sulphuric acid. The *ammonium*, $C_{19}H_{11}O_2N_2(NH_4), 4H_2O$, and *barium* salts, $C_{38}H_{22}O_4N_4Ba, 11H_2O$, have been prepared. The base, $C_{18}H_{12}N_2$, forms colourless needles, m. p. 182° (not sharp), and is resolved by fractional crystallisation of the hydriodide into a small quantity of 8:8'-*diquinolyl* and an isomeric *diquinolyl*, m. p. 187° .

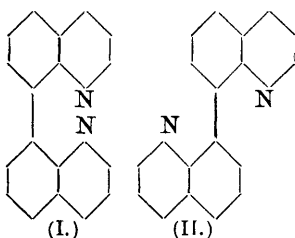
The dicarboxylic acid has been synthesised in the following way. Oxidation of 2:2'-dinitro-4:4'-dimethyldiphenyl by potassium dichromate and sulphuric acid leads to the formation of mono- and di-carboxylic acids in the ratio of 1:4. These are separated by fractional precipitation from a solution of the ammonium salts by hydrochloric acid. 2:2'-*Dinitro-4-methyldiphenyl-4'-carboxylic acid* (annexed formula) forms crystals, m. p. $235.5-236^\circ$; the *ammonium* salt, *barium* salt, $C_{28}H_{18}O_{12}N_4Ba, 4H_2O$, and *silver* salt have been prepared. 2:2'-*Dinitrodiphenyl-*



4:4'-*dicarboxylic acid*, $C_{14}H_8O_8N_2$, forms white crystals, m. p. $335-337^\circ$; its *ammonium* salt and *barium* salt, $C_{14}H_6O_8N_2Ba, 3H_2O$, are yellow, and the methyl ester has m. p. $155-156^\circ$ (Ullmann and Bielecki, Abstr., 1901, i, 586, give $159-160^\circ$). By the reduction of these dinitro-compounds with tin and hydrochloric acid, the corresponding diamino-derivatives are obtained. 2:2'-*Diamino-4-methyldiphenyl-4'-carboxylic acid*, $C_{14}H_{14}O_2N_2$, forms stout, yellow crystals, m. p. $169-171^\circ$; the *hydrochloride*, $C_{14}H_{14}O_2N_2, 2HCl$, has m. p. $280-285^\circ$ (decomp.), whilst 2:2'-*diaminodiphenyl-4:4'-dicarboxylic acid*, $C_{14}H_{12}O_4N_2$, forms very small, rhombic plates, m. p. $307-309^\circ$;

its *diacetyl* derivative, $C_{18}H_{16}O_6N_2$, has m. p. 250° ; the *hydrochloride*, $C_{14}H_{12}O_4N_2 \cdot HCl$, is insoluble. Using arsenic acid as the oxidising agent, this dicarboxylic acid undergoes Skraup's reaction, forming 8:8'-diquinolyl-5:5'-dicarboxylic acid, apparently identical with the acid obtained from dimethyldiquinolyl, yet on dry distillation under reduced pressure, pure 8:8'-diquinolyl (m. p. 205°) was obtained.

The relationships of these two isomeric diquinolyls are discussed. It is not possible to decide yet whether they are structural isomerides;

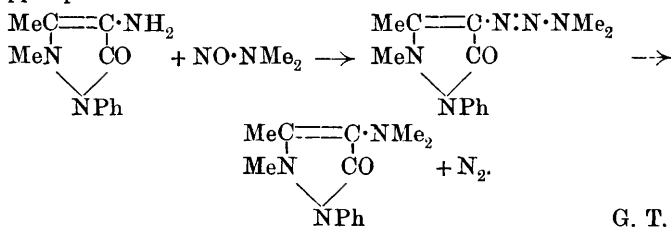


that of m. p. 187° might be the 8:7'- or 8:6'-modification, but this is considered to be improbable. They may be stereoisomerides of the annexed formulæ; their simultaneous production from the same dicarboxylic acid would support this, and the difference in behaviour of the acid obtained from different reactions might be accounted for by a certain fine difference between the acids themselves. Lastly,

they may be analogous to the *ana*-substituted quinoline isomerides, which have not yet been explained (Lellmann and co-workers, Abstr., 1887, 502, 737, 973; 1888, 296, 499).

W. R.

Preparation of 4-Dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone. SOCIÉTÉ CHIMIQUE DE L'AVANCHET (D.R.-P. 203753).—The alkylation of 4-amino-1-phenyl-2:3-dimethyl-5-pyrazolone leads to quaternary compounds, and the yield of "pyramidone" (4-dimethylamino-1-phenyl-2:3-dimethylpyrazolone) is accordingly diminished. An indirect alkylation can be effected by treating the aminopyrazolone with nitrosodimethylamine either alone at 110° or in the presence of copper powder:



G. T. M.

Preparation of 5:5-Dialkyliminobarbituric Acids (5:5-Dialkylmalonylguanidines). BASLER CHEMISCHE FABRIK (D.R.-P. 204795).—The dialkylmalonic acids can be condensed with guanidine when the acid and a salt of the base are suspended in concentrated sulphuric acid and the mixture treated with fuming sulphuric acid, chlorosulphonic acid, or phosphoric oxide.

5:5-Diethylmalonic acid and guanidine thiocyanate or hydrochloride were thus condensed to 2-imino-4:6-dioxy-5:5-diethylpyrimidine (diethylmalonylguanidine), and 2-imino-4:6-dioxy-5:5-dipropylpyrimidine was similarly prepared from 5:5-dipropylmalonic acid and guanidine hydrochloride.

G. T. M.

Intramolecular Transformations. OTTO DIMROTH (*Annalen*, 1909, 364, 183—226).—It has been shown previously that esters of 5-hydroxy-1-phenyl-1:2:3-triazole-4-carboxylic acid readily undergo desmotropic change (compare Abstr., 1905, i, 98, 384). With the object of ascertaining whether the corresponding 5-amino-compounds behave in a similar manner, these substances have been prepared and their chemical behaviour studied. It is found that they also undergo intramolecular change when fused, yielding isomerides which, unlike the parent substances, possess acidic properties. The change under these conditions is a reversible one, but complete conversion into the acidic form may be effected by treating the neutral isomeride with sodium ethoxide or pyridine.

The velocity with which the reaction proceeds in this case, unlike that of the corresponding hydroxy-derivative, is exceedingly small. The isomeric esters when hydrolysed yield isomeric acids, which when heated evolve carbon dioxide, yielding the same acidic substance, m. p. 139°. This substance is not 5-amino-1-phenyl-1:2:3-triazole, consequently it must be derived from the ester having acidic properties. It is also found that 5-amino-1-phenyl-1:2:3-triazole and 5-amino-1:4-diphenyl-1:2:3-triazole when fused completely change into their corresponding isomerides, which are also soluble in alkalis.

Consideration of the properties of the acidic isomerides shows that these are not the result of a desmotropic change; instead, it is definitely proved that they are produced by the phenyl group changing places with a hydrogen atom of the amino-group. 1:2:3-Triazoles may be regarded as cyclic diazoamino-compounds, and this intramolecular change is similar to that which diazoamino-compounds are known to undergo when treated with bases.

The position of the imino-hydrogen atom in the ring is not yet definitely known.

[With G. WERNER.]—*Methyl 5-amino-1-phenyl-1:2:3-triazole-4-carboxylate*, $\begin{array}{c} \text{N} \\ | \\ \text{N} \cdot \text{C}(\text{CO}_2\text{Me}) \end{array} \begin{array}{c} \text{NPh} \\ \text{N} \end{array} \Rightarrow \text{C} \cdot \text{NH}_2$, is obtained by the condensation of

phenylazoimide with methyl cyanoacetate in the presence of sodium methoxide; it crystallises in small, white needles, m. p. 173°, and is converted by boiling with pyridine or sodium ethoxide dissolved in alcohol for three hours into *methyl 5-anilino-1:2:3-triazole-4-carboxylate*, $\text{C}_{10}\text{H}_{10}\text{O}_2\text{N}_4$, crystallising in groups of small, slender needles, m. p. 154°. The corresponding *ethyl* ester, $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_4$, forms slender, felted needles, m. p. 129—130°; it passes into the isomeric *ethyl 5-amino-1-phenyl-1:2:3-triazole-4-carboxylate* to the extent of 33—34% in alcoholic solution and 42—44% in benzene; the *acetate*, $\text{C}_{13}\text{H}_{14}\text{O}_3\text{N}_4$, crystallises in needles, m. p. 90°.

[With G. WERNER and FRITZ HESS.]—*5-Amino-1-phenyl-1:2:3-triazole-4-carboxylic acid*, $\text{C}_9\text{H}_8\text{O}_2\text{N}_4$, formed by boiling the corresponding ester with alcoholic potassium hydroxide for thirty minutes, crystallises in small prisms, m. p. 142° (decomp.); the isomeric *5-anilino-1:2:3-triazole-4-carboxylic acid*, obtained from its ester by boiling with alcoholic potassium hydroxide for twelve to fifteen hours, crystallises in four-cornered scales, m. p. 153° (decomp.). Either of the preceding

acids when fused evolve carbon dioxide and yield 5-anilino-1-phenyl-1:2:3-triazole, and when warmed with 20% sulphuric acid yield *glycollic acid phenylamidine*, $\text{OH}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{NHPh}$, crystallising in colourless needles, m. p. 130°; it is very unstable, and is decomposed by dilute alkalis, forming glycollanilide and ammonia.

[With J. MARSHALL and FRITZ HESS.]—1-Phenyl-1:2:3-triazole-5-carboxylic acid hydrazide, $\text{C}_9\text{H}_9\text{ON}_5$, obtained by heating the ester (Abstr., 1902, i, 403) with hydrazine hydrate under pressure at 120°, forms long, colourless needles, m. p. 143°; it is converted by nitrous acid into the *azoimide*, glistening leaflets, m. p. 99° (decomp.), and by boiling ethyl alcohol into the *urethane*, $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_4$, colourless needles, m. p. 98°. The latter substance when boiled with dilute alkali yields

5-amino-1-phenyl-1:2:3-triazole, $\begin{array}{c} \text{N}\cdot\text{NPh} \\ | \\ \text{N}-\text{CH} \end{array} \text{C}\cdot\text{NH}_2$, crystallising in needles or leaflets, m. p. 110°.

Methyl 5-chloro-1-phenyl-1:2:3-triazole-4-carboxylate, $\text{C}_9\text{H}_6\text{O}_2\text{N}_3\text{Cl}$, prepared by the action of phosphorus pentachloride on methyl 1-phenyl-5-triazolone-4-carboxylate, crystallises in a labile form, colourless needles, m. p. 85–86°, and a stable form, compact, rhombic crystals, m. p. 87–88°. It may also be obtained by the action of amyl nitrite on a solution of methyl 5-amino-1-phenyl-1:2:3-triazole-4-carboxylate in methyl alcohol containing hydrogen chloride.

5-Chloro-1-phenyl-1:2:3-triazole-4-carboxylic acid crystallises in slender, white needles, m. p. 136° (decomp.), and when fused yields 5-chloro-1-phenyl-1:2:3-triazole, $\text{C}_8\text{H}_6\text{N}_3\text{Cl}$, slender, white needles, m. p. 50°. The latter substance is converted by alcoholic ammonia at the ordinary temperature into 5-amino-1-phenyl-1:2:3-triazole, which, when diazotised and coupled with β -naphthol, yields 1-phenyltriazole-5-azo- β -naphthol, $\text{C}_{18}\text{H}_{13}\text{ON}_5$, crystallising in red plates, m. p. 215° (decomp.).

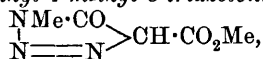
5-Anilino-1-phenyl-1:2:3-triazole, $\text{C}_8\text{H}_8\text{N}_4$, prepared by fusing 5-amino-1-phenyl-1:2:3-triazole or as described above, crystallises in large, glistening leaflets, m. p. 139°; it forms a *silver salt*, $\text{C}_8\text{H}_7\text{N}_4\text{Ag}$, and a *hydrochloride*, m. p. 128°; the *acetate*, $\text{C}_{10}\text{H}_{10}\text{ON}_4$, crystallises in white needles, m. p. 137–138°; the *urethane*, $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_4$, forms white leaflets, m. p. 147°; the *nitroso-derivative*, $\text{C}_8\text{H}_7\text{ON}_5$, forms yellow crystals, m. p. 115–116° (decomp.).

5-Amino-1:4-diphenyltriazole (compare Dimroth and Werner, Abstr., 1903, i, 127), when diazotised and coupled with β -naphthol, yields 1:4-diphenyltriazole-5-azo- β -naphthol, $\text{C}_{24}\text{H}_{17}\text{ON}_5$, red needles, m. p. 204°. The diazo-solution when treated with cuprous chloride yields 5-chloro-1:4-diphenyltriazole (compare Abstr., 1905, i, 98).

[With FRITZ HESS.]—5-Anilino-4-phenyltriazole, $\text{C}_{14}\text{H}_{12}\text{N}_4$, prepared by boiling 5-amino-1:4-diphenyltriazole with pyridine, crystallises in needles, m. p. 167°; it forms *salts* with alkalis and acids.

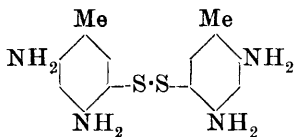
5-Methylamino-1-phenyl-1:2:3-triazole, $\text{C}_9\text{H}_{10}\text{O}_4$, is obtained by the action of methylamine on 5-chloro-1-phenyltriazole; it crystallises in slightly yellow, compact prisms, m. p. 102°, and when boiled with water or pyridine passes into 5-anilino-1-methyl-1:2:3-triazole, $\text{C}_9\text{H}_{10}\text{N}_4$, white leaflets, m. p. 172°.

Methyl 5-hydroxy-1-methyltriazole-4-carboxylate, $C_5H_7O_3N_3$, prepared by the action of methylazoimide on methyl malonate in the presence of sodium methoxide, forms hexagonal crystals, m. p. 136° ; when fused, it passes into *methyl 1-methyl-5-triazolone-4-carboxylate*,



crystallising in yellow needles, m. p. 75° . Either the enolic or ketonic ester when treated with phosphorus pentachloride yields *methyl 5-chloro-1-methyltriazole-4-carboxylate*, crystallising in long, white leaflets, m. p. 112° ; the corresponding acid crystallises in white needles, m. p. 167° , and passes into 5-chloro-1-methyl-1:2:3-triazole when fused, which substance when treated with aniline yields 5-anilino-1-methyl-1:2:3-triazole, identical with that just described. 5-Chloro-1-phenyl-1:2:3-triazole is converted by aniline into 5-anilino-1-phenyltriazole, $C_{14}H_{12}N_4$, small, glistening, square plates, m. p. 142° , and by sodium ethoxide at the ordinary temperature into 5-ethoxy-1-phenyl-1:2:3-triazole (compare Abstr., 1905, i, 98). W. H. G.

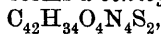
Action of Sulphur on *m*-Tolylenediamine. I. and II. GUSTAV SCHULTZ and HEINRICH BEYSCHLAG (*Ber.*, 1909, 42, 743—752, 753—757).—*m*-Diamines are characterised by the ease with which elementary sulphur is introduced into the molecule. The gentle boiling of alcoholic *m*-tolylenediamine and sulphur for five to six hours leads to the evolution of hydrogen sulphide and the formation of a mixture of polysulphides, from which *dithio-m-tolylenediamine* (annexed formula), m. p. 215° , has been isolated in tufts of yellow needles by fractional crystallisation from alcohol. The constitution of the disulphide is proved from its formation by the reduction with stannous chloride and hydrochloric acid of 2:3:2':3'-tetranitroditolyl 5:5'-disulphide,



$C_6H_2Me(NO_2)_2 \cdot S_2 \cdot C_6H_2Me(NO_2)_2$,

which decomposes before melting at 265° , and is obtained by the action of an alcoholic solution of crystallised sodium sulphide on alcoholic 5-chloro-2:4-dinitrotoluene.

Dithio-*m*-tolylenediamine forms a *benzoyl* derivative,

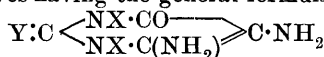


and a *benzylidene* compound, $C_{42}H_{34}N_4S_2$, m. p. 152 — 153° , yields 4-acetyl-amino-1:5-dimethylbenzthiazole, m. p. 180 — 181° , by warming with zinc dust, glacial acetic acid, and acetic anhydride, and gives, by treating its solution in dilute hydrochloric acid with hydrogen sulphide, 2:4-diamino-*m*-tolyl mercaptan, which forms yellow needles, and, on account of its extreme oxidisability, is best kept in the form of the *hydrochloride*, $C_7H_{10}N_2S_2 \cdot 2HCl$.

Since dithio-*m*-tolylenediamine dissolved in boiling alcohol takes up, per mol., six atoms of sulphur without evolution of hydrogen sulphide, giving a mixture of polysulphides, whilst 2:4-diamino-*m*-tolyl mercaptan under similar conditions combines with sulphur with the evolution of hydrogen sulphide, giving the same mixture of polysulphides, it is probable that the entrance of sulphur into *m*-tolylene-

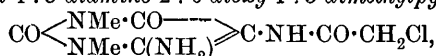
diamine is due to the initial formation of the mercaptan, which then changes into the disulphide, to which the addition of sulphur leads to the formation of higher unstable polysulphides. These polysulphides then react with the unchanged base and with the intermediately formed mercaptan to give the mixture of lower stable polysulphides which is ultimately isolated. C. S.

Preparation of *o*-Diaminopyrimidines containing Halogenated Acyl Groups. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 206454).—It has now been found that 4:5-diaminopyrimidine derivatives having the general formula



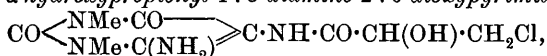
(where X is hydrogen or an alkyl group and Y an oxygen or sulphur atom, or an imino- or a cyanimino-group) readily react with halogenated carboxy-acids to give derivatives with an acyl group in position 5.

5-Chloroacetyl-4:5-diamino-2:6-dioxyl-3-dimethylpyrimidine,



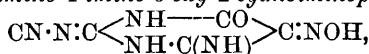
white crystals, m. p. 210°, is produced by heating together at 120° chloroacetic acid and 4:5-diamino-2:6-dioxyl-3-dimethylpyrimidine.

β-Chloro-α-hydroxypropionyl-4:5-diamino-2:6-dioxypyrimidine,



m. p. 215°, is obtained in a similar manner by replacing chloroacetic by β-chlorolactic acid in the foregoing condensation. G. T. M.

Preparation of 5-Oximino-4-iminopyrimidine Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 206453).—5-Oximino-4-imino-2:6-dioxypyrimidine is produced by condensing ethyl oximinocynoacetate and carbimide with sodium ethoxide in absolute alcohol. A similar condensation between ethyl oximinocynoacetate, dicyanodiamide, and potassium ethoxide leads to the formation of 5-oximino-4-imino-6-oxy-2-cyanoiminopyrimidine,



red needles, insoluble in water and the organic media, but yielding sparingly soluble salts with aqueous alkalis. Other condensations with ethyl oximinocynoacetate are indicated in the patent, but the products have already been described (compare Abstr., 1900, i, 416; 1901, i, 54).

G. T. M.

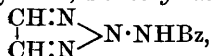
Derivatives of Osotetrazine and of Osotriazole. HANS VON PECHMANN and WILHELM BAUER (*Ber.*, 1909, 42, 659—674).—By oxidising the dibenzoylhydrazones of diacetyl and of glyoxal to the corresponding dibenzoylosotetrazines and hydrolysing the latter, the authors hoped to obtain osotetrazine and its dimethyl homologue. The hydrolysis of the dibenzoylosotetrazines, however, yields the corresponding amino-osotriazoles, and thus furnishes another addition to the several recent instances of the conversion of tetrazines into amino-triazoles. Consequently, the substances described previously (Abstr.,

1900, i, 314) as benzoyldimethylosotetrazine and dimethylosotetrazine are 1-benzoylamino-3:4-dimethyl-1:2:5-triazole, m. p. 95°, and 1-amino-3:4-dimethyl-1:2:5-triazole, m. p. 95°, respectively. The evidence for the constitutions of the two compounds is the following: (1) By benzoylation the original dibenzoyldimethylosotetrazine is not reproduced, but Stollé's 1-dibenzoylamino-3:4-dimethyl-1:2:5-triazole, m. p. 115° (this vol., i, 123); (2) the formation of the *benzylidene* compound, $\begin{matrix} \text{CMe:N} \\ \text{CMe:N} \end{matrix} > \text{N} \cdot \text{N} \cdot \text{CHPh}$, m. p. 80°; (3) by the action of nitrous

acid aminodimethyl-1:2:5-triazole yields 3:4-dimethyl-1:2:5-triazole, m. p. 70° (with 3H₂O, m. p. 97°), the constitution of which is proved by nitrating 1-phenyl-3:4-dimethyl-1:2:5-triazole (Abstr., 1888, 1287) in the cold, reducing the *nitro*-compound, C₁₀H₁₀O₂N₄, m. p. 227°, to 1-aminophenyl-3:4-dimethyl-1:2:5-triazole, $\begin{matrix} \text{CMe:N} \\ \text{CMe:N} \end{matrix} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, m. p. 132°, and oxidising the latter by potassium permanganate and dilute sulphuric acid, whereby 3:4-dimethyl-1:2:5-triazole, identical with the preceding, is obtained.

An aqueous solution of diacetyl and benzhydrazide yields *diacetylbenzoylhydrazone*, CH₃·CO·CMe·N·NHBz, m. p. about 167° (completely at 185°), which by recrystallisation from hot glacial acetic acid gives *diacetylbenzoylosazone*, NHBz·N·CMe·CMe·N·NHBz, m. p. 286·5° (decomp.), which is also obtained by heating an excess of alcoholic benzhydrazide and diacetyl for six hours at 100°. The osazone by oxidation with alkaline 25% potassium ferricyanide yields Stollé's 2:3-dibenzoyl-5:6-dimethyl-1:2:3:4-tetrazine (*loc. cit.*), m. p. 140°, which differs from the corresponding diphenyltetrazine in being colourless and in not being capable of reduction to the osazone. By hydrolysis with concentrated hydrochloric acid the dibenzoyldimethyltetrazine yields 1-benzoylamino-3:4-dimethyl-1:2:5-triazole. 1-Amino-3:4-dimethyl-1:2:5-triazole, obtained by hydrolysing the preceding compound in a sealed tube, forms a *hydrochloride*, m. p. 131°, *mercurichloride*, m. p. 145°, *picrate*, m. p. 124—125°, and a *platinichloride*, decomposing at 215°; it is unaffected by mild oxidising agents, is converted into diacetyl by potassium dichromate or lead peroxide and sulphuric acid, and yields ββγγ-tetrabromobutane by the action of bromine water.

Compounds similar to the preceding have been obtained from glyoxal. When the sodium hydrogen sulphite compound is heated with dilute sulphuric acid until sulphur dioxide is eliminated, the solution treated with an excess of sodium acetate, and heated with benzhydrazide, *glyoxalbenzoylosazone*, NHBz·N·CH·CH·N·NHBz, is obtained as a white powder, which melts above 300°, and gives, by oxidation with alkaline potassium ferricyanide, 1-benzoylamino-1:2:5-triazole,



m. p. 151°, which by hydrolysis with dilute hydrochloric acid in a sealed tube at 90—100° yields 1-amino-1:2:5-triazole, m. p. 51° (*picrate*, m. p. 130°, decomp.; *hydrochloride*, m. p. 114°, decomp.), from which Pechmann's osotriazole is obtained by the action of nitrous acid. C. S.

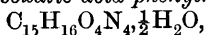
Oxidation of Uric Acid in Alkaline Solution. ROBERT BEHREND and ROLAND SCHULTZ (*Annalen*, 1909, 365, 21—37).—Attempts have been made to confirm the conclusion previously drawn (Abstr., 1904, i, 950), namely, that hydroxyglycurilcarboxylic acid is first formed during the oxidation, and that this is transformed partly into uroxic acid and partly into a substance which yields allantoin when acidified.

When a larger quantity of permanganate was used, the chief product was biuret together with a small amount of the potassium salt of a *dibasic acid*, $C_5H_7O_4N_5$. It is possible that the latter compound was formed by the oxidation of guanine contained in the crude uric acid.

Attempts have been made to establish the constitution of uroxic acid. Behrend's formula (*loc. cit.*), namely, diureidomalonic acid, $C(CO_2H)_2(NH \cdot CO \cdot NH_2)_2$, is supported by a study of the alkali salts and also by the behaviour of the acid towards methyl alcohol. The normal potassium salt is neutral to litmus and phenolphthalein in aqueous solution, whereas the acid potassium salts of diureides of the type of uric acid are distinctly alkaline. The behaviour of the normal salts is thus completely in harmony with the view that uroxic acid is a substituted malonic acid containing two carboxyl groups. The readiness with which the acid loses carbon dioxide and yields allantoic acid when shaken for several days with cold 95% methyl alcohol is also in harmony with this formula, whereas Medicus' formula (*Ber.*, 1876, 9, 462) would necessitate the rupture by cold methyl alcohol of a ring which is stable even in the presence of concentrated alkali.

Normal phenylhydrazine uroxanate, $C_5H_8O_6N_4 \cdot 2C_6H_5N_2$, crystallises in colourless plates, m. p. 130—132° (decomp.), after turning yellow at 120°. Aniline and hydroxylamine also yield sparingly soluble salts; the latter has m. p. 155° (decomp.).

When boiled with water the phenylhydrazine uroxanate yields the *phenylhydrazine salt of mesoxalic acid phenylhydrazone*,



which crystallises in yellow needles. It darkens at 140—150°, melts at 154—158°, solidifies again at 160°, and melts a second time at 183° (decomp.). Hydrochloric acid decomposes this salt, yielding *mesoxalic acid phenylhydrazone*, $C_9H_8O_4N_2$, which crystallises in minute needles, m. p. 170—171° (decomp.).

When heated with water, uroxic acid yields allanturic acid, mesoxalic acid, and carbamide.

J. J. S.

Production of Azoxy- and Azo-compounds of the Benzene Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 204653).—The sulphides of the heavy metals can be employed in the production of the reduction products of nitrobenzene. This substance when boiled with iron pyrites and 60% aqueous sodium hydroxide yields about 90% of azoxybenzene. When the reaction is carried out at 140°, further reduction occurs and 85—90% of azobenzene is obtained.

G. T. M.

***p*-Nitrodiazobenzene Chloride.** HANS T. BUCHERER and S. WOLFF (*Ber.*, 1909, 42, 881—887).—In preparing a nitrous acid-free

solution of *p*-nitrodiazobenzene by acidifying the sodium isodiazotate ("nitrosamine" paste), the authors noticed that the solution always showed the presence of free nitrous acid, and the paste, when acidified with acetic acid instead of hydrochloric acid, gave this reaction only after some time. The conclusion is drawn that the nitrous acid is produced by the hydrolytic decomposition of the diazonium hydroxide into nitrous acid and *p*-nitroaniline. After proving that excess of nitrous acid in a diazo-solution can be removed by means of hydrogen peroxide or potassium permanganate (whereby it is oxidised to nitric acid), the authors investigated the action of various reagents on a solution of *p*-nitrodiazobenzene chloride in order to ascertain if, on slowly liberating the diazonium hydroxide, the above reaction would proceed, which would be shown by the combination of the *p*-nitroaniline with some of the diazo-salt present to form the corresponding diazoamino-compound. The addition of solutions of sodium hydroxide, hydrogen carbonate, carbonate, acetate, ammonia, ammonium carbonate, soap, or a mixture of soap and sodium carbonate gave rise to the formation of a diazoamino-compound in varying degrees, but with ammonium acetate an almost quantitative yield of *p*-dinitrodiazoaminobenzene was obtained. It is considered that this is due to the rapid removal of the nitrous acid liberated in the hydrolysis owing to the formation of ammonium nitrite, which at once decomposes. The addition of ammonium chloride or carbamide to the diazo-solution produced no appreciable effect. Preliminary experiments with diazotised sulphanilic acid and *o*-nitrodiazobenzene chloride showed that the reactions do not proceed quite in the same way as those described above.

J. C. C.

Preparation of *p*-Aminodiazobenzene and its Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 205037).—Acetyl-*p*-phenylenediamine is diazotised with sodium nitrite in hydrochloric acid, a further quantity of hydrochloric acid is added, and the sodium heated at 70° for one hour. At the end of this time the solution no longer gives the azo-coupling reaction with sodium β -naphthol-3:6-disulphonate (*R* salt) in cold aqueous sodium carbonate. This diazo-solution now contains *p*-aminodiazobenzene, which only gives an azo-derivative with *R* salt either very slowly at the ordinary temperature or more rapidly on warming.

G. T. M.

Iodothyreoglobulin. A. NÜRENBERG (*Biochem. Zeitsch.*, 1909, 16, 87—110).—Iodothyreoglobulin is the name given by Oswald to the protein substance in the colloid matter of the thyroid gland which contains iodine. The elementary analyses given are very like those of Oswald. Among its hydrolytic cleavage products, arginine, histidine (?), lysine, tyrosine, glutamic acid, glycine, alanine, leucine, phenylalanine, aspartic acid, and proline were separated. The iodine is united to the aromatic groups, especially to tyrosine and tryptophan.

W. D. H.

Partial Hydrolysis of Certain Proteins. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1909, 58, 373—389).—The distinction

between proteins will probably rest not wholly in the kind and amount of the final cleavage products, so much as on the way the individual amino-acids are linked together. For this purpose, partial hydrolysis with the resulting yield of polypeptides is of great utility. In the present preliminary attempt in this direction, polypeptides were separated from the partial hydrolysis of edestin, elastin, and keratin. From the digest, amino-acids were precipitated by phosphotungstic acid, and the polypeptides were separated from the filtrate; one of these from edestin contained glutamic acid and tryptophan, another glutamic acid, tryptophan, and leucine, and a third, tyrosine, glycine, and leucine. From keratin a polypeptide containing cystine, glutamic acid, and tyrosine, and another containing histidine and leucine were separated. From elastin, *l*-leucyl-*d*-alanine and *d*-alanyl-*l*-leucine were separated.

W. D. H.

Amyloid Protein. M. MAYEDA (*Zeitsch. physiol. Chem.*, 1909, 58, 469—484).—The yield of hexone bases from the amyloid substance of the liver is the same as in the normal organ. The same is true for the spleen, except that the amount of histidine is a little higher than usual. There is no ground for believing that amyloid is specially rich in bases, or that it has anything in common with histone.

W. D. H.

The Protein Component of Chondro-mucoid. M. MAYEDA (*Zeitsch. physiol. Chem.*, 1909, 58, 485—486).—The amount of hexone bases from the protein component of chondro-mucoid is about the same as in amyloid protein (see preceding abstract).

W. D. H.

Schmiedeberg's Ferratin. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1909, 58, 282—289. Compare Scaffidi, this vol., i, 196).—Schmiedeberg's ferratin is simply the nucleo-protein of the liver, which has a variable percentage of iron. It is not a ferri-albuminic acid, and has nothing in common with ferri-albuminic acids artificially prepared.

W. D. H.

The Combination of Iron and the Nucleo-protein of the Liver. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1909, 59, 19—21).—The amount of iron in the nucleo-protein of the liver is very variable; possibly the nucleo-protein is mixed with small and variable amounts of another compound rich in iron. At any rate the iron is very loosely bound, and can be liberated by the action of dilute sodium carbonate solution at the boiling heat.

W. D. H.

Nucleo-protein of Pus. FERDINANDO STRADA (*Biochem. Zeitsch.*, 1909, 16, 195—202).—The nucleo-protein which is precipitable by acetic acid from pus serum has been named pyin. Elementary analyses are given which differ mainly in the percentage of phosphorus (0.6 to 1.6%), according as the pus was autolysed or not previously. Its cleavage products were not investigated. It does not set up amyloid degeneration when injected into animals.

W. D. H.

Preparation of Bismuth Paranucleate. G. RICHTER (D.R.-P. 202955).—*Bismuth paranucleate*, an insoluble, white powder, is produced by mixing solutions of calcium paranucleate and bismuth nitrate in concentrated aqueous sodium chloride and washing successively with sodium chloride solution, water, alcohol, and ether. G. T. M

Tanning and Adsorption Compounds of Gelatin. LÜPPO-CRAMER (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 21—23).—Colloidal vanadic hydroxide is an active tanning agent; a 1% solution of vanadic chloride coagulates a 10% gelatin solution immediately. Gelatin films, which have been tanned by dipping into vanadic chloride solution, are of a grey colour; the adsorbed vanadium compound can be removed by solutions of alkali hydroxides or oxalates. Egg-albumin and gum arabic are also quickly transformed into insoluble compounds by vanadic chloride solution.

Nickel and cobalt salts have no appreciable tanning action on gelatin; if, however, gelatin films are dipped in sodium hydroxide solution and then exposed to the action of nickel and cobalt salts, tanning results from the action of the colloidal hydroxides.

That the higher oxides of many metals have the faculty of tanning, whilst the lower oxides of the same metals produce no such effects, is due to the fact that the salts corresponding with the higher oxides are more generally hydrolysed, and that the hydroxides are very stable in the hydrosol form. H. M. D.

Composition of Different Silks. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1909, 58, 334—336).—Total hydrolysis may yield results of little value in distinguishing between proteins; the amino-acids obtained may be equal in kind and quantity, and yet their different methods of linking together may result in proteins of different characters. Partial hydrolysis reveals the difference. In Italian silk fibroin, two dipeptides (glycyl-*D*-alanine and a glycyltyrosine) and a tetrapeptide were thus found. W. D. H.

Composition of Different Silks. I. Neuchang Silk. EMIL ABDERHALDEN and AUGUSTE RILLIET (*Zeitsch. physiol. Chem.*, 1909, 58, 337—340).—Before it is possible to undertake the partial hydrolysis alluded to in the preceding abstract, total hydrolysis is a necessary first step. The Chinese silk here investigated yielded: glycine, 19.7; alanine, 23.8; leucine, 1.6; serine, 1.0; aspartic acid, 2.9; glutamic acid, 1.7; tyrosine, 9.8; proline, 1.85%; total 63.55.

W. D. H.

Kephalin. FRITZ FALK (*Biochem. Zeitsch.*, 1909, 16, 187—194).—The kephalin obtained from sciatic nerve has an N:P ratio of 1:1, as Thudichum and, later, Koch stated. That obtained from brain, however, has an N:P ratio of 2:1. Methods of preparation are given in full, and many details as to solubilities; it was not obtained crystalline. It has m. p. 176—180°. Thudichum described among its decomposition products three bases, stearic acid, and an unsaturated fatty acid called kephalic acid, which, according to Cousin, belongs to

the linoleic series. In the present research it was obtained in crystalline form, m. p. 122° ; its identification is not yet completed; its elementary composition gives figures lying between those required by the formulæ $C_{19}H_{38}O_4$ and $C_{18}H_{36}O_4$. W. D. H.

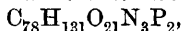
Preparation of Glucothionic Acid. PHCÆBUS A. LEVENE (*Biochem. Zeitsch.*, 1909, 16, 246—249. Compare Mandel and Neuberg, Abstr., 1908, i, 1029).—Details are given of a modified method for the purification of glucothionic acids, more especially for the removal of nucleic acids.

The analysis of an acid barium salt agreed fairly well with the formula $(C_{14}H_{20}O_{14}NS)_2Ba \cdot 2H_2O$. J. J. S.

"Glucothionic Acids." CARL NEUBERG (*Biochem. Zeitsch.*, 1909, 16, 250—253).—A reply to Levene (preceding abstract). Largely polemical. The conclusions arrived at previously (Abstr., 1908, i, 1029) are adhered to. J. J. S.

Lipoids. II. Unsaturated Phosphatides of the Kidney. SIGMUND FRANKEL and ALEXANDER NOGUEIRA (*Biochem. Zeitsch.*, 1909, 16, 366—377. Compare Abstr., 1908, i, 377).—Three unsaturated phosphatides have been prepared from the ox-kidney. One of these, present in only small quantity, has the properties of kephalin; when dry it is dark yellow and of a waxy consistence; it begins to melt at 125° and decomposes at 135° . The Hübl iodine number is 70·38.

The second compound, an *unsaturated triaminodiphosphatide*,



is precipitated from the extract of the kidneys after removal of the kephalin as a *cadmium* compound, $C_{78}H_{131}O_{21}N_3P_2 \cdot 2HCl \cdot 2CdCl_2$. The free phosphatide is dibasic in character, and has iodine number 82, whilst that of the cadmium compound is 63·48. Two of the nitrogen atoms are in the form of choline, that is, combined with methyl groups. It is a pale yellow powder, m. p. 205° , and optically inactive in dilute ethereal solution.

Lastly, a *diaminomonophosphatide*, found in small quantities, has no basic properties, but forms a *cadmium* salt, $C_{34}H_{74}O_{10}N_2P \cdot 2CdCl_2$, m. p. 215° , which has an iodine value of 25·81 and is much less unsaturated than the previous compound; the free phosphatide has a value of 37·83. Only one of the nitrogen atoms is in the form of choline. E. F. A.

Lipoids. III. Interaction between the Unsaturated Phosphatides of the Kidney and Dyes. SIGMUND FRANKEL and ALEXANDER NOGUEIRA (*Biochem. Zeitsch.*, 1909, 16, 378—382).—Dyes are excreted by the kidney in a changed state, methylene-blue, for example, being converted into a leuco-derivative. The behaviour of the three unsaturated phosphatides of the kidney (see previous abstract), which have a marked affinity for oxygen, towards methylene-blue has been studied outside the organism.

Triaminodiphosphatide decolorises methylene-blue slightly in the cold, more strongly on heating to 50° . The blue colour does not re-

appear on shaking with air, but is reformed to some extent, although not entirely on adding acetic acid or on boiling. Chloroform extracts from the reduced liquid the same soluble methylene blue as occurs in human urine after administration of the dye. The leuco-derivative corresponds with the chromogen of Voisin and Hauser.

The diaminomonophosphatide reduces methylene-blue strongly to a chromogen, but the primary colour is completely restored on adding acetic acid and boiling.

The kephalin-like substance produces a greenish-blue solution. The original colour is not restored on shaking with air, but a clouded blue liquid is produced by boiling with acetic acid. A similar green dye is often found in dog's urine after administration of methylene-blue, but seldom in human urine.

None of the phosphatides react with indigo-carmin. The most completely saturated of the three has the strongest decolorising action towards methylene-blue.

E. F. A.

Plasteins. II. PHCEBUS A. LEVENE and DONALD D. VAN SLYKE (*Biochem. Zeitsch.*, 1909, 16, 203—206. Compare Abstr., 1908, i, 932).—The viscosity of plastein solutions in alkali is less than that of native proteins, and is nearly as low as that of Witté's peptone. The viscosity sinks slightly after a short time and then remains practically constant. The viscosity of such native proteins as fibrin sinks more gradually and continues to fall until lower than that of plastein. Whether plastein is a decomposition product of protein cleavage which settles out on account of its insolubility or whether it is synthetically formed from secondary proteoses is left uncertain.

W. D. H.

Mechanical Destruction of Pepsin. A. O. SHAKLEE and SAMUEL J. MELTZER (*Proc. Amer. Physiol. Soc.*, 1908, xxix—xxx; *Amer. J. Physiol.*, 23).—Shaking a solution of pepsin at room temperature diminishes its activity and finally destroys it. This action is more rapid at 33°. It is not due to oxidation, but occurs just the same in inert gases. Mere shaking in the animal body lessens its strength, as was determined by introducing a small bottle of pepsin solution into a dog's stomach.

W. D. H.

Electrical Transportation of Ferments. I. Invertin. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1909, 16, 81—86).—In order to avoid injurious changes in reaction, unpolarisable electrodes (zinc in solutions of zinc sulphate) were employed. The experiments were made in a U-tube, the bend of which, containing the ferment, could be closed by taps and so separated from the side-tubes which contained water. The latter were fitted with glass tubes containing the electrode, and zinc sulphate.

Results obtained both without, and in presence of, acetic acid showed that, as indicated by the absorption method, invertin is an acid.

N. H. J. M.

Enzymes which Hydrolyse (1) Salicin and (2) Arbutin. WILHELM SIGMUND (*Monatsh.*, 1909, 30, 77—87).—The leafy twigs of

various species of *Salix* and *Populus* contain an enzyme which is capable of hydrolysing salicin to dextrose and saligenin; this the author names *salikase*. The action of the enzyme, which differs from emulsin, was shown by autolytic experiments and by means of the precipitate obtained on adding alcohol to the aqueous extract of the twigs.

Similarly, the twigs of *Calluna vulgaris* and of *Vaccinium Myrtillus* contain an enzyme, to which the name *arbutase* is given, capable of hydrolysing arbutin into quinol and dextrose. T. H. P.

Basiphil Rennets. C. GERBER (*Compt. rend.*, 1909, 148, 56—58).—As a result of the study of the time of clotting of milk produced by rennets of different origin in the presence of varying quantities of acids and alkalis, the conclusion is drawn that there are two extreme types of rennet, namely, oxyphil and basiphil. The former include the rennets from calf and pig, the latter those from *Maclura* and the decapod crustaceans. Between the extreme types, there are other rennets which can be classified according to their action in the presence of various mineral and organic acids. S. B. S.

Rennet Action. W. VAN DAM (*Zeitsch. physiol. Chem.*, 1908, 58, 295—330).—The investigation was undertaken to determine why certain specimens of cow's milk do not readily curdle with rennet. It was found by the electrical conductivity method that the coagulation-time is inversely proportional to the hydrogen ions present. The main reason of want of satisfactory curdling is poorness in calcium salts, and this can be corrected by giving the cows calcium phosphate in their food. W. D. H.

Theory of the Curdling of Milk by Rennet. GERHARD WERNCKEN (*Zeitsch. Biol.*, 1908, 52, 47—71).—Differences in the internal friction of solutions of caseinogen and casein (called in the paper casein and paracasein respectively) are so small as to come within the errors of analysis. Caseinogen solutions show a tryptophan reaction after a comparatively short lapse of time; nevertheless, the theory that casein is the result of fermentative change in caseinogen is considered untenable. W. D. H.

Coagulation of Fresh Milk by the Rennet of the Papaw Tree (*Carica Papaya*). C. GERBER (*Compt. rend.*, 1909, 148, 497—500).—The rennet in papayotin-Merck is much more resistant to high temperatures than that of yeast and of pepsin, and clots milk at 0° even when calcium is absent. The product of the quantity of ferment by the time taken to clot a given quantity of milk remains constant when the milk is perfectly fresh, but when the milk is four hours' old it clots too slowly with small quantities of ferment, so that the above-mentioned product increases when the quantity of ferment is diminished. G. B.

Tyrosinase. ALEXIS BACH (*Ber.*, 1909, 42, 594—601. Compare Abstr., 1906, i, 616; 1907, i, 268, 810; 1908, i, 237, 746).—Numerous

experiments which have been made do not support Gonnermann's hypothesis (*Pflüger's Archiv*, 1900, 82) that tyrosinase is a hydrolysing enzyme and that the products of hydrolysis of tyrosine are subsequently oxidised by atmospheric oxygen. Gessard's view (*Abstr.*, 1900, i, 468) that the specific action of tyrosinase is due to the presence of certain metallic salts is also shown to be untenable.

Experiments with some hundred different plant-juices and extracts prove that the oxidation of tyrosine by means of peroxydase, hydrogen peroxide, and a plant-juice or ferment preparation takes place only when the juice or preparation itself oxidises the base, namely, contains tyrosinase. In many cases the activity of the tyrosinase is concealed by the presence of reducing substances, but when these are removed by precipitation with alcohol, the activity of the tyrosinase can be demonstrated.

The activity of purified tyrosinase towards tyrosine is appreciably diminished by the addition of neutral peroxydase, whether hydrogen peroxide is present or not. If the plant extract or tyrosinase preparation contains reducing or other substances which lower its activity, the addition of peroxydase and hydrogen peroxide produces an initial acceleration in the oxidation, but after a short time the inhibiting action of the peroxydase can be noticed. This initial acceleration is not due to the oxidation of the tyrosine, but to the decomposition of the reducing or other substances present.

J. J. S.

Artificial Oxydases and Peroxydases. V. MARTINAND (*Compt. rend.*, 1909, 148, 182).—The oxides of alkalis and alkaline earths which form soluble peroxides and percarbonates give reactions similar to organic peroxydase. Salts of metals which form several peroxides react in a similar way when they correspond with the higher oxides of the metal; those corresponding to the lower oxides do not act in this manner.

S. B. S.

Action of Acids on Peroxydase. GABRIEL BERTRAND and MILE. M. ROZENBAND (*Compt. rend.*, 1909, 148, 297—300. Compare *ibid.*, 1907, 145, 340).—In the case of laccase and tyrosinase, certain acids inhibit the ferment in minute doses, whilst other acids are almost without effect. As regards the action of acids in peroxydase (from wheat-bran), no such division into two groups can be traced, the inhibitory effect being of the same order of magnitude as the electrical conductivity, although not proportional to it.

G. B.

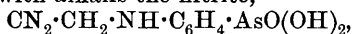
Some New Properties of the Oxydases of *Russula Delica*. JULES WOLFF (*Compt. rend.*, 1909, 148, 500—502).—The oxydase from *Russula Delica* is most active on tyrosine and many other substances when the solution is neutral to phenolphthalein. Some colouring matters are oxidised both by this oxydase and by laccase, but others are only oxidised by the ferment from *Russula*.

G. B.

Preparation of Hydroxyarylsarsinic Acids. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 205616).—*p*-Hydroxyphenylarsinic acid, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$, yellow prisms, m. p. 173—174°.

has now been prepared directly from phenol and crystallised arsenic acid by heating at 150° for four hours. The product soluble in water is evaporated to dryness, and the arsenic acid extracted from the residue with acetone. 4-Hydroxy-3-tolylarsinic acid is similarly obtained from *o*-cresol and arsenic acid at 140° . With *m*-cresol and arsenic acid the reaction takes place at 170° . 4-Hydroxy-2-tolylarsinic acid, $\text{HO}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{AsO}(\text{OH})_2$, sinters at 160° and decomposes at $183\text{--}185^{\circ}$.
G. T. M.

Preparation of *p*-Arylglycinearsinic Acids. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 204664).—*Phenylglycine-p-arsinic acid*, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$, is prepared either by mixing sodium *p*-aminoarsinate and chloroacetic acid in hot water or by hydrolysing with alkalis the nitrite,



produced by warming together in aqueous solution, *p*-aminophenylarsinic acid, potassium cyanide, and formaldehyde (40%).

G. T. M.

Preparation of Sulphur Derivatives of *p*-Aminophenylarsinic Acid. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 205617).—*p*-Aminophenylarsenious sulphide, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsS}$, yellowish-white powder, m. p. 180° , is obtained by passing hydrogen sulphide into an acidified solution of *p*-aminophenylarsinic acid. The free sulphur is removed by carbon disulphide, and the new sulphide dissolved in aqueous sodium hydroxide and reprecipitated by acids, which dissolve it when present in excess. This sulphide is also produced by passing hydrogen sulphide into a methyl-alcoholic solution of *p*-aminophenylarsenious oxide.

p-Acetylaminophenylarsenic sesquisulphide, $\text{O}(\text{NHAs}\cdot\text{C}_6\text{H}_4\text{As})_2\text{S}_3$, white, lustrous needles, m. p. 208° , is produced by dissolving acetyl-*p*-aminophenylarsinic acid in 25% aqueous ammonia, saturating the solution with hydrogen sulphide, and precipitating with dilute hydrochloric acid.

Phenylglycinearsenic disulphide, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsS}_2$, yellowish-white powder, decomposing at 142° , is produced by saturating with hydrogen sulphide an aqueous solution of phenylglycin-*p*-arsinic acid.

G. T. M.

Preparation of the Salts of the Mercury Derivatives of Fluorescein. HERMANN PAULY and VIKTOR TRAUMANN (D.R.-P. 201903).—The sodium salt of dimercurifluorescein is produced by adding mercuric chloride to a solution of fluorescein in sodium hydroxide. The yellowish-red precipitate then obtained is dissolved in sodium carbonate, and the red sodium salt isolated by evaporating the solution.

The sodium salt of tetramercurifluorescein is similarly prepared by treating the foregoing dimercuri-derivative with more mercuric chloride in alkaline solutions. These mercuric derivatives of fluorescein have the property of giving very fast shades of red with fabrics mordanted with chromium, iron, uranium, nickel, cobalt, aluminium, and cerium.

G. T. M.

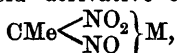
Organic Chemistry.

Formation of Mineral Oils from the Salts of Fatty Acids and the Metals of the Alkaline Earths. A. KÜNKLER and H. SCHWEDHELM (*Seifensieder-Zeit.*, 1908, 35, 1285—1286, 1341—1342, 1365—1366, and 1393—1394).—Stearin was heated with calcium carbonate under pressure at varying temperatures in order to find out to what extent the decomposition of the resulting calcium stearate would lead to the formation of substances resembling the mineral oils. At 270° a decomposition sets in with the formation of solid products, and after eight hours' heating at 320° it is complete. The first decomposition products of calcium stearate and palmitate are paraffin wax, kerosene, and viscid oils. The products from calcium oleate are entirely liquid. The authors discuss the bearing of these experiments on the hypothesis that mineral oils are the products of the thermal decomposition of calcium and magnesium salts of the higher fatty acids derived from decaying animal matter. F. M. G. M.

Optical and Certain other Properties of Grosny Naphtha. MICHAEL A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 109).—The author has made an investigation, detailed results of which are to be given later, on the optical and other properties of all the distillation products of Grosny naphtha. The distillates having densities up to 8° on the saccharometer exhibit a dextro-rotation which increases with the sp. gr., colour, and viscosity. The viscosity and sp. gr. of the transparent distillates attain the values for castor oil, the fact that Grosny naphtha does not give lubricating oil depending on the different conditions employed in the works and in the laboratory, in which latter vacuum without steam is used. T. H. P.

Optical Properties of Cheleken Ozokerite. MICHAEL A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 109—110).—The author has investigated the products of Cheleken ozokerite distilling within the limits 130—280° at ordinary pressure. The solid distillates of a white to dark yellow colour dissolve to the extent of 2—5% in benzene or chloroform, the solutions exhibiting dextro-rotation. There is no doubt but that a genetic relation exists between ozokerite and naphtha. T. H. P.

Coloured and Colourless Salts of Ethylnitrolic Acid. ARTHUR HANTZSCH and GEORG KANASIRSKI (*Ber.*, 1909, 42, 889—893. Compare Graul and Hantzsch, *Abstr.*, 1899, i, 187).—Ethylnitrolic acid only absorbs generally in the ultra-violet, whereas its red alkali salts exhibit selective absorption; the acid is, therefore, a ψ -acid, and the red salt is a quinonoid derivative of the type



similar to those of the dinitro-paraffins (*Abstr.*, 1907, i, 500). The

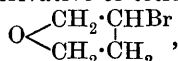
colourless salts obtained from the coloured are much more stable, and, moreover, cannot be reconverted into the red isomerides. It has been found that the red potassium salt, when heated under petroleum at 45—50° in the light, is converted into the colourless; on a bright day the conversion is complete in one and a-half hours, on a dull day six hours are necessary. It is not decomposed at 110°, and molecular-weight determinations (1) in water, f. p. method, gave the ion number 2.2, 2.0, 2.1; (2) in methyl alcohol, b. p. method, 1.77 and 1.56, showing that the salt is unimolecular. Attempts to alkylate or acylate the colourless salt were without success, as also was an attempt to prepare the free acid. The dry potassium salt dissolved in xylene decomposes at 120° into methylcarbimide and potassium nitrite, and as its absorption in the ultra-violet is even less than that of the ethylnitrolic acid, the constitution $\begin{array}{c} \text{MeC:N} \\ \text{KO}\cdot\text{N}\cdot\text{O} \end{array} \text{O}$ is assigned to this potassium ethyl isonitrolate (compare Wieland, this vol., i, 216).

W. R.

Allylcarbinol: Passage to the Furfuran Series. H. PARISELLE (*Compt. rend.*, 1909, 148, 849—851).—The author gives a method for obtaining allylcarbinol in 20—25% yield from allyl bromide, trioxymethylene, and magnesium (compare Wagner, Abstr., 1894, i, 563; Carré, *Compt. rend.*, 1908, 146, 1283); diallyl and the formal of allylcarbinol, $\text{CH}_2(\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2)_2$, b. p. 175—177°, are also formed.

$\gamma\delta$ -Dibromobutyl alcohol, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, obtained by the action of bromine on allyl carbinol, has b. p. 112—114°/11 mm.: Wagner (*loc. cit.*) gave b. p. 131—141°/16 mm.

The action of potassium hydroxide on this bromide in ethereal solution yields the bromo-derivative of tetrahydrofuran,



b. p. 150—151°, which, when heated with powdered potassium hydroxide, yields dihydrofuran, $\text{O} \begin{array}{c} \text{CH}_2\cdot\text{CH} \\ \text{CH}_2\cdot\text{CH} \end{array}$.

T. H. P.

The Lecithin of Egg-yolk. HUGH MACLEAN (*Zeitsch. physiol. Chem.*, 1909, 59, 223—229).—Work on this phosphatide shows that some of the nitrogen is present in the form of choline, and part in some unknown form. Control experiments show that loss of choline during the analytical methods used will not account for the residual nitrogen.

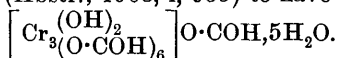
W. D. H.

Lipoids of the Brain. I. Sphingomyelin. OTTO ROSENHEIM and M. CHRISTINE TEBB (*Proc. physiol. Soc.*, 1909, li—liii; *J. Physiol.*, 38).—Sphingomyelin is the phosphorised constituent of so-called protagon, and may be separated from the non-phosphorised constituents of this mixture by combining fractional precipitation by means of acetone from alcohol-chloroform solutions with recrystallisation from pyridine. The term galactoside is adopted for the non-phosphorised substances just referred to.

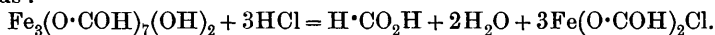
Sphingomyelin is a white, crystalline, non-hygroscopic substance which exhibits the phenomenon of sphæro-rotation previously described. It contains 4% of phosphorus, and the P : N ratio is 1 : 2 ; it is therefore a diamino-monophosphatide. On hydrolysis it yields choline and fatty acids, but not glycerol. On partial hydrolysis, it furnishes a substance which has some resemblance to the simplest nucleic acids, but this, on complete hydrolysis, yields phosphoric acid, a base, and a crystalline alcohol instead of a carbohydrate.

W. D. H.

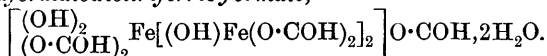
Iron Formates. E. BELLONI (*Arch. Pharm.*, 1909, 247, 123—130).—An investigation on the simple and complex formates of iron. The salt described by Scheurer-Kestner (*Ann. chim. phys.*, 1863, [iii], 68, 480) as a normal ferric formate, and when prepared by dissolving ferric hydroxide in formic acid, is shown to have the composition represented by the formula $\text{Fe}_3(\text{O}\cdot\text{COH})_7(\text{OH})_2\cdot 4\text{H}_2\text{O}$; it is consequently analogous with the basic chromium formate which Werner has shown recently (Abstr., 1908, i, 935) to have the formula



When the salt is treated with hydrochloric acid, it is decomposed, thus :



From this it follows that only one formyl group can function as an ion, and that two formyl groups are attached to each atom of iron ; consequently, since the complex is univalent, eight of the nine valencies of the iron must be satisfied within the complex itself. Two of the four mols. of water are held very firmly, and are therefore situated in the complex ; the compound is consequently a diaquo-salt, in agreement with which is the fact that the aqueous solution reacts acid. The conclusion is drawn, therefore, that the salt is probably *diaquohexaformatodioltriferric formate*,



It has not yet been found possible to replace the formyl group outside the complex by other acid radicles.

An aqueous solution of the salt when kept for some time exposed to the air deposits a brick-red precipitate, which is shown to be a *basic formate*, $\text{Fe}(\text{OH})_2(\text{O}\cdot\text{COH})$. The latter substance, when kept for about two months, has the composition $\text{Fe}_3(\text{O}\cdot\text{COH})(\text{OH})_8$.

The complex salts, $\text{Fe}_2(\text{O}\cdot\text{COH})_4\text{Cl}_2\cdot 3\text{H}_2\text{O}$ (Scheurer-Kestner, *loc. cit.*), $\text{Fe}(\text{O}\cdot\text{COH})_2\text{Cl}\cdot 1\frac{1}{2}\text{H}_2\text{O}$ (Rosenheim and Müller, Abstr., 1904, i, 468), and $\text{Fe}_2\text{Cl}_2(\text{O}\cdot\text{COH})_4\cdot \text{H}_2\text{O}$ (Benrath, Abstr., 1905, i, 734), are shown to be identical with that prepared by the action of hydrochloric acid on hexaformatodioltriferric formate, which has the formula $\text{Fe}(\text{O}\cdot\text{COH})_2\text{Cl}\cdot 1\frac{1}{2}\text{H}_2\text{O}$.

W. H. G.

Sodium Acetates at 30°. M. DUKELSKI (*Zeitsch. anorg. Chem.*, 1909, 62, 114—117).—An investigation of the phase-equilibrium of mixtures of sodium hydroxide, water, and acetic acid, or anhydride,

shows that the compounds capable of existence in the solid form at 30° are: $C_2H_3O_2Na, \frac{1}{2}H_2O$, $C_2H_3O_2Na, 3H_2O$, $C_2H_3O_2Na, C_2H_4O_2$, and $C_2H_3O_2Na, 2C_2H_4O_2$.

The results are expressed in a triangular diagram.

C. H. D.

Glycerides of Fatty Acids. II. Occurrence of the Mixed Glycerides of Palmitic and Stearic Acids in Mutton Tallow. ALOIS BÖMER [and, in part, G. HEIMSOETH] (*Zeitsch. Nahr. Genussm.*, 1909, 17, 353—396. Compare Abstr., 1907, i, 820).—It is shown that dipalmitylstearin and distearylpalmitin are present in the mixture of glycerides of saturated fatty acids occurring in mutton tallow; the separation of the various glycerides from one another is extremely difficult, and is only attained by repeated fractional crystallisation. No proof could be obtained of the presence of tripalmitin in the fat. The quantity of dipalmitylstearin, m. p. 57.5° , and distearylpalmitin, m. p. 63.6° , present in the mutton tallow examined was from 4 to 5%.

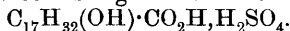
W. P. S.

Crotonic Anhydride. ANDREAS LUNIAK (*Ber.*, 1909, 42, 915—916).—*Crotonic anhydride*, $(CHMe:CH\cdot CO)_2O$, is obtained in 80% yield when dry sodium crotonate is heated with crotonyl chloride (b. p. $34\text{--}36^\circ/18$ mm., $D^{20} 1.0905$: Henry gives $D^{16} 1.295$, Abstr., 1899, i, 257) for three hours, and subsequently during eight hours after addition of ether. It is a colourless liquid, b. p. $113.5\text{--}114.5^\circ/12$ mm., $246\text{--}248^\circ/766$ mm., $D^{20} 1.0397$, $n_D^{20} 1.47446$.

W. R.

Essential Constituent of Turkey-red Oil and its Derivatives. ADOLF GRÜN and M. WOLDENBERG (*J. Amer. Chem. Soc.*, 1909, 31, 490—506).—Turkey-red oil, obtained by the action of strong sulphuric acid on castor oil, consists essentially of a mixture of ricinoleic acid and its derivatives. The present paper contains an account of experiments carried out with the object of elucidating the course of the reaction between ricinoleic acid and sulphuric acid, and is a continuation of previous work (Grün, Abstr., 1907, i, 111; Grün and Wetterkamp, Abstr., 1908, i, 8).

When sulphuric acid is added gradually to ricinoleic acid at 0° , a clear liquid is obtained consisting of the additive compound,

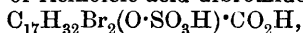


If the product is left for some time, $\theta\lambda$ -dihydroxystearic acid, ricinoleic ricinoleate, ricinoleic lactide, and a small amount of ricinoleic acid sulphuric ester are produced. Attempts were made to prepare the sulphuric ester of methyl ricinoleate by the action of sulphuric acid and of chlorosulphonic acid on the methyl ester, but in each case the resulting product was chiefly the sulphuric ester of the acid itself. Ricinoleic acid sulphuric ester can be prepared by treating ricinoleic acid with an ethereal solution of chlorosulphonic acid at -5° . The compound is very stable towards alkali hydroxide at the ordinary temperature, but when boiled with water for four hours yields a product consisting of ricinoleic acid (38%) and the lactide (62%).

By the action of chlorosulphonic acid on ricinostearoleic acid (Ulrich, *Zeitsch. Chem.*, 1867, 3, 545), the sulphuric ester,

$\text{Me} \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{O} \cdot \text{SO}_3\text{H}) \cdot \text{CH}_2 \cdot \text{C} \cdot \text{C} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H}$, is obtained as a clear, yellowish-brown oil; its *barium* salt forms a light yellow powder.

The *sulphuric* ester of ricinoleic acid dibromide,



obtained as a clear brown liquid by the action of chlorosulphonic acid on the dibromide, is decomposed by water. An attempt to prepare the sulphuric ester of methyl ricinoleate dibromide resulted in the production of the ester of the dibromide of the acid itself.

Methyl λ-hydroxystearate, $\text{Me} \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{OH}) \cdot [\text{CH}_2]_{10} \cdot \text{CO}_2\text{Me}$, m. p. 58°, obtained by reduction of methyl ricinoleate, crystallises in white, silky plates. *λ-Hydroxystearic acid*, m. p. 78°, forms minute, white crystals; its *sulphuric* ester, m. p. 71—73°, is very stable, and is not decomposed by hot water.

By the action of phosphoric oxide on ricinoleic acid, two amorphous *polymerides* have been obtained, one of which is soluble in ether and is converted into potassium ricinoleate when heated with alcoholic potassium hydroxide, whilst the other is of a rubber-like consistence, is insoluble in all organic solvents, and cannot be reconverted into ricinoleic acid.

E. G.

Preparation of Glyoxylic Acid as a Reagent. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1909, 6, 51—52).—A method is described for the preparation of glyoxylic acid from magnesium and oxalic acid. The magnesium salt of glyoxylic acid so obtained gives the reactions well in testing for tryptophan.

W. D. H.

Citric Acid Fermentation. REGINALD O. HERZOG and A. POLOTZKY (*Zeitsch. physiol. Chem.*, 1909, 59, (2), 125—128).—The authors find that the amount of citric acid formed depends very much on the nature of the sugar supplied. Lactose yielded very little, sucrose much more, and maltose still more. Xylose was more effective than arabinose. Erythritol gave no citric acid, and mannitol only little; notable quantities, however, were obtained from dextrose, mannose, lævulose, and glycerol. Further investigation is needed of this formation of citric acid from glycerol. The authors, unlike Mazé and Perrier, did not obtain citric acid from ethyl alcohol.

E. J. R.

Humus Substances. RUDOLF MIKLAUZ (*Chem. Zentr.*, 1909, i, 937—938; from *Zeitschr. Moorkult. Torfverwert.*, 1908, 285—327).—The action of mineral acids on peat is less the more completely the peat is humified. Humic acids from peat are altered by prolonged boiling with acids, the percentages of carbon and hydrogen increasing and diminishing respectively. Attempts to obtain pure substances by means of dilute alkali failed.

Dopplerite differs from peat in being much more strongly acid; the humic acid obtained from it by means of alkali does not, however, appreciably differ from that obtained from peat.

N. H. J. M.

Ester-Acids of Thiocarboxylic Acids with Aliphatic Alcohol-Acids. III. BROR HOLMBERG (*J. pr. Chem.*, 1909, [ii], 79, 253—270. Compare Abstr., 1907, i, 283).—The paper gives an account of the three acids which are theoretically obtained from carbamylglycollic acid by replacing the oxygen by sulphur. Of these three acids, carbamylthioglycollic acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, thiocarbamylglycollic acid, $\text{NH}_2 \cdot \text{CS} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, and thiocarbamylthioglycollic acid, $\text{NH}_2 \cdot \text{CS} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, the first has long been known. It can be readily obtained by the interaction of aqueous sodium chloroacetate and solid ammonium thiocarbamate and subsequent acidification; so prepared, it has m. p. $139-139.5^\circ$ (decomp.), and a K value 0.0266 by the conductivity method, and 0.0261 calculated from the rate of decomposition of ethyl diazoacetate, both values being greater than Ostwald's value, 0.0246. Thiocarbamylglycollic acid, prepared as previously described (*loc. cit.*), has m. p. $111-112^\circ$, and K value 0.113 and 0.108 by the preceding methods; the *ammonium*, *sodium*, and *barium* salts are mentioned. The *anhydride*, $\text{NH} \begin{smallmatrix} \text{CS} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$, m. p. 143° (decomp.), is deposited by the evaporation of a warm solution of the acid in acetic anhydride, and has weak acid properties. When warmed with an equal weight of bromoacetic acid on the water-bath, thiocarbamylglycollic acid is changed into the isomeric carbamylthioglycollic acid.

Thiocarbamylthioglycollic acid, $\text{NH}_2 \cdot \text{CS} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, is obtained almost quantitatively by the interaction of a concentrated aqueous solution of sodium chloroacetate and solid ammonium dithiocarbamate and subsequent acidification. Owing to its tendency to yield the *anhydride*, the acid must be rapidly filtered and purified by the precipitation of its solution in acetone with chloroform. It darkens at 100° , has m. p. $136-137^\circ$, resolidifies, and then melts at $168-169^\circ$ (decomp.), the m. p. of the *anhydride*; the *sodium*, *calcium*, *lead*, and *barium* salts are described. Thiocarbamylthioglycollic acid is very unstable, yielding thioglycollic and thiocyanic acids in alkaline solution, and its *anhydride*, rhodanin (rhodanic acid), in acid solution; even in neutral solution a slow decomposition into these three substances occurs. The ready formation of rhodanin from the acid is contributory evidence for the correctness of the constitution, $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CS} \cdot \text{S} \end{smallmatrix}$, ascribed by Liebermann and others to this substance.

Trithiocarbodiglycollamide, $\text{CS}(\text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2)_2$, prepared from potassium trithiocarbonate and chloroacetamide, or from ethyl trithiodiglycollate and cold concentrated ammonium hydroxide, forms glistening, yellow leaflets from water, and begins to decompose at 195° , but is not melted at 205° ; the *aniline* salt, $\text{CS}(\text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}, \text{PhNH}_2)_2$, prepared from the acid and aniline in slightly warmed acetone, forms yellow needles, m. p. $119-119.5^\circ$ (decomp.). C. S.

Catalytic Preparation of Ketones. JEAN B. SENDERENS (*Compt. rend.*, 1909, 148, 927—929. Compare Abstr., 1908, i, 494, 495; this vol., i, 127).—The [author continues his study of the catalytic

action of heated alumina on primary alcohols and aliphatic acids. Under the conditions described previously, methyl ether is obtained in good yield from methyl alcohol at 250—370°. Propyl alcohol in presence of heated alumina forms an ethylenic hydrocarbon and only 30% of propyl ether. *iso*Butyl alcohol forms *diisobutylene*. The use of other catalysts did not increase the yield of ether in the last two cases.

When the vapour of acetic anhydride is passed over alumina at 300—380°, acetone and carbon dioxide are obtained. The preparation of acetone from acetic acid has already been described. The higher ketones are more conveniently obtained, in a state of purity and with good yields, when anhydrous thorium dioxide is used as the catalyst. The following ketones have been prepared from the free acids at about 400°; diethyl ketone, dipropyl ketone, and *diisopropyl* ketone. Formic acid yields carbon dioxide and formaldehyde in presence of thorium dioxide at 200—250°.

W. O. W.

Transformation of Non-cyclic Diketones into Cyclic Compounds. EDMOND E. BLAISE and A. KÖHLER (*Compt. rend.*, 1909, 148, 852—854).—The authors have investigated 1:6-, 1:7-, and 1:8-diketones in order to ascertain up to which term in the series diketones are convertible into cyclic compounds.

1:6-Diketones are readily transformed into cyclic derivatives by the action of alkali in boiling alcoholic solution. Contrary to the statement made by Perkin and Marshall (*Trans.*, 1890, 57, 241), octane- $\beta\eta$ -dione and its homologues yield practically pure 2-acidyl-1-alkyl- Δ^1 -cyclopentenones, $\text{CR} \begin{smallmatrix} \text{C}(\text{CO}\cdot\text{R}')\cdot\text{CH}_2 \\ \text{CH}_2\text{---CH}_2 \end{smallmatrix}$, under these conditions.

2-Propionyl-1-ethyl- Δ^1 -cyclopentene, $\text{CEt} \begin{smallmatrix} \text{C}(\text{COEt})\cdot\text{CH}_2 \\ \text{CH}_2\text{---CH}_2 \end{smallmatrix}$, prepared from decane- $\gamma\theta$ -dione, is a colourless liquid, b. p. 94—95°/14 mm., with an odour resembling that of camphor, and forms a *semicarbazone*, m. p. 188°, and an *oxime*, b. p. 127°/9 mm. When oxidised by means of permanganate, 2-propionyl-1-ethyl- Δ^1 -cyclopentene yields propionic and γ -propionylbutyric acids.

Nonane- $\beta\theta$ -dione is converted into 2-acetyl-1-methyl- Δ^1 -cyclohexene by cold concentrated sulphuric acid, but not by alkali (compare Perkin and Kipping, *Trans.*, 1890, 57, 13; 1891, 59, 214). Undecane- $\gamma\iota$ -dione, on the other hand, is not converted into a cyclic compound by sulphuric acid.

With 1:6-diketones, then, this transformation occurs readily, and does not appear to be influenced by the weight of the alkyl radicles attached to the carbonyl groups. But with 1:7-diketones, the change takes place less easily, and depends on the alkyl radicles united to the carbonyl groups.

Decane- $\beta\iota$ -dione is not converted into a cyclic compound either by alkali or by sulphuric acid.

T. H. P.

New Method for Determining the Constitution of Sugars. MAURICE HANRIOT (*Compt. rend.*, 1909, 148, 640—643. Compare this vol., i, 206).—The aldopentoses and aldohexoses can be classified in

four groups according to the configuration of the substituents of the three carbon atoms adjacent to the CHO group. Since the isomerism of the chloralic acids depends only on the configuration of these three carbon atoms, it follows that the sugars of each group must give the same chloralic acid. This has been verified for the three groups of which dextrose, galactose, and mannose respectively are examples.

To determine the partial constitution of a sugar, it is converted into its chloralose; if this cannot be identified, it is oxidised to the corresponding chloralic acid; if this is not identical with any of the acids already described, the sugar must belong to the group of which talose and ribose are examples. Lævulose reacts with chloral to form a chloralose, $C_8H_{11}O_6Cl_3$, m. p. 228° . On oxidation this furnishes an acid, $O \begin{array}{l} \diagup CH \cdot C(OH)(CO_2H) \cdot CH \cdot CCl_3 \\ \diagdown CH \cdot C(OH)(CO_2H) \cdot O \end{array}$. This has m. p. $200-210^\circ$, and is very unstable. Attempts to prepare a chloralose from sorbose have been unsuccessful. W. O. W.

β -Hydroxy- δ -methylfurfuraldehyde as the Cause of Some Colour Reactions of Hexoses. WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 217-226).—On dry distillation, or on heating with dilute acids, hexoses lose 3 molecules of water, yielding β -hydroxy- δ -methylfurfuraldehyde, the proportion obtained from ketoses being much higher than that from aldoses. The behaviour of this substance being similar to that of furfuraldehyde, it has frequently been mistaken for that compound. On its formation depend the test of Fiehe for artificial honey (*Zeitsch. Nahr. Genussm.*, 1908, 16, 75), Seliwanoff's reaction (Abstr., 1887, 459), and Baudouin's sesamé oil reaction (Villavecchia and Fabris, Abstr., 1893, ii, 197; 1894, ii, 126; 1898, i, 445). It also plays an important part in the reactions of Molisch (Abstr., 1886, 923) and Udranszky (Abstr., 1888, 863, 878, and 1889, 449). A. J. W.

Styracitol. Y. ASAHINA (*Arch. Pharm.*, 1909, 247, 157-160).—The formation of β -hexyl iodide from styracitol (Abstr., 1908, ii, 59) and the preparation of a tetrabenzoate and tetranitrate of this compound show that it is an anhydrohexitol, $C_6H_8O(OH)_4$. The optical rotatory power of styracitol given previously (*loc. cit.*) is incorrect; it should be $[\alpha]_D^{12} - 56.47^\circ$ (1.0095 grams in 50 grams of water). The tetrabenzoate, $C_6H_8O(OBz)_4$, crystallises in white, glistening leaflets, m. p. 142° , $[\alpha]_D^{17} - 150.42^\circ$ (0.604 gram in 37.2 grams of chloroform). The tetranitrate, $C_6H_8O(O \cdot NO_2)_4$, prepared by adding styracitol to a mixture of concentrated sulphuric acid and fuming nitric acid, crystallises in white, glistening needles, m. p. 106° , $[\alpha]_D^{17} - 31.82^\circ$ (0.654 gram in 20.025 grams of acetone). Styracitol is converted by concentrated sulphuric acid into styracitoldisulphuric acid; the barium salt, $C_6H_{10}O_5(SO_3)_2Ba$, is a white powder. As yet, only oxalic acid has been obtained by oxidising styracitol with 50% nitric acid. W. H. G.

Mechanism of the Oxidation of Dextrose by Bromine in Neutral and Acid Solutions. H. H. BUNZEL and ALBERT P. MATHEWS (*J. Amer. Chem. Soc.*, 1909, 31, 464—479).—Dextrose has both weakly basic and weakly acidic properties. A neutral or acid solution contains non-dissociated molecules, $C_6H_{12}O_6$, the free base, $C_6H_{12}O_6 \cdot H_2O$, and the ions $C_6\bar{H}_{11}O_6$ and $C_6\bar{H}_{13}O_6^+$. These are formed according to the following reactions: (1) $C_6H_{12}O_6 \rightleftharpoons C_6\bar{H}_{11}O_6 + H^+$ (2) $C_6H_{12}O_6 + HCl \rightleftharpoons C_6\bar{H}_{13}O_6^+ + Cl^-$, and (3) $C_6\bar{H}_{12}O_6 + H_2O \rightleftharpoons C_6H_{12}O_6 \cdot H_2O$.

The object of the present investigation was to ascertain which of these components is most readily oxidised by bromine. The velocity of oxidation of dextrose has been determined in solutions containing varying quantities of hydrobromic, hydrochloric, sulphuric, and phosphoric acids up to a concentration of 0.5*N*, both in the presence and absence of sodium bromide. The determinations were made by measuring the rate of disappearance of the bromine.

It has been found that the course of the oxidation in presence of an excess of dextrose is represented quantitatively by the equation $dx/dt = a(A - x)[K^v + K_4/(B + 2x)^2]$, in which $a(A - x)$ is the concentration of the active bromine, $(B + 2x)$ the concentration of the hydrogen ions, and K^v and K_4 the constants of two reactions. All the results of the experiments agree quantitatively with the hypothesis that dextrose undergoes ionisation in aqueous solution to form the ions $C_6\bar{H}_{11}O_6$ and $C_6\bar{H}_{13}O_6^+$, and that these ions are the particles actually oxidised by the bromine. The oxidation of dextrose by bromine in neutral or acid solution yields a large proportion of gluconic acid. Since the solution, even if neutral at first, rapidly becomes acid owing to the formation of hydrobromic acid, the reaction of the $-$ ion will be quickly suppressed and the oxidation of the $+$ ion only will take place. Hence it is evident that the oxidation of the $+$ ion results in the formation of gluconic acid. In view of the large amount of gluconic acid obtained by Nef (*Abstr.*, 1908, i, 7) in the oxidation of dextrose by Fehling's solution, it seems probable that gluconic acid is also derived from some other source than the $+$ ion, but whether from the $-$ ion or from the non-dissociated molecule cannot be definitely stated. E. G.

Spontaneous Oxidation of Sugars. ALBERT P. MATHEWS. **Spontaneous Oxidation of Cysteine.** ALBERT P. MATHEWS and SYDNEY WALKER. **Action of Cyanides and Nitriles on the Spontaneous Oxidation of Cysteine.** ALBERT P. MATHEWS and SYDNEY WALKER (*J. Biol. Chem.*, 1909, 6, 3—20, 21—28, 29—38).—Lævulose, galactose, dextrose, maltose, and lactose oxidise rapidly in the air in alkaline solutions. This shows that for oxidation it is necessary to form a salt of the sugar, which ionises, and the resulting disturbance of electrical equilibrium in the anion causes its easy oxidation. Lævulose oxidises most rapidly; the other sugars oxidise at about an equal speed, approximately one-quarter that of lævulose.

In the body, oxydases are believed to include (1) activators of oxygen, and (2) activators of the reducing substances by dissociation; the latter, which are more important, are specific, the former not. Cysteine is rapidly oxidised to cystine in neutral media, that is, about the reaction of blood. Cyanides and most nitriles check or hinder this action, probably by uniting with the sulphur group which the oxygen ordinarily attacks. This suggests a similar action of these poisons on cellular respiration.

W. D. H.

Conjugated Phosphoric Acids of Plant Seeds. PHÆBUS A. LEVENE (*Biochem. Zeitsch.*, 1909, 16, 399—405).—Phytin consists partly of a condensation product of inosite with phosphoric acid (compare Neuberg, *Abstr.*, 1908, i, 394), but partly, also, of a condensation product of phosphoric acid with glycuronic acid. A complete separation of the two constituents was not possible (compare following abstract).

G. B.

Phytin. CARL NEUBERG (*Biochem. Zeitsch.*, 1909, 16, 406—410. Compare *Abstr.*, 1908, i, 394; Levene, preceding abstract).—Mainly polemical. Neuberg has shown that phytin is inosite-phosphoric acid; Levene claims to have resolved it into this substance and into glycuronic acid-phosphoric acid. Eight different phytin preparations are now found to give no glycuronic acid reaction.

E. F. A.

Cellulose Hydrates. CHARLES F. CROSS and EDWARD J. BEVAN (*Chem. Zeit.*, 1909, 33, 368).—Polemical. A reply to Ost and Westhoff (this vol., i, 210).

L. DE K.

Preparation of Esters of Cellulose and their Transformation Products by the Action of Acid Anhydrides in the Presence of Salts. KNOLL & Co. (D.R.-P. 206950).—Other acid anhydrides besides acetic anhydride condense with cellulose to form various stable esters. *Propionylcellulose* is produced by dissolving cotton wool in a mixture of propionic anhydride and glacial acetic acid containing a small proportion of ammonium sulphate. A butyryl ester is similarly obtained by dissolving cellulose or hydrocellulose at 70° in a mixture of butyric anhydride and glacial acetic acid containing methylamine sulphate.

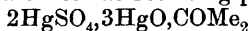
F. M. G. M.

Formation of Hydrocelluloses by means of Sulphuric Acid. GEORG BÜTTNER and J. NEUMANN (*Zeitsch. angew. Chem.*, 1909, 22, 585. Compare this vol., i, 86).—A reply to Schwalbe (*ibid.*, 136). The importance and usefulness of analytical data for hydrocelluloses are emphasised.

J. J. S.

Distillation of Wood with Superheated Steam. GEORG BÜTTNER and HANS WISLICENUS (*J. pr. Chem.*, 1909, [ii], 79, 177—234).—A systematic investigation of the destructive distillation of wood has not been undertaken since Violette's original researches. The present paper deals with the dry distillation, and the distillation with superheated steam, of cellulose and of wood, on the small and on the large

scale, and with the estimation of the products. Concordant determinations of the acetic acid, methyl alcohol, ketones, and reducing agents in the crude pyroligneous acid can be obtained only by suitable preliminary treatment of the crude distillate. The acetic acid is estimated by treating the crude aqueous distillate with dilute sulphuric acid, distilling with steam, and titrating the distillate with *N*/10-sodium hydroxide and phenolphthalein, volatile acids other than acetic being present in negligibly small amount. The methyl alcohol and the ketones (calculated as acetone) are estimated by filtering a measured volume of the crude distillate, neutralising with solid sodium carbonate, again filtering, making the filtrate strongly alkaline, and distilling, the first half of the distillate being shaken with animal charcoal, filtered, and made up to volume; in one portion of this solution the methyl alcohol is determined by Zeisel's method, whilst in another portion the ketones are estimated by Denigès' mercuric sulphate method, after preliminary treatment with hydrogen peroxide to destroy impurities which cause the resulting precipitate,



(dried at 90°), to be coloured. The reducing agents are estimated by warming the crude distillate with ammoniacal *N*/10-silver nitrate, and determining, after filtration, the excess of silver nitrate by ammonium thiocyanate. The water, coke, and tar are determined by direct weighing, and the gaseous constituents are measured at the ordinary temperature and pressure. All %'s are calculated on cellulose or wood dried at 120°.

Preliminary experiments were performed on cellulose (filter paper), which was subjected to dry distillation in an iron tube heated to a dark red heat in an ordinary gas furnace, the volatile products passing through a condenser and being collected in two receivers and a gas-holder. Analysis of the products gives (on 41.62 grams of cellulose) 20.07% charcoal, 5.97% tar, 2.76% acetic acid, 0.04% ketones, and 7.56% reducing agents, the outstanding feature being the absence of methyl alcohol. In the next experiment the tube was heated in a Heraeus electrical resistance furnace to ensure more equable heating; the distillation occurred between 140° and 470°, and the results were very similar to the preceding, the chief difference being an increase of 10% in the amount of charcoal. Again, methyl alcohol is not produced. In another experiment with the electric furnace, the temperature was raised to 140°, when steam at 125° was admitted, and the distillation continued up to 460°. Methyl alcohol is not formed, the % of reducing agents is doubled, and the charcoal decreases 7.5%. Next, with the same apparatus, the temperature was raised to 150°, steam at 140° admitted, and the distillation continued up to a very high, unmeasured temperature; the cellulose is completely destroyed, no charcoal, tar, or methyl alcohol is formed, only a trace of ketone, 1.7% acetic acid, and 5.18% reducing agents being produced, apart from gaseous products.

Similar experiments on wood have been performed on the small scale. The iron tube, packed with beech wood or hornbeam, was heated to 150° in the electric furnace, steam at 140° admitted, and the distillation continued up to 350°. The %'s are as follows: charcoal

35.1, tar 4.30, acetic acid 10.30, methyl alcohol 0.27, ketones 0.41, and reducing agents 8.49. A comparative examination of the products of the distillation of cellulose and of wood shows that the formation of acetic acid is largely, and of methyl alcohol is entirely, due to the lignin of the wood.

The rapid distillation of beech wood with steam at 350—425° leads to an increase in the amount of gas, tar, and reducing agents, the % of acetic acid being unchanged. This result is important, because dry distillation, as ordinarily practised, must proceed slowly in order to avoid a decrease in the amount of acetic acid formed.

In these experiments with superheated steam, the aqueous distillate is necessarily very dilute. It is shown, however, that the decomposition of wood by steam begins at 240°, and that all the valuable products come over in the fraction between 240—300°; the carbonisation of the wood can then be completed at a higher temperature without any valuable product collecting in the distillate.

Attempts have been made to increase the yield of acetic acid by the oxidation of the reducing agents (mainly acetaldehyde) formed in the distillation. Distillation of wood with a mixture of air and superheated steam is of no use, as also is the passing of air through the crude acetic acid. The addition of hydrogen peroxide, however, to the crude aqueous distillate (containing 8% of acetic acid and 7.53% of reducing agents) and distillation with a few c.c. of dilute sulphuric acid yields a distillate containing 18.86% of acetic acid.

The experience gained in these experiments has been applied on a manufacturing scale. A description and sections of the plant are given, but the results are disappointing; for example, in an experiment on 15,800 grams of beech wood, the yield of acetic acid is only 3.34%, whilst the amounts of methyl alcohol, reducing agents, and ketones are 0.24, 2.64, and 0.19% respectively.

It has been noticed that, whilst the average temperature of the retort is about 300°, the escaping gases and vapours have a temperature of 400—500°, proving that an exothermic reaction must occur among the products of the distillation of wood with superheated steam.

C. S.

New General Method for Preparation of Aliphatic Amines. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1909, 148, 898—901. Compare Abstr., 1908, i, 594, 713).—In the presence of heated thorium dioxide or tungsten trioxide, primary alcohols react readily with ammonia to form water and a primary amine without the formation of an ethylenic hydrocarbon. Under the same conditions, alcohols react with primary amines to give secondary and tertiary amines. This observation has led to the discovery of a method for preparing aliphatic amines which is more convenient than Merz's method (Abstr., 1884, 984). The alcohol vapour and dry ammonia, or the vapour of a primary amine, are passed over a few grams of the catalyst at 350—370°. The product condenses to a liquid containing a primary and secondary amine with a small quantity of the tertiary amine and also water, ammonia, and unaltered alcohol; the latter is removed by distillation. The following amines have been prepared in

this way: *iso*Amylamine, diisoamylamine, ethyl*iso*amylamine, *propyl*-*iso*amylamine, $\text{Pr}^a(\text{C}_5\text{H}_{11})\text{NH}$, b. p. 141° , *isobutyliso*amylamine, $\text{C}_9\text{H}_{21}\text{N}$, b. p. 158 — 160° .

The application of the method to aromatic, secondary, and cyclic alcohols will form the subject of a further communication.

W. O. W.

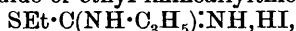
Homologues of Arginine. ERNST WINTERSTEIN and ALBERT KÜNG (*Zeitsch. physiol. Chem.*, 1909, 59, 141—164).—Thiocarbamide, by shaking with mercuric oxide in ethereal suspension, passes largely into the condition of cyanamide. By heating $\alpha\beta$ -dibromopropionic acid with ammonia and ammonium carbonate, *isoserine* is obtained, and not $\alpha\beta$ -diaminopropionic acid as expected. By the action of $\alpha\beta$ -dibromopropionic acid on guanidine carbonate, an amorphous, nitrogenous substance is obtained in addition to guanidine hydrobromide. By the condensation of cyanamide with $\alpha\beta$ -diaminopropionic acid, a lower homologue of arginine is formed, namely, α -amino- β -guanidinepropionic acid. The hydrochloride,



forms colourless, transparent, monoclinic (?) prisms, decomp. 180 — 181° ; the *picrate* crystallises in slender needles, decomp. 200° . After the reaction between lysine and cyanamide, no higher homologues of arginine could be separated out.

W. D. H.

Thiodine. ROGER DOURIS (*Bull. Sci. Pharmacol.*, 1908, 15, 629—631).—This drug is prepared by heating equimolecular proportions of thiosinamine (allylthiocarbamide) and ethyl iodide in a reflux apparatus. Contrary to the supposition of its discoverer, Weiss, the ethyl group in thiodine is attached to the sulphur atom, for, on oxidation, ethanesulphonic acid is formed. Thiodine is therefore either the hydride of ethyl iminoallylthiocarbamate,



or of ethyl allyliminothiocarbamate, $\text{SEt} \cdot \text{C}(\text{NH}_2, \text{HI}) : \text{N} \cdot \text{C}_3\text{H}_5$. The substance forms colourless crystals, m. p. 69° ; the corresponding hydrochloride is crystalline and very hygroscopic. The *picrate* has m. p. 123° .

G. B.

Oxidation of Glutamic and Aspartic Acids by Hydrogen Peroxide. HENRY D. DAKIN (*J. Biol. Chem.*, 1909, 5, 409—412).—Glutamic acid (like monoaminomonocarboxylic acids) is readily oxidised when the ammonium salt is warmed with hydrogen peroxide, with the liberation of ammonia, carbon dioxide, and formation of succinic acid. A similar reaction is brought about by yeast (Ehrlich) and putrefactive organisms. With aspartic acid, essentially the same reaction occurs, but the change is complicated by the fact that the primary product of the reaction, namely, the semialdehyde of malonic acid, is very unstable and breaks up easily into acetaldehyde and carbon dioxide.

W. D. H.

Cyanohydrins. A. J. ULTÈE (*Rec. trav. chim.*, 1909, 28, 1—23).—Lapworth (*Trans.*, 1903, 83, 995) has shown that the addition of hydrogen cyanide to aldehydes and ketones is accelerated by an

alkaline catalyst, but, hitherto, attempts to isolate the cyanohydrin formed by distillation of the reaction product have failed. The failure is due to the reversible action of the alkali regenerating the hydrogen cyanide and aldehyde or ketone. Accordingly, if after the reaction is completed the catalyst is neutralised by a trace of sulphuric acid, the cyanohydrin produced can be readily isolated by distilling the reaction mixture under reduced pressure. Utilising this fact, the author has prepared a number of cyanohydrins, some of which have been described previously, in a pure state, and determined their physical constants. Contrary to the generally accepted statement of Urech (*Annalen*, 1872, 164, 259), the cyanohydrins do not precipitate silver nitrate solution, and the amount of cyanohydrin present at the equilibrium condition, resulting when the latter is treated with a trace of alkali, has been determined for each compound by estimating the free hydrogen cyanide as silver cyanide. α -Hydroxyisobutyronitrile, which, although already described (compare Urech, *loc. cit.*; Tiemann and Friedländer, *Abstr.*, 1882, 56; Pinner, *Abstr.*, 1884, 1292; Henry, *Abstr.*, 1899, i, 182; Bucherer and Grolée, *Abstr.*, 1906, i, 405), has not hitherto been obtained pure, is a colourless, inodorous liquid, b. p. $82^{\circ}/23$ mm., m. p. -19° , D^{19}_D 0.9320, n^{19}_D 1.40002, which very largely dissociates when heated at $170-175^{\circ}$. At the condition of equilibrium, equimolecular quantities of acetone and hydrogen cyanide combine to the extent of 94.15% at 0° , 88.60% at 25° . α -Hydroxy- α -methylbutyronitrile is a liquid, D^{19}_D 0.9303, n^{19}_D 1.41525, which does not crystallise on cooling, but forms a hard, vitreous mass. In the equilibrium mixture, 95.57% of the cyanohydrin is present at 0° , 90.36% at 25° . α -Ethyl- α -hydroxybutyronitrile, a liquid, b. p. $97.5^{\circ}/18.5$ mm., D^{18}_D 0.9300, n^{18}_D 1.42585, is the first of the series which is not completely miscible with water. At 0° addition takes place to the extent of 95.90%, and at 25° 91.29%. α -Hydroxy- α -methylvaleronitrile, $\text{OH}\cdot\text{CMePr}\cdot\text{CN}$, is a liquid, b. p. $100^{\circ}/21$ mm., D^{18}_D 0.9166, n^{18}_D 1.42585, which is present in the equilibrium mixture to the amount of 93.87% at 0° , 88.08% at 25° . α -Hydroxy- $\alpha\beta$ -dimethylbutyronitrile has b. p. $97^{\circ}/19$ mm., D^{13}_D 0.9334, n^{13}_D 1.42755. The amount present at equilibrium is 95.88% at 0° , 91.32% at 25° . α -Hydroxy- α -methylhexonitrile, $\text{CH}_2\text{Pr}\cdot\text{CMe}(\text{OH})\cdot\text{CN}$, is a liquid, b. p. $114^{\circ}/21$ mm., $D^{13.5}_D$ 0.9102, $n^{13.5}_D$ 1.42915, of which 94.24% is present at equilibrium at 0° , 87.45% at 25° . α -Hydroxy- $\alpha\gamma$ -dimethylvaleronitrile, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CN}$, a colourless, odourless liquid, b. p. $109^{\circ}/24$ mm., D^{20}_D 0.9047, n^{21}_D 1.42595, is more readily dissociated, only 82.51% being present in equilibrium at 0° , and 69.84% at 25° . α -Hydroxy- $\alpha\beta\beta$ -trimethylbutyronitrile could not be obtained pure; the substance recrystallised from light petroleum has m. p. $103-104^{\circ}$: Carlinfanti (*Abstr.*, 1898, i, 234) observed $82-87^{\circ}$. α -Hydroxy- α -propylvaleronitrile, $\text{CPr}^2_2(\text{OH})\cdot\text{CN}$, which has b. p. $119^{\circ}/21$ mm., D^{18}_D 0.9077, n^{18}_D 1.43366, is present in the equilibrium mixture to the extent of 92.88% at 0° , 84.81% at 25° . β -Chloro- α -hydroxy- α -methylpropionitrile (Bischoff, *Ber.*, 1872, 5, 865) is a liquid, b. p. $110^{\circ}/22$ mm., D^{15}_D 1.2027, n^{15}_D 1.45362. The amount present in equilibrium at 0° is 97.75%, at 25° 94.94%. 1-Cyanocyclohexanol forms very hygroscopic crystals, m. p. 29° , b. p. $125.5-126^{\circ}/17.5$ mm. It is only slightly dissociated at 25° , the equilibrium mixture containing 98.61% of the

nitrile. The latter condenses with aniline, giving colourless needles of 1-anilinocyclohexanonitrile, $\text{CH}_2\langle\text{CH}_2\cdot\text{CH}_2\rangle\text{C}(\text{NHPh})\cdot\text{CN}$, m. p. 73° .

Ethyl α -cyano- α -hydroxypropionate (compare Gerson, Abstr., 1887, 260) is a colourless liquid, b. p. $105-105.5^\circ/19$ mm., D^{16}_4 1.0988, n^{17}_D 1.42435, of which 98.17% is present in the equilibrium mixture at 25° . Ethyl β -cyano- β -hydroxybutyrate is a colourless, odourless liquid, b. p. $127-128^\circ/16.5$ mm., m. p. 8.5° , $D^{13.5}_4$ 1.0886, $n^{13.5}_D$ 1.43557, which is more readily dissociated than the preceding compound, the equilibrium mixture at 0° containing 94.02%, and at 25° 87.71%, of the ester.

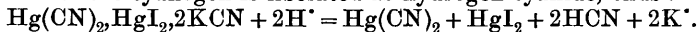
When ethyl lævulate containing a small quantity of potassium cyanide is treated with hydrogen cyanide and the product after remaining overnight distilled under reduced pressure, a solid, m. p. $29-30^\circ$, is obtained which seems to be identical with Tollens and Block-Kreckeler's cyanovalerolactone (Abstr., 1887, 800). All the above cyanohydrins with the exception of β -chloro- α -hydroxy- α -methylpropionitrile were analysed by hydrolysis with potassium hydroxide and estimation of the cyanide by titration with $N/10$ -silver nitrate solution, this being found the most accurate method.

E. H.

Mercuric Oxycyanide. ERWIN RUPP and S. GOY (*Arch. Pharm.*, 1909, 247, 100-107. Compare Abstr., 1908, i, 770).—Mercuric oxycyanide when treated with potassium iodide behaves as a mixture of mercuric oxide and mercuric cyanide. The reaction proceeds in one of the following ways, depending on the proportion of potassium iodide present :

- (1) $\text{HgO}, \text{Hg}(\text{CN})_2 + 2\text{KI} + \text{H}_2\text{O} = \text{HgI}_2 + \text{Hg}(\text{CN})_2 + 2\text{KOH}$;
- (2) $2[\text{HgO}, \text{Hg}(\text{CN})_2] + 10\text{KI} + 2\text{H}_2\text{O} =$
 $4\text{KOH} + 2[\text{HgI}_2, 2\text{KI}] + [\text{Hg}(\text{CN})_2, \text{HgI}_2, 2\text{KCN}]$;
- (3) $\text{HgO}, \text{Hg}(\text{CN})_2 + 8\text{KI} + \text{H}_2\text{O} = 2[\text{HgI}_2, 2\text{KI}] + 2\text{KCN} + 2\text{KOH}$.

The complex salt, $\text{Hg}(\text{CN})_2, \text{HgI}_2, 2\text{KCN}$, crystallises in silky, white needles ; its aqueous solution reacts acid towards litmus and neutral towards phenolphthalein. When the salt is acted on by an acid, only one-half of the cyanogen is liberated as hydrogen cyanide, thus :



In the presence of an excess of potassium iodide a state of equilibrium exists, represented by the equation : $2[\text{HgI}_2, 2\text{KI}] + 4\text{KCN} \rightleftharpoons [\text{Hg}(\text{CN})_2, \text{HgI}_2, 2\text{KCN}] + 6\text{KI}$. The complex cyanide separates when the solution is concentrated, although the aqueous solution is practically a solution of potassium cyanide and potassium mercuric iodide, as represented by the left-hand side of the equation. Mercuric oxycyanide also behaves as a mixture of mercuric oxide and mercuric cyanide towards iodine, hydrochloric acid, hydrobromic acid, and hydriodic acid.

W. H. G.

Preparation of Aromatic Nitro-compounds. CHEMISCHE FABRIK GRÜNAU LANDSHOFF & MEYER ATKIEN-GESELLSCHAFT (D.R.-P. 207170).—The nitrous fumes obtained by the electrical oxidation of atmospheric nitrogen are absorbed by a weak basic oxide, such as zinc or copper oxide, and the product when heated at 500° evolves again the oxides of nitrogen, from which nitric acid can be prepared.

When, however, a mixture of benzene and air is passed over the mixed zinc nitrite-nitrate at 300—350°, nitration of the hydrocarbon occurs, and pure nitrobenzene is produced in quantitative yield. At higher temperatures a decomposition sets in. The residual zinc oxide may be used in subsequent operations. Toluene, when nitrated by this method at about 400°, gives *m*-nitrotoluene (11%) and the para-isomeride (89%). In combination with Sabatier's reduction process, this method furnishes a means of preparing aniline directly and continuously from benzene compounds. F. M. G. M.

2 : 5- and 4 : 5-Dinitro-*m*-xylenes. JAN J. BLANKSMA (*Rec. trav. chim.*, 1909, 28, 92—96).—It has been stated previously (Abstr., 1906, i, 11) that by nitrating *s*-nitro-*m*-xylene with nitric acid, D 1·52, 4 : 5-dinitro-*m*-xylene, m. p. 132°, is formed. The latter compound is also obtained by nitrating 5-nitroaceto-*m*-xylidide, removing the acetyl group by hydrolysis, and eliminating the amino-group by diazotisation. Since Klages (Abstr., 1896, i, 290) prepared the same compound, but regarded it as 2 : 5-dinitro-*m*-xylene, the present work was undertaken in order definitely to determine its constitution.

4 : 6-Dinitro-*m*-xylene on partial reduction gives 6-nitro-4-amino-*m*-xylene, which, when acetylated with a mixture of acetic anhydride and acid, gives 6-nitroaceto-*m*-xylidide, m. p. 160°. Nitration of the latter with nitric acid, D 1·52, or a mixture of nitric and sulphuric acids, gives 5 : 6-dinitroaceto-*m*-xylidide, m. p. 217°, identical with that prepared by nitrating 5-nitroaceto-*m*-xylidide. Elimination of the amino-group from 5 : 6-dinitro-*m*-xylidine, m. p. 120° (Klages gives 115°, and 226° for the acetyl derivative), by the diazo-reaction gives 4 : 5-dinitro-*m*-xylene, of which the constitution is therefore proved.

The 4 : 5-dinitro-*m*-xylene is transformed by nitration into 4 : 5 : 6-trinitro-*m*-xylene. A new proof of the constitution of the latter is furnished by transforming it into 4 : 6-dinitro-5-amino-*m*-xylene by heating with alcoholic ammonia and eliminating the amino-group, giving 4 : 6-dinitro-*m*-xylene.

2-Nitroaceto-*m*-xylidide, m. p. 147°, prepared by acetylating Noelting, Braun, and Thesmar's 2-nitro-4-amino-*m*-xylene (Abstr., 1901, i, 588), on nitration with nitric acid, D 1·52, gives clear yellow crystals of 2 : 5-dinitroaceto-*m*-xylidide, m. p. 233°. The latter, on hydrolysis, gives 2 : 5-dinitro-*m*-xylidine, from which the amino-group is eliminated, giving 2 : 5-dinitro-*m*-xylene, colourless crystals, m. p. 101°, which become yellow on exposure to light. The constitution of the latter substance is proved by its transformation into 2 : 4 : 5-trinitro-*m*-xylene when nitrated.

Methods are described for the preparation of 2 : 5- and 4 : 5-dinitro-*m*-xylenes from *m*-xylene. The four possible isomeric dinitro-*m*-xylenes have now been described. E. H.

Benzeneselenonic Acid and Related Compounds. HOWARD W. DOUGHTY (*Amer. Chem. J.*, 1909, 41, 326—337).—Benzeneselenonic acid, $C_6H_5 \cdot SeO_3H$, is formed when benzene and selenic acid are heated together on a water-bath or in a sealed tube at 110°. It has m. p. 142°, and gives off carbon dioxide and water when heated

at 180°. The barium salt crystallises from cold or warm solutions with 3H₂O, from hot solutions with 2H₂O.

Phenyl silver selenide, SeAgPh, is obtained as a yellow precipitate when a solution of benzeneselenonic acid is mixed with the equivalent quantity of silver nitrate and sulphur dioxide is then added.

Benzeneseleninic acid is precipitated when benzeneselenonic acid is treated with concentrated hydrochloric acid in the cold. It crystallises without water of crystallisation. When heated at 130°, it forms *benzeneseleninic anhydride*, m. p. 164°, subliming about 130°; the anhydride is not changed by heating at its melting point, but decomposes at 200°. It is very hygroscopic, and on exposure to the air it absorbs moisture, forming benzeneseleninic acid. H. M. D.

New Method for the Preparation of β -Halogen Derivatives of Naphthalene GEORGES DARZENS and ERNEST BERGER (*Compt. rend.*, 1909, 148, 787—788).—In addition to esters of phosphorous and phosphoric acids, β -halogen derivatives of naphthalene are obtained when the sodium derivative of β -naphthol is treated with a halogen or oxy-halogen derivative of phosphorus.

The best yield (55%) was obtained with phosphorus trichloride, which was dissolved in dry toluene and heated for an hour on the water-bath with the sodium derivative of β -naphthol suspended in the same solvent. The product was then treated with water and distilled in steam. W. O. W.

Hydrogenation of Fluorene. LEOPOLD SPIEGEL (*Ber.*, 1909, 42, 916—920. Compare Abstr., 1908, i, 331).—Polemical. A reply to Schmidt. The reduction product of fluorene is not a decahydro-fluorene, but the perhydride, C₁₃H₂₂, D²² 0.9203, M_D 55.66 (Abstr., 1908, i, 16; this vol., i, 19). W. R.

Preparation of 3-Chloro-6-nitroaniline. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 206345).—3-Chloro-6-nitroaniline and its sulphonic acid, which are of importance in connexion with the production of azo-dyes, are now readily prepared by the following series of operations.

3-Chloroacetanilide is sulphonated with fuming acid (20% SO₃) at the ordinary temperature, and the mixture then treated with mixed nitric and sulphuric acids at -5°. On pouring the nitration product into a large volume of water and warming at 70—80°, the acetyl group is removed, and the addition of potassium chloride leads to the formation of potassium 3-chloro-6-nitroaniline-4-sulphonate. This salt, which is only sparingly soluble in cold water, gives a yellow diazo-derivative. When boiled with 3.5 parts of sulphuric acid (55° B_e), the sulphonic group is eliminated, and 3-chloro-6-nitroaniline, m. p. 124—125°, is produced. F. M. G. M.

Bromination of the Dinitroanilines. JAN J. BLANKSMA (*Rec. trav. chim.*, 1909, 28, 97—104).—2:3-, 3:4-, and 3:6-Dinitroanilines were prepared according to the method described by Wender (Abstr., 1890, 884).

When 3:6-dinitroaniline, dissolved in glacial acetic acid, is heated with bromine (1 mol.) in a sealed tube on a water-bath, the product consists of 4-bromo-3:6-dinitroaniline, yellow crystals, m. p. 186°, which on similar treatment gives 2:4-dibromo-3:6-dinitroaniline, m. p. 140°. The constitution of the 4-bromo-3:6-dinitroaniline is proved by the production of the acetyl derivative, m. p. 152°, together with 4-bromo-2:3-dinitroacetanilide, m. p. 185°, by the nitration of 4-bromo-3-nitroacetanilide, prepared according to Noelting and Collin's method (Abstr., 1884, 1011).

The constitution of 4-bromo-2:3-dinitroacetanilide is established by the fact that the amine obtained by hydrolysis gives 4:6-dibromo-2:3-dinitroaniline, not 2:4:6-tribromo-3:5-dinitroaniline (Abstr., 1902, i, 600) when treated with excess of bromine.

2:3-Dinitroaniline, when brominated in a sealed tube, gives 6-bromo-2:3-dinitroaniline, deep red crystals, m. p. 158° (not 4-bromo-2:3-dinitroaniline, which has the same m. p.), which on further bromination gives 4:6-dibromo-2:3-dinitroaniline, m. p. 100°.

Bromination of 3:4-dinitroaniline under similar conditions gives clear yellow crystals of 6-bromo-3:4-dinitroaniline, m. p. 186°, which can be again brominated, giving 2:6-dibromo-3:4-dinitroaniline, yellow crystals, m. p. 201°.

6-Bromo-3-nitroaniline, prepared according to Wheeler's method (Abstr., 1896, i, 23), on acetylation gives colourless crystals of 6-bromo-3-nitroacetanilide, m. p. 183°, which when nitrated gives 6-bromo-3:4-dinitroacetanilide, colourless crystals, m. p. 165°. The latter on hydrolysis gives an amine identical with the 6-bromo-3:4-dinitroaniline obtained from 3:4-dinitroaniline, thus establishing the constitution of the former compound.

The author confirms the observation of Körner and Contardi (Abstr., 1908, i, 523) that bromination of 3:5-dinitroaniline gives 2-bromo-3:5-dinitroaniline. The latter, with excess of bromine, gives 2:4:6-tribromo-3:5-dinitroaniline.

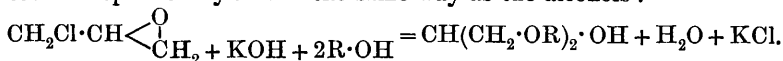
All attempts to prepare 1:3-dibromo-2:5-dinitrobenzene, of which a small quantity is probably formed in the nitration of 1:3-dibromo-5-nitrobenzene, by eliminating the amino-group from 2:4-dibromo-3:6-dinitroaniline failed. E. H.

Colouring and Dyeing Properties of Picric Acid. LÉO VIGNON (*Compt. rend.*, 1909, 148, 844—846).—The intensity of colour of solutions of picric acid in water, alcohol, benzene, and ether varies in the same sense as the electrical conductivities of the solutions. Aqueous solutions of picric acid are able to dye wool, but only when their electrical conductivities exceed a certain minimum value, which may be attained either by a sufficient concentration of the picric acid or by the addition of a small proportion of an acid, such as hydrochloric, to solutions of lower concentrations. With alcoholic solutions of picric acid containing 1 part of hydrochloric acid per 10,000, the fixation of colouring matter by wool is very slight, in spite of a moderately high conductivity.

The fixation of picric acid by wool seems to be due to a chemical action between the fibre of the wool and the highly-ionised colouring

matter. This chemical action is apparently not a salt-forming phenomenon, since, although picric acid dissolved in benzene forms salts with organic bases (compare Abstr., 1908, ii, 664), such solutions have no dyeing action on wool. T. H. P.

Action of Potassium Hydroxide on Epichlorohydrin in Presence of Monohydric Phenols. VIRGILIO ZUNINO (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 254—256. Compare Abstr., 1899, i, 410; 1900, i, 535).—Phenols dissolved in potassium hydroxide solution behave towards epichlorohydrin in the same way as the alcohols:



The reaction proceeds spontaneously even in the cold, but the yields obtained are small; this result is perhaps related to Menshutkin's laws of etherification of the alcohols, the phenols behaving like tertiary alcohols. The hydroxy-compounds employed were phenol, *m*- and *o*-cresols, thymol, and carvacrol, the following ethers being obtained.

The *diphenyl ether*, $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{OPh})_2$, b. p. 287—288°, a liquid of pleasant odour. *Di-o-tolyl ether*, $\text{C}_{17}\text{H}_{20}\text{O}_3$, b. p. 296°, a faintly yellow liquid with a pleasant odour. *Di-m-tolyl ether*, $\text{C}_{17}\text{H}_{20}\text{O}_3$, b. p. 253—254°, a pale, lemon-yellow liquid. *Dithymyl ether*, $\text{C}_{23}\text{H}_{32}\text{O}_3$, a rather dense liquid, b. p. 215°. *Dicarvacryl ether*, $\text{C}_{23}\text{H}_{32}\text{O}_3$, b. p. 245—246°, a dense liquid, becoming mobile on heating. T. H. P.

Preparation of *o*-Nitro-*p*-cresol. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 206638).—Formerly, the technically important *o*-nitro-*p*-cresol was obtained by boiling the solution of diazotised *o*-nitro-*p*-toluidine; it has now been more easily prepared by nitrating *p*-tolyl carbonate, $\text{CO}(\text{O}\cdot\text{C}_7\text{H}_7)_2$, needles, m. p. 117°, when the nitro-group enters the ring in the ortho-position to the methyl group.

o-Nitro-*p*-tolyl carbonate, $\text{CO}(\text{O}\cdot\text{C}_7\text{H}_6\cdot\text{NO}_2)_2$, yellow needles, m. p. 143—144°, when hydrolysed with boiling aqueous sodium hydroxide or carbonate furnishes *o*-nitro-*p*-cresol, m. p. 77°. F. M. G. M.

Tetrahydronaphthyl Glycols (cis and trans) and their Combination. HENRI LEROUX (*Compt. rend.*, 1909, 148, 931—934).—By treating dibromodihydronaphthalene with silver acetate, an ester is obtained which, on hydrolysis, yields a mixture of glycols isomeric with Bamberger's tetrahydronaphthyl glycol, $\text{C}_6\text{H}_4\begin{array}{c} \text{CH}_2\cdot\text{CH}\cdot\text{OH} \\ \diagup \quad \diagdown \\ \text{CH}_2\cdot\text{CH}\cdot\text{OH} \end{array}$ (Abstr., 1893, i, 591). The product has m. p. 110°, and by repeated crystallisation from benzene gives two compounds. The more soluble of these is *trans*-tetrahydronaphthyl glycol, m. p. 118°; the second is a compound, m. p. 140°, formed by union of an equal number of molecules of the *cis*- and *trans*-isomerides. Bamberger's compound appears to be the *cis*-glycol.

trans-Tetrahydronaphthyl glycol crystallises in striated tablets; its *diacetate* crystallises in prisms, m. p. 59°. The *dibenzoate* has m. p. 127°. The *diphenylurethane* occurs in needles, m. p. 175°.

The compound of the *cis*- and *trans*-glycols, which has also been obtained by mixing its constituents in benzene solution, differs from the *trans*-compound in being very soluble in water; treatment with acetic anhydride and pyridine leads to the formation of a mixture of *cis*- and *trans*-diacetates. Similar compounds have been obtained by the combination of other *cis*- and *trans*-isomerides; thus the compound of *cis*-hexane-1:2-diol with its *trans*-isomeride has m. p. 73°.

W. O. W.

Formation of an Ether by the Dehydration of the Alcohol by Heat. PAUL CARRÉ (*Bull. Soc. chim.*, 1909, [iv], 5, 286—287).—*m*-Nitrobenzyl alcohol is converted by distillation into *m*-nitrobenzyl ether, $O(CH_2 \cdot C_6H_4 \cdot NO_2)_2$, m. p. 114°, which is changed quantitatively by phosphorus pentachloride into *m*-nitrobenzyl chloride, m. p. 47°.

The ortho- and para-isomerides do not behave in a similar manner on distillation.

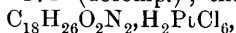
C. S.

New Method for obtaining Substituted Thiocarbamates of Monohydric Alcohols. M. S. ROSCHDESTVENSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 107—108. Compare Orndorff and Richmond, *Abstr.*, 1900, i, 156).—Substituted thiocarbamates of monohydric alcohols may be readily prepared by the action of phenyl or other thiocarbimide on the alkyl oxides derived from the alcohols at the ordinary temperature, the reaction being instantaneous and quantitative. With phenylthiocarbimide, menthol gives a compound, m. p. 74—75°; benzyl alcohol, a compound, m. p. 82—82.5°, and *a*-terpineol, one, m. p. 109°.

This reaction, which is being extended to other thiocarbimides, and to mercaptans, phenols, and polyhydric alcohols, may be employed for the resolution of racemic alcohols and mercaptans.

T. H. P.

Aminoaryl Alcohols. I. Preparation of α -Amino- α -phenylisopropyl Alcohol. HERMANN EMDE [with E. RUNNE] *Arch. Pharm.*, 1909, 247, 130—140. Compare *Abstr.*, 1908, i, 203).—Phenylacetone when treated with sodium ethoxide and amyl nitrite yields oximinophenylacetone, together with a substance, m. p. 188°, which crystallises in slender, white needles. Oximinophenylacetone is reduced by stannous chloride, yielding α -amino- α -phenylacetone, the platinichloride of which crystallises in yellow needles ($1H_2O$), decomposing at 183°, and compact, reddish-brown prisms, decomposing at 194° (compare Kolb, *Abstr.*, 1896, i, 576; Gabriel, *Abstr.*, 1908, i, 466); the *aurichloride* crystallises in flat, golden-yellow needles, m. p. 83°, decomposing at 138—140°. β -Amino- β -phenylisopropyl alcohol, $NH_2 \cdot CHPh \cdot CHMe \cdot OH$, is prepared by reducing the corresponding ketone with sodium amalgam; it forms flexible, glassy crystals, sinters at 83°, m. p. 85°; the *hydrochloride*, $C_9H_{13}ON \cdot HCl$, crystallises in white leaflets, m. p. 170—171° (decomp.); the *platinichloride*,



forms small, orange-red plates, m. p. 189° (decomp.); the *aurichloride*, $C_{18}H_{26}O_2N_2 \cdot HCl \cdot HAuCl_4$, forms golden-yellow needles, m. p. about 85° (decomp.); the *picrate* crystallises in short needles, m. p. $180-181^{\circ}$ (decomp.).
W. H. G.

***l*-Campholic Acid and its Derivatives.** MARCEL GUERBET (*Bull. Soc. chim.*, 1909, [iv], 5, 272—276. Compare this vol., i, 100).—*l*-Campholic acid is obtained in 75% yield by heating *l*-borneol and recently fused potassium hydroxide in a sealed tube for twenty-four hours at 280° , dissolving the product in dilute hydrochloric acid and ether, shaking the ethereal solution with dilute sodium hydroxide, and precipitating the *l*-campholic acid from the latter at 0° by carbon dioxide. The acid has m. p. $106-107^{\circ}$, b. p. 250° , $[\alpha]_D^{25} - 46.5^{\circ}$, and resembles the *d*-isomeride in its chemical behaviour. The *anhydride*, $(C_{10}H_{17}O)_2O$, m. p. $57-58^{\circ}$, is obtained by heating the acid with acetic anhydride, and separates unchanged by the spontaneous evaporation of its solution in cold water. The *chloride*, $C_{10}H_{17}OCl$, has b. p. 222° , and the *amide*, $C_{10}H_{17}O \cdot NH_2$, prepared from the chloride and aqueous ammonia in the presence of ether, has m. p. $78-79^{\circ}$, and is hydrolysed by alkalis only with difficulty. *l*-Campholic acid cannot be directly esterified. The esters are prepared from the chloride or the anhydride and the corresponding alcohol; the *methyl* ester and the *ethyl* ester have b. p. 211° (corr.) and 228° (corr.) respectively. C. S.

Synthesis of Dimethylnorcampholide. GUSTAV KOMPPA and S. V. HINTIKKA (*Ber.*, 1909, 42, 898—899).—This is a continuation of the investigation of the action of magnesium alkyl derivatives on anhydrides related to camphoric anhydride (compare Abstr., 1908, i, 352), and it has been found that the *dimethylnorcampholide* (annexed formula) prepared from the interaction of magnesium methyl iodide and 1:3-cyclopentanedicarboxylic anhydride is identical with Semmler's lactone of δ -hydroxycamphenilonic acid (this vol., i, 170), m. p. $94.5-95^{\circ}$, crystallising from light petroleum in large, rectangular plates.
W. R.

Transformation of Pinonic Acid into *m*-Xylylacetic Acid. PHILIPPE BARBIER and VICTOR GRIGNARD (*Compt. rend.*, 1908, 148, 646—648).—Pinonic acid undergoes an unexpected transformation when heated at 100° with water and bromine. After neutralising the product with sodium hydrogen carbonate and filtering, the liquid gives a precipitate of *m*-xylylacetic acid (Claus, Abstr., 1890, i, 979) on the addition of hydrogen chloride. Crude pinonic acid may be used in this preparation. This reaction is in accordance with the accepted constitution for pinonic acid, and is analogous to the conversion of methylheptenone into dihydro-*m*-xylene under the influence of hydrogen bromide.

Methyl m-xylylacetate is a liquid having a raspberry-like odour, b. p. $120-121^{\circ}/11$ mm.
W. O. W.

Action of Nitric Acid on Benzoyl Chloride in Presence of Acetic Anhydride. WILLIAM J. KARSLAKE and R. C. HUSTON (*J. Amer. Chem. Soc.*, 1909, 31, 479—483).—Pictet and Genequand

(Abstr., 1902, i, 584) and Pictet and Khotinsky (Abstr., 1907, i, 175) have shown that when acetic acid and acetic anhydride are used as solvents in the nitration of aromatic compounds, the actual nitrating agent is probably either diacetylorthonitric acid or acetyl nitrate, or both. This question has now been studied by means of experiments on the nitration of benzoyl chloride.

When a mixture of benzoyl chloride, acetic anhydride, and nitric anhydride is heated at 60°, oxides of nitrogen are evolved, and a solid residue is obtained, which dissolves in boiling water to form a solution from which benzoic acid separates on cooling. Neither nitroderivatives nor acetyl derivatives of benzoic acid are produced in this reaction.

If benzoyl chloride is warmed at 40° with a mixture of nitric acid and acetic anhydride, *o*-acetylbenzoic acid (acetophenone-*o*-carboxylic acid), benzoic acid, and *m*-nitrobenzoic acid are obtained, the relative amounts of these compounds depending on the proportions of the reagents used. Benzoyl chloride is not capable of acetylation by acetic anhydride alone, or of nitration or acetylation by acetyl nitrate, but by the action of diacetylorthonitric acid it seems to be hydrolysed to benzoic acid, which is then nitrated or acetylated.

Acetophenone-*o*-carboxylic acid, $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, was first obtained by Gabriel and Michael (Abstr., 1878, 229). The *chloride* is an oil; the *amide*, m. p. 116.5°, forms small, colourless prisms, and the anilide melts at 156—157°. The barium, *strontium*, lead, and *silver* salts are described. E. G.

Preponderance of Temperature in Direct Decompositions: Case of Benzoic and Salicylic Esters. ALBERT COLSON (*Compt. rend.*, 1909, 148, 643—645. Compare Abstr., 1908, i, 1).—A continuation of the study of the decomposition of esters by heat. Methyl benzoate differs from its homologues in remaining unaltered at 300—310°; when heated for seven hours at 350°, however, it yields a small quantity of carbon dioxide. Ethyl salicylate decomposes at 300° in accordance with the equation $\text{C}_9\text{H}_{10}\text{O}_3 = \text{PhOH} + \text{C}_2\text{H}_4 + \text{CO}_2$. Under the same conditions, methyl salicylate gives carbon dioxide and anisole with small quantities of phenol. Allyl benzoate gives carbon dioxide and a hydrocarbon.

The author considers that these experiments lend support to his contention that temperature is the determining cause of chemical reactions. If this is the case in the classical conversion of aromatic acids into hydrocarbons, the lime acts merely as an accelerating agent. To test this point, ethyl and methyl salicylates were heated with lime in sealed tubes at 235° for seven hours. The tubes were found to contain a considerable amount of carbon dioxide, together with unaltered lime, indicating that neither the lime nor the heat of formation of calcium carbonate should be regarded as the determining cause of the reaction. W. O. W.

Preparation of Anhydrides of Cyclic and Aliphatic Acids. AUGUSTE BÉHAL (*Compt. rend.*, 1909, 148, 648—650. Compare this vol., i, 145—164).—When tri-*o*-chlorophenylmethane is boiled with

excess of acetic acid for ten hours, hydrogen chloride is liberated and benzoic acid, benzoic anhydride, acetic anhydride, and acetic benzoic anhydride are formed. Benzoyl chloride also appears to be produced, but cannot be isolated, inasmuch as it reacts rapidly with acetic acid, giving a mixture of the foregoing substances. As in the cases previously studied, certain salts exercise an accelerating influence; thus, in the present instance, 86% of the total amount of hydrogen chloride is evolved in two hours, and the reaction is complete in six hours when carried out in presence of a small quantity of cobalt chloride.

W. O. W.

Preparation of 3:5-Di-iodotyrosine. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1909, **59**, 320—324).—In the preparation of 3:5-di-iodotyrosine (iodogorgonic acid: compare Abstr., 1905, i, 350; Abstr., 1908, i, 420), the formation of resinous products may be avoided by working at 0° and adding iodine until there is a permanent excess.

G. B.

***allo-* and *iso*-Cinnamic Acids.** CARL LIEBERMANN (*Ber.*, 1909, **42**, 1027—1036).—Billmann (this vol., i, 155) has shown that the difference between *allocinnamic* and the two *isocinnamic* acids is due to trimorphism. Giesel has now found a quantity of *isocinnamic* acid (m. p. 58°) which has been kept ten to fifteen years in the dark undisturbed; this is shown by crystallographic means to be identical with Liebermann's *iso*-acid. Billmann has shown that all three acids when heated in a steam-drying oven (at 105°) are converted into an acid, m. p. 42°, and this in the fused condition, when inoculated with *isocinnamic* acid (m. p. 58°) or with *allocinnamic* acid, immediately crystallises as a mass of the inoculating acid. These observations are confirmed; both *iso*-acids are not only immediately converted into the *allo*-acid on inoculation, but pass over into it, particularly the *iso*-acid (m. p. 42°), of their own accord.

E. F. A.

New Synthesis of Inactive $\alpha\delta$ -Diaminovaleric Acid and of Proline. EMIL FISCHER and GÉZA ZEMPLÉN (*Ber.*, 1909, **42**, 1022—1026).—Benzoylpiperidine is oxidised by permanganate to benzoyl-*d*-aminovaleric acid, $\text{COPh}\cdot\text{NH}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$, which, when treated with bromine and phosphorus, forms *α-bromobenzoyl-δ-aminovaleric acid*, and this is converted by ammonia into *monobenzoyl ornithine*, from which inactive ornithuric acid (dibenzoyl- $\alpha\delta$ -diaminovaleric acid) is easily obtained on benzylation. The method is analogous to that used by J. von Braun (this vol., i, 229) for the synthesis of lysine from ϵ -benzoylaminohectic acid. Bromo- δ -benzoylaminovaleric acid when boiled with hydrochloric acid yields proline in quantity. It is obtained on bromination of benzoyl- δ -aminovaleric acid as an amorphous solid, and forms an amorphous silver salt. The crude product interacts with aqueous ammonia, forming inactive δ -benzoylornithine, $\text{COPh}\cdot\text{NH}\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$; this crystallises in colourless plates, m. p. 260° (decomp.), and is very similar to the active form (Fischer, Abstr., 1901, i, 192); the yield represents about 20% of the original weight of piperidine taken.

E. F. A.

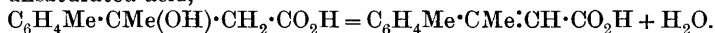
[Esters of Salicylic Acid and the Higher Aliphatic Acids.] NATHAN SULZBERGER (D.R.-P. 206056).—The esters of salicylic acid and the higher aliphatic acids are easily absorbed by the skin without producing local irritation, and within the organism they undergo fission, giving rise to salicylic acid. They are produced by condensing the alkyl salicylates with the alkali salts of oleic, stearic, erucic, brassidic, elaidic, ricinolic, palmitic, and hydroxystearic acids, either alone or in the presence of phosphoryl chloride.

Ethyl oleylsalicylate [*o*-oleoyloxybenzoate], $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{33}$, an oily mass solidifying and melting at 10° , and *ethyl stearyl salicylate* [*o*-stearyloxybenzoate], $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{35}$, a white, crystalline mass, m. p. 48—49°, produced in this way, are substances having an antiseptic action. F. M. G. M.

Action of a Mixture of Ethyl α -Bromopropionate and *p*-Tolualdehyde on Zinc. M. STRECHALKOVSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 18—22).— β -*p*-Tolyl- α -methylhydracrylic acid, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, prepared by the action of zinc on a mixture of ethyl α -bromopropionate and *p*-tolualdehyde in presence of sulphuric acid and decomposing the compound obtained by means of water, crystallises from water in hexagonal prisms, m. p. 108—110°, and has the normal molecular weight in boiling ether. Its sodium (H_2O) and silver salts were prepared and analysed. The ethyl ester, $\text{C}_{13}\text{H}_{18}\text{O}_3$, b. p. 182°/125 mm., n_D^{19} 1.5022, D_4^{19} slightly greater than 1, is a viscous liquid with an odour resembling that of honey, and is readily soluble in alcohol or ether.

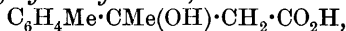
On heating the hydroxy-acid with sulphuric acid, it yields a neutral unsaturated product, b. p. about 200°, which should be, and is probably, α -*p*-tolylpropylene (compare Errera, Abstr., 1885, 655). T. H. P.

Action of Zinc on a Mixture of *p*-Tolyl Methyl Ketone and Ethyl Bromoacetate. I. MATSCHUREVITSCH (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 56—66).—The action of zinc on a mixture of *p*-tolyl methyl ketone and ethyl bromoacetate yields the ester of β -*p*-tolyl- β -methylhydracrylic acid, which, however, readily loses water, giving an unsaturated acid,



β -*p*-Tolyl- β -methylhydracrylic acid can, however, be obtained by isolating and hydrolysing its silver salt.

β -p-Tolyl- β -methylhydracrylic acid,

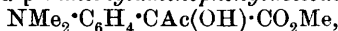


is a faintly yellow, viscid liquid, which, on distillation or on boiling with dilute sulphuric acid, yields α -*p*-tolylpropylene. The silver salt was prepared.

β -p-Tolycrotonic acid, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, crystallises from water in needles and from alcohol in prisms, rhombs, or needles, m. p. 132—134°. Its silver, calcium, $\text{Ca}(\text{C}_{11}\text{H}_{11}\text{O}_2)_2\cdot 3\text{H}_2\text{O}$, barium, and potassium salts were prepared. On dry distillation, the acid yields β -*p*-tolylpropylene (compare Errera, Abstr., 1891, 1020). The ethyl ester, $\text{C}_{13}\text{H}_{16}\text{O}_2$, is a colourless, mobile liquid, b. p. 172°/25 mm., D_4^{23} 1.02091, with a faint odour recalling that of methyl *p*-tolyl ketone, and dissolves readily in alcohol, ether, or benzene. T. H. P.

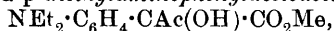
Condensation of Methyl Diketobutyrate with Aromatic Hydrocarbons and Amines. ALFRED GUYOT and V. BADONNEL (*Compt. rend.*, 1909, 148, 847—849. Compare this vol., i, 158, 236).

—*Methyl α-hydroxy-a-p-dimethylaminophenylacetoacetate*,



obtained by the interaction of molecular proportions of dimethylaniline and methyl diketobutyrate in acetic acid solution, crystallises from carbon disulphide in colourless leaflets, m. p. 81°.

Methyl α-hydroxy-a-p-diethylaminophenylacetoacetate,



prepared from diethylaniline and methyl diketobutyrate, crystallises in small prisms, m. p. 56°.

These two esters are hydrolysed quantitatively into acetic acid and dialkylaminophenylglycollic acid, $\text{NR}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$, by aqueous potassium hydroxide, whilst with hot concentrated sulphuric acid a dialkylamino-derivative of benzaldehyde, $\text{NR}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$, is obtained. Cupric acetate oxidises the esters to methyl dialkylaminophenylglyoxylates, $\text{NR}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO}_2\text{Me}$. With phenylhydrazine, the esters give the corresponding simple hydrazones, m. p. 106° and 153° respectively.

Diketobutyric esters also condense with aromatic hydrocarbons, giving, firstly, a hydroxyphenylacetoacetic ester, such as $\text{OH} \cdot \text{CPhAc} \cdot \text{CO}_2\text{R}$, which then fixes a second molecule of hydrocarbon, forming an ester of diphenylacetoacetic acid, $\text{CPh}_2\text{Ac} \cdot \text{CO}_2\text{R}$; thus toluene yields (1) *methyl α-hydroxy-p-tolylacetoacetate*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CAc}(\text{OH}) \cdot \text{CO}_2\text{Me}$, a colourless oil, b. p. 190°/15 mm., and (2) *methyl ditolylacetoacetate*, $\text{CAc}(\text{C}_6\text{H}_4\text{Me})_2 \cdot \text{CO}_2\text{Me}$, which crystallises in colourless prisms, m. p. 119°, b. p. 235°/15 mm., and is resolved quantitatively into acetic acid and ditolylacetic acid by means of alcoholic potassium hydroxide.

T. H. P.

3-Amino-o-phthalic Acid and Certain of its Derivatives.

MARSTON T. BOGERT and FABEL LOUIS JOUARD (*J. Amer. Chem. Soc.*, 1909, 31, 483—490).—In an earlier paper (*Abstr.*, 1908, i, 651), a description has been given of 4-amino-o-phthalic acid and its derivatives. The work has now been extended to the 3-amino-compounds.

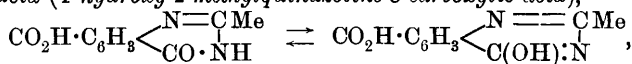
Onnertz (*Abstr.*, 1902, i, 101) first prepared 3-amino-o-phthalic acid, but was unable to purify it. It has now been obtained in the pure state by reducing the corresponding nitro-acid with tin and hydrochloric acid. The compound is a white, crystalline solid, which gradually becomes yellow. When heated rapidly, it melts at 177° (decomp.), or when heated slowly, at 191° (decomp.). If the acid is boiled with water, a fluorescent solution is obtained, which deposits orange-yellow crystals of a *substance*, m. p. 240° (decomp.), which has not been identified. The *hydrochloride* of the acid, m. p. 227° (corr.), and the potassium hydrogen, ammonium hydrogen, silver, and *barium* salts are described. The *hydrochlorides* of the *methyl* and *dimethyl* esters have m. p. 153° (corr.) and 172—174° (decomp.) respectively.

Methyl 3-acetylamino-o-phthalate, $\text{NHAc} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{Me})_2$, m. p. 92—93° (corr.), exhibits strong triboluminescence, even under water.

3-Amino-*o*-phthalic anhydride, m. p. 193—194° (corr.), crystallises in pale yellow needles; its acetyl derivative melts at 185—186° (corr.).

3-Amino-*o*-phthalimide has m. p. 266—267° (corr.); its *hydrochloride* and *potassium* derivative are described. 3-Acetylamino-*o*-phthalimide melts at 242° (corr.), and the *diacetyl* compound at 152—154° (corr.). 3-Phenylcarbmino-*o*-phthalimide, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5\cdot(\text{CO})_2\cdot\text{NH}$, sinters at about 260°, and darkens and melts at about 335°. 3-Amino-*o*-phthalanil melts at 186—188° (corr.), and its acetyl derivative at 195.5° (corr.). 3-Acetylaminophthal-*o*-tolyl, m. p. 214—215° (corr.), forms straw-coloured prisms. The *phenylhydrazide* of 3-amino-*o*-phthalic acid, m. p. 284—285° (decomp.), reacts with acetic anhydride with formation of a substance, m. p. 223—224° (corr.), which has not been further investigated.

Methyl 3-azophthalate, $\text{N}_2[\text{C}_6\text{H}_3(\text{CO}_2\text{Me})_2]_2$, m. p. 224—225° (corr.), obtained by the action of aluminium amalgam on methyl *o*-nitrophthalate, forms pale salmon needles. 2-Methyl-4-quinazoline-5-carboxylic acid (4-hydroxy-2-methylquinazoline-5-carboxylic acid),



m. p. 342° (decomp.), obtained by boiling acetylamino-*o*-phthalimide with potassium hydroxide solution and acidifying the product, crystallises in colourless needles; its *methyl* ester melts at 273—274° (corr.).

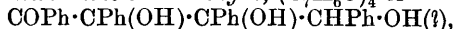
E. G.

Condensation of Mesoxalic Esters with Phenolic Esters.

ALFRED GUYOT and G. ESTÉVA (*Compt. rend.*, 1909, 148, 719—720. Compare this vol., i, 158, 236).—In presence of concentrated sulphuric acid, mesoxalic esters undergo condensation with phenolic ethers, giving a mixture of two products, namely, a substituted phenyltartronic ester and a substituted diphenylmalonic ether. When sulphuric acid and the phenolic ester are present in excess, only the latter is obtained. The following compounds were obtained by condensing methyl or ethyl mesoxalate with anisole and phenetole. Methyl *p*-methoxyphenyltartronate, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})(\text{CO}_2\text{Me})_2$, long needles, m. p. 118°. Methyl *di-p*-methoxymalonate, $\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2(\text{CO}_2\text{Me})_2$, pearly leaflets, m. p. 90°; the *ethyl* ester occurs in brilliant spangles, m. p. 72°. Methyl *p*-ethoxyphenyltartronate, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})(\text{CO}_2\text{Me})_2$, prisms, m. p. 112°. Methyl *di-p*-ethoxyphenylmalonate, $\text{C}(\text{C}_6\text{H}_4\cdot\text{OEt})_2(\text{CO}_2\text{Me})_2$, leaflets, m. p. 118°; the *ethyl* ester occurs in brilliant spangles, m. p. 92.5°.

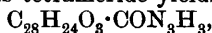
W. O. W.

Chemical Actions of Light. XIII. GIACOMO L. CIAMICIAN and PAUL SILBER (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 216—220. * Compare Abstr., 1908, i, 555).—One hundred grams of benzaldehyde were exposed to the action of light for two years and five months, at the end of which time it was almost completely resinified. It was then found to contain (1) the trimeric benzaldehyde obtained by Mascarelli (Abstr., 1906, i, 962) by the interaction of benzaldehyde and iodoxybenzene under the influence of light; (2) benzoic acid; (3) hydrobenzoin; (4) a tetrameric benzaldehyde, $(\text{C}_7\text{H}_6\text{O})_4$ or



* and *Ber.*, 1909, 42, 1886—1891.

which is a white powder, m. p. 160—170°, and has the normal molecular weight in acetic acid, but gives a value corresponding with the formula $(C_7H_6O)_9$ in benzene; this tetrameride yields a *semicarbazone*,



which forms a white powder, m. p. 232° (compare Abstr., 1903, i, 562).

Dibenzylideneacetone, when exposed to the action of sunlight in alcohol, in which it is mainly suspended, is converted into a resin, which separates from a mixture of ether and light petroleum as an almost white powder, m. p. 125—135°, having the composition $(C_{17}H_{15}O)_2$.

The greater reactivity of *isosafrole* containing a propenyl group compared with safrole containing an allyl group is also evident when these two compounds are exposed to the action of light in presence of a little iodine; the safrole then remains practically unaltered, whilst the *iso*-compound is transformed into a resin from which *diisosafrole* can be separated in small proportion (compare Angeli and Mola, Abstr., 1895, i, 24).

A similar difference is exhibited in the behaviour of the methyl ethers of eugenol and *isoeugenol* in presence of iodine and under the influence of light. The former undergoes no change even after prolonged exposure, but the latter yields a *compound*, crystallising from methyl alcohol in slender needles, m. p. 96°, and having the composition of *diisoeugenol* methyl ether, although apparently not identical with the one described by Széki (Abstr., 1906, i, 660) and by Francesconi and Puxeddu (this vol., i, 226).

Under the influence of sunlight, benzaldehyde condenses with many different compounds (compare Klinger and Standke, Abstr., 1891, 900; Klinger and Kolvenbach, Abstr., 1898, i, 467; Benrath, Abstr., 1906, i, 535). The authors find that benzaldehyde forms condensation products with both safrole and *isosafrole* having the composition $C_7H_6O, C_{10}H_{10}O_2$, the former having m. p. 150—180°, and the latter, m. p. 170—180°.

T. H. P.

Separation of *o*- and *p*-Chlorobenzaldehydes. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 207157).—*o*- and *p*-Chlorobenzaldehydes can be separated by taking advantage of the slight difference in their boiling points: the ortho, b. p. 208°, and the para, b. p. 213°/748 mm. The first fraction when cooled to -20° gives solid *o*-chlorobenzaldehyde (m. p. +11°, and not -4°), whilst the end fraction when similarly refrigerated yields the para-isomeride.

F. M. G. M.

Variations in the Density of Anisaldazine at the Clearing Temperature. F. CONRAT (*Physikal. Zeitsch.*, 1909, 10, 202—206).—The variation of the density of anisaldazine with the temperature in the neighbourhood of the clearing point has been investigated by means of a dilatometer. Whereas the isotropic modification is quite normal in its behaviour, it is found that the anisotropic form shows an abnormally large rate of increase in volume as the clearing temperature is approached. In addition to the sharp change in the density which accompanies the transition from the anisotropic to the

isotropic modification, there is a comparatively small change which takes place before the transition temperature is reached

H. M. D.

Aldehydic Compounds. ANGELO ANGELI and VINCENZO CASTELLANA (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 221—225).—Salicylaldehyde does not give a hydroxamic acid when treated with dihydroxyammonia in presence of alkali, although the corresponding ethoxy-aldehyde readily reacts. Negative results are also given by protocatechualdehyde and its carbonate.

m-Hydroxybenzaldehyde, however, yields *m*-hydroxybenzhydroxamic acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NOH})\cdot\text{OH}$, which separates from ethyl acetate in large crystals, m. p. about 72° , dissolves readily in water, turns red in the air, and gives an intense violet coloration with ferric chloride; dilute sulphuric acid hydrolyses it, yielding hydroxylamine and *m*-hydroxybenzoic acid. It yields a green copper salt. *m*-Hydroxybenzhydroxamic acid is also obtained in quantitative yield from ethyl *m*-hydroxybenzoate by the action of an alcoholic solution of hydroxylamine in presence of sodium ethoxide (compare Jeanrenaud, *Abstr.*, 1889, 870).

The aldehydes of the pyrrole and indole groups, which can be obtained by treating the pyrroles and indoles with chloroform and potassium hydroxide, do not yield hydroxamic acids (compare Angelo and Marchetti, *Abstr.*, 1907, i, 551; this vol., i, 12). But the authors have obtained, by the action of amyl formate on 2-methylindole in presence of sodium ethoxide, a sodium salt of methylindolealdehyde, which they regard as a hydroxymethylene derivative of the constitution $\text{N} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{C}:\text{CH}\cdot\text{OH}$. Analogy is drawn between the aromatic hydroxyaldehydes and certain of the nitroso-indoles, phenols, and naphthols, which must be regarded as oximes, the new arrangement of the molecules being determined by the iminic hydrogen in the case of the indoles, and by the phenolic hydrogen in the case of the phenols and naphthols. The view that a similar rearrangement is produced with the aromatic hydroxyaldehydes, owing to the presence of the hydroxyl hydrogen, is supported by the fact that, when the hydroxyl is converted into alkoxyl, these compounds give hydroxamic acids.

Vanillin does not yield a hydroxamic acid, but *isovanillin* readily does so.

T. H. P.

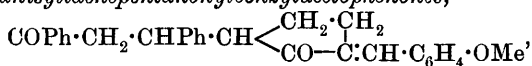
Behaviour of the Compounds $\text{CRPh}\cdot\text{NOH}$ towards Nitrogen Peroxide. GIACOMO PONZIO (*Gazzetta*, 1909, 39, i, 324—326).—When, in compounds of the formula $\text{CRPh}\cdot\text{NOH}$, $\text{R}=\text{Ph}$ or Me , nitrogen peroxide converts them into dinitro-derivatives, whilst when $\text{R}=\text{COPh}$, oxidation to benzil takes place. The present experiments show that when $\text{R}=\text{CH}_2\cdot\text{OH}$, a dinitro-compound is formed, whilst when $\text{R}=\text{CO}_2\text{H}$ a dioxime-peroxide is obtained. In the latter case, analogy with the formation of aliphatic nitrolic acids indicates that benznitrolic acid, $\text{CHPh}\cdot\text{N}_2\text{O}_3$, is an intermediate product.

Oximinophenylacetic acid, $\text{CO}_2\text{H}\cdot\text{CPh}\cdot\text{NOH}$, reacts with nitrogen peroxide in cold ethereal solution, yielding diphenylglyoxime peroxide,

$\begin{matrix} \text{CPh:NO} \\ | \\ \text{CPh:NO} \end{matrix}$. Benzoylcarbinoloxime, $\text{OH}\cdot\text{CH}_2\cdot\text{CPh:NOH}$, yields phenyl-dinitromethane when similarly treated. C. H. D.

Methods for the Preparation of Stereoisomeric Benzylidene-anisylidenecyclopentanones and Similar Unsymmetrical Derivatives of Cyclic Ketones. HANS STOBBE (*Ber.*, 1909, 42, 921—928).—Stereoisomeric unsymmetrical substituted cyclic ketones of the type $\text{CHR}'\cdot\text{C} \begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CO}-\text{C}:\text{CHR}'' \end{smallmatrix}$, where R' and R'' represent two aryl groups, can be synthesised by either of the following methods: (1) A compound of the type of Stobbe and Volland's (*Abstr.*, 1902, i, 472; 1903, i, 115) β -cyclopentanonylbenzylacetophenone is condensed with anisaldehyde, and the resulting anisylidene derivative or derivatives decomposed by distillation under reduced pressure. (2) An aqueous-alcoholic solution of anisaldehyde and benzaldehyde is condensed with cyclopentanone in the presence of 10% sodium hydroxide solution at the ordinary temperature.

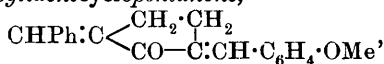
[With ROBERT GEORGI and RICHARD HÄRTEL].—Anisaldehyde condenses with β -cyclopentanonylbenzylacetophenone in the presence of a few drops of sodium hydroxide solution, yielding two stereoisomeric β -anisylidenepentanonylbenzylacetophenones,



termed anisylidene diketones A and B, which can be separated by crystallisation from dilute alcohol, in which the A compound, m. p. 126°, is more readily soluble than the B compound, m. p. 146°. Both compounds are colourless, and form yellow additive compounds with sulphuric acid. When the condensation takes place at 15—20°, only some 10—15% of B is obtained, whereas at 50° this compound is the chief product. The two are stereoisomeric, as they can each be transformed into the other by the following methods: Action of light on the crystals or on their benzene solutions; action of heat or boiling their benzene solutions with a small amount of iodine.

When heated, both diketones are decomposed, and when distilled under 12 mm. pressure yield unaltered substance, benzylidene-anisylidenecyclopentanone and a stereoisomeride, dianisylidenecyclopentanone, and benzylideneacetophenone.

Benzylideneanisylidenecyclopentanone,



is readily soluble in alcohol, from which it separates in yellow lamellæ, m. p. 153°; the *stereoisomeride* crystallises from alcohol, in which it is sparingly soluble, in dark lemon-yellow, felted needles, m. p. 147°. Both compounds combine with bromine or sulphuric acid, and may be transformed each into the other. J. J. S.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. III. EMIL FISCHER (*Ber.*, 1909, 42, 1015—1022. Compare *Abstr.*, 1908, i, 892; this

vol., i, 161).—*p*-Methylcarbonatobenzoyl chloride combines with benzene in presence of aluminium chloride, forming *p*-methylcarbonatobenzophenone, $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_5$, which yields, on hydrolysis, the known *p*-hydroxybenzophenone. In a similar manner, 3:4:5-trihydroxybenzophenone has been obtained from 3:4:5-trimethylcarbonatobenzoyl chloride. This differs from the isomeric alizarin-yellow, and confirms the supposition that alizarin-yellow is 2:3:4-trihydroxybenzophenone; it should be possible to prepare it from pyrogallol-carboxylic acid.

p-Methylcarbonatobenzophenone crystallises in colourless, obliquely-cut, microscopic prisms or needles, m. p. $94-95^\circ$ (corr.), to a colourless liquid; it is hydrolysed to *p*-hydroxybenzophenone, m. p. 135° (corr.), by heating with sodium hydroxide.

3:4:5-Trihydroxybenzophenone, prepared by the interaction of benzene, aluminium chloride and 3:4:5-trimethylcarbonatobenzoyl chloride at 70° , and subsequent hydrolysis, crystallises with H_2O in faintly yellow, thin, glistening plates, but is colourless when anhydrous. It has m. p. $177-178^\circ$ (corr.), reduces silver nitrate and Fehling's solution, and, like alizarin-yellow, dyes with mordants.

Gallacetophenone semicarbazone is a bright yellow, glistening, crystalline powder consisting of microscopic, short, thick prisms or tablets, m. p. 225° (quickly heated) to a red liquid and decomposes at a higher temperature. The so-called monoacetylpyrogallol obtained by Einhorn and Hollandt (Abstr., 1898, i, 577) is shown to be in reality gallacetophenone.

Ethyl 3:4:5-trimethylcarbonatobenzoate, $\text{C}_6\text{H}_2(\text{O}\cdot\text{CO}_2\text{Me})_3\cdot\text{CO}_2\text{Et}$, forms colourless, thin prisms or needles, m. p. $86-87^\circ$ (corr.); on cautious hydrolysis, ethyl gallate, m. p. $154-155^\circ$ (corr.), is obtained.

E. F. A.

Preparation of Alkyl- and Aryl-aminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 205881).—The alkyloxyanthraquinones when heated with primary arylamines, or primary or secondary alkylamines, give rise to aryl- and alkyl-aminoanthraquinone derivatives respectively. The dimethyl or diethyl ethers of quinizarin when heated with *p*-toluidine give rise to quinizarin-green.

1:4-Di-*p*-tolylaminoanthraquinone is similarly obtained by heating with *p*-toluidine at $160-180^\circ$ the methyl ether of 1-nitro-4-hydroxyanthraquinone.

Other instances of this condensation are described, but the products have already been prepared.

F. M. G. M.

Action of Potassium Hydroxide on Borneol, Camphor, and isoBorneol; Racemic Campholic Acid. MARCEL GUERBET (*Compt. rend.*, 1909, 148, 720-723; *J. Pharm. Chim.*, 1909, 29, 321-324. Compare Abstr., 1908, i, 100).—The production of campholic acid by the action of potassium hydroxide on borneol has been described in a previous communication; it is now found that the product of the reaction invariably contains camphor.

Campholic acid, which is obtained from camphor in small yield by Delalande's reaction (*Ann. Chim. Phys.*, 1841, [iii], i, 120), can be

prepared in practically theoretical yield by heating camphor with twice its weight of fused potassium hydroxide at 280–290° in a sealed tube. A small amount of *isocampholic* acid is formed simultaneously. Under the same conditions, *isoborneol* yields a mixture of *r*-borneol, *r*-camphor, and *r-campholic acid*; the latter, which is identical with the racemic acid prepared by mixing equal parts of the *d*- and *l*-acids, crystallises in transparent, hexagonal tablets, m. p. 109°. It is less soluble in alcohol than either of the active acids. The *sodium* salt crystallises with 8H₂O. The *anhydride* has m. p. 66°. The *amide* has m. p. 90°. W. O. W.

Preparation of *iso*Bornyl Esters of Fatty Acids. CHARLES WEIZMANN and THE CLAYTON ANILINE Co. (D.R.-P. 207155).—In the presence of a small proportion of a metallic salt, such as anhydrous zinc chloride, pinene hydrochloride and boiling glacial acetic acid readily condense, giving a yield of about 70% of *isobornyl* acetate, suitable for the production of camphor. Other fatty acids, such as formic and butyric acids, may be employed in this condensation.

F. M. G. M.

Preparation of *iso*Bornyl Esters from Camphene and Monobasic Organic Acids. ALBERT VERLEY, EDOUARD URBAIN, and ANDRÉ FEIGE (D.R.-P. 207156).—Aqueous sulphuric acid (4·5 parts of 60–66% H₂SO₄) is shaken thoroughly at 20–30° with camphene (1 part) and concentrated acetic acid (1 part), and the mixture then allowed to settle into two layers, the upper of which consists of *isobornyl* acetate, with a trace of borneol, whilst the lower, containing the sulphuric and unaltered acetic acids, is employed in subsequent operations. *iso*Bornyl formates, propionates, and butyrates can be prepared similarly.

F. M. G. M.

Fenchyl Derivatives. IWAN L. KONDAKOFF (*J. pr. Chem.*, 1909, [ii], 79, 271–280).—The solid chloride obtained from fenchyl alcohol is regarded as an impure bornyl chloride by Wallach, who doubts the existence of a solid fenchyl chloride corresponding with fenchyl alcohol.

The author, however, by treating the chloride or bromide obtained from *l*-fenchyl alcohol with alcoholic potassium hydroxide, obtains an undecomposable residue, from which the solid chloride or bromide is isolated; this chloride is regarded as a true fenchyl chloride on account of its m. p., 92° (lower than that of bornyl chloride; the preceding bromide also has m. p. 65°, whilst bornyl bromide has m. p. 90°), its inability to yield camphene, and its property of giving, in addition to liquid hydrocarbons, a mixture of fenchyl alcohol and fenchone.

A new solid, *fenchyl chloride*, has been prepared from *l*-fenchyl alcohol. It is purified by fractional distillation and freezing, and has m. p. 22°, b. p. 80–82°/11 mm., D₂₀ 1·004, *n*_D 1·4802, and [*a*]_D²⁰ –8·89°, is not completely changed to fenchene by alcoholic potassium hydroxide, and at 180° yields fenchyl (and *isofenchyl*?) alcohol and a *fenchene*, which has b. p. 155–160°, D_{18·5} 0·869, *n*_D 1·468802, and [*a*]_D –29·49°. The paper concludes with a reply to Wallach's contention that *isofenchyl* alcohol, which yields *isofenchone* by oxidation, must be a secondary and not a tertiary alcohol. C. S.

Constituents of Essential Oils. *enol*-Camphenilanaldehyde Acetate and Further Derivatives of Camphenilanaldehyde. Production of Terpinolene by the Inversion of Carvenene (Terpinene?). FRIEDRICH W. SEMMLER (*Ber.*, 1909, 42, 962—966. Compare this vol., i, 239; Bredt, *Abstr.*, 1900, i, 134).—It is shown that the camphene nucleus remains unchanged in the formation of camphenilanaldehyde from camphene, because camphenilanaldehyde when treated with acetic anhydride and sodium acetate yields *enol-camphenilanaldehyde acetate*, $C_9H_{14}\cdot CH\cdot OAc$, a colourless oil, b. p. 113—116°/10 mm., D_{20} 1.0125, n_D 1.4816, which, when oxidised by ozone, yields camphenilone. The acetate is reduced by sodium and alcohol, yielding *camphenityl alcohol*, $C_{10}H_{17}\cdot OH$, a colourless solid, m. p. about 58—59°, b. p. 105—106°/10 mm.; the same compound is produced by reducing the aldehyde in the same manner; it is converted by phosphorus pentachloride into *camphenityl chloride*, $C_{10}H_{17}Cl$, a colourless liquid, b. p. 83—85°/10 mm., D_{20} 0.9909, n_D 1.4862, which, when reduced with sodium and alcohol, yields camphene together with a small quantity of *isocamphene*.

Inversion of Carvenene.—Carvenene prepared from carvenone does not yield any terpinolene tetrabromide when treated with bromine. When inverted with alcoholic sulphuric acid, it yields *isocarvene* (compare this vol., i, 171), which, when treated with bromine, yields a considerable quantity of terpinolene tetrabromide. If pure *isocarvenene* ($\Delta^{1,4}$ -dihydrocymene) should not yield terpinene nitrosite, we have the transition: terpinolene \longleftrightarrow carvenene. W. H. G.

Essential Oils. HEINRICH HAENSEL (*Haensel's Bericht*, October—March, 1909. Compare this vol., i, 111).—Oil from the leaves of the *marsh mallow* (*Althaea officinalis*) has been obtained for the first time; yield 0.022%, D_{20} 0.9209, acid number 88.7, saponification number 122.6, ester number 33.9; it appears to contain valeric and palmitic acids as constituents. *Angelica-root oil* (*loc. cit.*), yield 0.22%, D_{15} 0.8580, consists chiefly of terpenes resembling phellandrene. *Cardamom oil*, freed from terpene, has D 0.948 and $a_D + 45.93^\circ$; the terpene constituent separated therefrom has D 0.846, $a_D - 1.76^\circ$. *Lemon oil* from Barcelona is colourless and has a faint aroma, D_{20} 0.8524, $a_D^{21} + 35.65^\circ$; when redistilled and dried $a_D^{17} + 21.16^\circ$, $a_D^{20} + 20.71$ (calc.); it apparently is largely adulterated. *Cubeb oil*, when obtained terpene-free, has D_{15} 0.9428, $a_D^{20} - 10.05^\circ$; the terpenes obtained therefrom have D_{15} 0.8662, $a_D^{20} - 15.45^\circ$. *Pine oil* usually contains such a large proportion of terpene that it requires highly rectified spirit for its solution; to avoid this it has now been prepared terpene-free, and has D 0.9384, $a_D - 15.56^\circ$, ester content 39.2%, compared with the ordinary oil D 0.8740, $a_D - 51.24^\circ$, ester content 9.8%. *Ginster oil* (*Abstr.*, 1903, i, 187), from *Spartium scoparium*, yield 0.031%, is a brown, strongly acid-smelling substance, D_{15} 0.8673, which partly solidifies at 0°. This oil gave an acid number 58.6, saponification number 88, and an ester number 29.4; it contained furfuraldehyde, and when hydrolysed gave palmitic acid and a white, solid paraffin, which separated from alcohol in needles, m. p. 48—49°. *Guaiacum-wood oil*, when shaken with ether and recrystallised from alcohol,

yields guaiol, which gives dihydroguaiene, b. p. $12^{\circ}/11$ mm., when warmed with zinc dust. Guaiol methyl ether has b. p. $141-143^{\circ}/9$ mm. *Hazel-nut-leaf oil*, prepared from the dried leaves of *Corylus Avellana*, yield 0.0425%, is a light brown, acid-reacting substance, only liquid when warm. It has a remarkably persistent aromatic odour, f. p. about 30° , D^{25} 0.8844, acid number 60.4, saponification number 85, ester number 24.6, after acetylation 158. This oil seems to contain a considerable quantity of free acids and alcohols, and when hydrolysed gave palmitic acid. *Oil from Vitex agnus castus* (sensitive plant), procured from Turkey, was obtained by steam distilling the leaves; yield 0.36%. It is a reddish-brown liquid possessing a strong odour resembling camphor; D^{20} 0.8993, acid number 5, saponification number 25.8, ester number 20.8, after acetylation 56.5. When saponified and distilled, palmitic acid, terpenes, cineol, and other substances were obtained. *Oil of cloves*, from Seychelles, had D^{20} 1.031, D^{15} 1.0349, $\alpha_D - 0.49^{\circ}$, and contained 80% eugenol, but no furfural. The terpene-free oil is optically inactive, has D^{15} 1.0695, and contains 86.12% eugenol. *Italian peppermint oil*, when freed from terpene, has been found to have somewhat different physical properties from that previously given (*loc. cit.*), namely, D^{20} 0.9014, $\alpha_D - 26.29^{\circ}$, ester number 15.0, after acetylation 185.5, content of esterified menthol 5.30%, content of free menthol 55.86%. The isolated terpenes have D^{20} 0.862 and $\alpha_D - 12.75^{\circ}$. *Sweet-orange oil* is found to vary somewhat considerably in physical properties according to the district in which the fruit is grown. *Bitter-orange oil*, when terpene-free, has D 0.9038, $\alpha_D^{18} + 11.80^{\circ}$; the isolated terpene portion has D 0.8489 and $\alpha_D^{17} + 96.18^{\circ}$. When prepared from unripe fruit this terpene-free oil has D 0.9179 and $\alpha_D + 9.63^{\circ}$. *Rosemary oil*, when purified and when freed from terpene, has respectively D^{15} 0.9090 and 0.9376, $\alpha_D + 5.03^{\circ}$ and $+ 7.35^{\circ}$, ester number 8.5 and 9.0, after acetylation 37.9 and 53.6, content of esterified borneol 2.97% and 3.15%, content of free borneol 10.92% and 16.27%, and the terpene-free oil boils at a higher temperature than oil which is only purified. Terpene-free *Star anise oil* has D^{22} 0.9856, $\alpha_D^{20} + 0.14^{\circ}$, freezing point $+ 18.5^{\circ}$.
J. V. E.

Essential Oils. SCHIMMEL & Co. (*Bericht*, April, 1909. Compare this vol., i, 112).—*Andropogon oil*, No. 2, obtained from a different plant to that giving the oil previously described (*loc. cit.*), was pale yellow, having an odour resembling aliphatic aldehydes and geraniol, D^{15} 0.9961, $\alpha_D - 2^{\circ}$, n_D^{20} 1.51236, acid number 3.6, ester number 7.3. It probably contains a small quantity of decaldehyde. *Oil of Artemisia lavandulaefolia*, obtained from wild Java plants, has D^{26} 0.924, $\alpha_D - 7.5^{\circ}$, and, when cooled, partly solidifies to a crystalline substance, $C_{12}H_{14}O_2(l)$. *Basilicum oil* (Abstr., 1907, i, 66), from *Ocimum minimum*, grown in the south of France, was identical in some respects with the oil from *Ocimum basilicum*, but differs therefrom in chemical composition. It contains 14% eugenol and probably linalool; D^{15} 0.9102, $\alpha_D - 11.97^{\circ}$, acid number 5.3, ester number 12.5, phenol content 14%. *Lemon-scented bay oil*, obtained from *Pimenta acris citrifolia*, is found to have D^{25} 0.882, $\alpha_D - 0.6^{\circ}$, and probably

65% citral. Leaves from the Isle of Tortola yield 1.11% of a pale yellow oil possessing a strong odour of lemon, and having D_{16}^{27} 0.8937, α_D -0.16° , citral content 44%, phenol content 10%. *Calmus oil*.—Two samples obtained from Java were yellow, possessing a faint calmus odour; the constants were: (I) D^{15} 1.0783, α_D $+0.9^\circ$, n_D^{20} 1.55043, ester number 12; (II) D^{15} 1.0771, α_D $+0.85^\circ$, n_D^{20} 1.55065, thus showing a considerable difference from ordinary calmus oil. A detailed account is given of the preparation of *Cananga oil* from the expressed plant juice. The composition of this oil seems to vary with the district in which the tree is grown and also with the climate. The difference between *Cananga oil* and *Ylang-ylang oil* lies in the fact that the former contains less ester, less alcohol, and more sesquiterpene than the latter. Under certain conditions of distillation it is considered possible to obtain the more valuable *Ylang-ylang oil* from cananga sap instead of *Cananga oil*.

Copaiba Balsam Oil.—It has been shown that several so-called Copaiba oils are mixtures of African Copaiba oil and Gurjun balsam oil. The constants for this oil are now given as D^{15} 0.9692, α_D -41.33° , acid number 60.75, saponification value (cold) 64.72. By means of steam about 62.5% of a yellow oil is separated, D^{15} 0.9180, α_D -78.8° , acid number 3.14, ester number 0.

Red-fir oil, obtained from the fresh needles and young twigs of small trees of *Pinus Douglasii taxifolia*, is a yellowish-green substance (yield 0.8—1%) having an odour resembling limonene; D^{23} 0.8680, α_D -62.5° , acid number 0, saponification number 86.6, after acetylation 92.1, free borneol content 27.18%. This oil contains no aldehyde, and the lower fractions give no nitrosochloride; the major fraction, b. p. 161—169°, contains camphene (*Pharm. Rev.*, 1908, 26, 326).

African Elemi oil is pale yellow to yellowish-green and moderately viscous. One sample gave 0.6% ash, acid number 55.3, saponification value 71.9, and the yield of ethereal oil was 8.1%, which contained considerable quantities of phellandrene, and had D^{15} 0.8686, α_D $+50.5^\circ$. A second sample gave 0.53% ash, acid number 37.8, saponification value 46.2, and contained 4.4% of ethereal oil. A sample of *Uganda Elemi oil* from *Canarium Schweinfurthii* was colourless to pale yellow; it contained 0.3% ash, and had acid number 29.4, saponification value 44.8, and when steam distilled gave 11.2% of a pale yellow oil having D^{15} 0.8451, α_D $+79.33^\circ$, and contained much phellandrene (*Bull. Imp. Inst.*, 1908, 6, 252).

Lemon oil from Messina is found to begin to boil at 175° and have the following limiting values, D^{15} 0.856 to 0.861, the rotation varies somewhat with the district and ripeness of the fruit, but lies between $+58^\circ$ and $+66^\circ$ at 20°, citral content 4 to 7.5%. *Bergamot oil* from Messina has the limiting values D^{15} 0.880 to 0.887, α_D $+7^\circ$ to $+25^\circ$, acid content calculated as acetic acid 0.15 to 0.2%, and with old oil up to 0.4%, ester content 33 to 44%, commences to boil at 180° or 72°/20 mm. (Berté and Romeo, Messina). *Sweet orange oil* from Messina (compare Abstr., 1907, i, 66) has the following limiting values, D^{15} 0.847 to 0.852, α_D^{20} $+96^\circ$ to 98° , α_D of the first 50% of distillate should be at least 1.5° higher than that of the

original oil, b. p. 176° to 177° or 79° to $81^{\circ}/20$ mm. *Bitter orange oil*, D^{15} 0.852 to 0.856, n_D^{20} $+88^{\circ}$ to 96° , and α_D of the first 50% of distillate should be at least 3° higher than that of the original oil. *Mandarin oil*, D^{15} 0.854 to 0.858, α_D $+67^{\circ}$ to 73° , and α_D of first 50% should average 3° higher than that of the original oil.

A sample of *Eucalyptus oil* distilled in Java had D^{20} 0.996, α_D $+4.3^{\circ}$, and commenced to boil at 150 — 200° , when 77% distilled; 200 — 240° , 16% distilled over; it appears to consist chiefly of cineol. Two other samples from Java: (I) (probably from *E. crebra*) contained little cineol, some phellandrene and cuminaldehyde; the constants are D^{15} 0.9036, α_D -20.93° . (II) (Probably from *E. piperita*) was a golden-yellow oil having D^{15} 0.8974, α_D -28.43° , and contained scarcely any cineol, but cuminaldehyde and a considerable quantity of phellandrene (*Jar. Land. Neder. Ind.*, 1907, 66). Oil from South Africa had $D^{15.5}$ 0.9227, α_D $+3^{\circ}17'$, and contained a considerable quantity of cineol, but no phellandrene.

Pine oil (Oleum templinum) has been definitely shown to contain borneol; the constants given for this oil are D^{15} 0.8556, n_D^{20} 1.47246, α_D -76.5° , ester number 5.3. Freed from terpene and saponified, the alcohols obtained had b. p. 190 — 225° ; the chief product had b. p. 205 — 215° , and consisted chiefly of borneol. In addition to this constituent an alcohol of b. p. 190 — 197° , D^{15} 0.9013, is present together with a sesquiterpene. *Siberian pine oil*, after heating with sulphuric acid and acetic acid to 60° and then saponifying with alcoholic potash, yields solid inactive camphene (compare *Chem. Zeit.*, 1908, 32, 922). *Australian pine-needle oil* from *Callitris glauca*, yield 0.6%, contains 12—16% bornyl acetate and geranyl acetate: by distilling the wood; a thick oil was obtained which contained a new phenol, *callitrol*.

Methyl sulphide has been detected in Réunion *Geranium oil* and also in African geranium oil. The sample of *Cochin wood oil* examined was brown with a green fluorescence; it had D^{15} 0.9633, α_D -37.5° , n_D^{20} 1.51236, acid number 7.8, ester number, 2.9. When steam distilled, 69.9% of a lemon-yellow oil was obtained, having D^{15} 0.9248, α_D -61.8° , n_D^{20} 1.50252. Acid number 0, ester number 1.6. *Japanese star anise oil*, from *Illicium religiosum*, differs from the Chinese oil by not containing anethole and only a small quantity of safrole; it also contains cineol and probably linalool. The constants found were D^{15} 0.9848, α_D -0.8° , acid number 1.8, ester number 12.9.

Kobuschii oil, from young twigs of Japanese plants, differs from the oil previously described (*Abstr.*, 1908, i, 666); it was pale yellow with an odour of citral, D^{15} 0.892, α_D $+6.13^{\circ}$, acid number 4.3, saponification value 19.1, after acetylation 56.48. It contained chiefly methylchavicol, together with citral, eugenol, and cineol. *Curled mint oil*, from the dry Hungarian plant, is similar in composition to the American and German product, but differs therefrom by its high carvone content, 72%, and its greater solubility. *Lovage root oil*—two fresh samples were examined: (I) one year roots, yield 0.22%, D^{15} 1.0310, α_D $+1.5^{\circ}$, n_D^{20} 1.55148, acid number 5.8, ester number 223.5. (II) Two year roots, yield 0.55%, D^{15} 1.0326, α_D $+0.75^{\circ}$, n_D 1.54944, acid number 6.1, ester number 224.5, after acetylation 227.8. *Linoloe oil*, when saponified and steam distilled, yields an unusually light oil, D^{15} 0.7727,

$\alpha_D + 1.75^\circ$, b. p. $42^\circ/18$ mm. This oil apparently contains isomeric octylenes and nonylenes, and an olefine of the formula $C_{10}H_{16}$ probably myrcene.

Matico oil, from the leaves of *Piper mandoni*, yields about 0.8% of a brown, balsam-smelling oil, D^{15}_D 0.9360, $\alpha_D + 1.08^\circ$, n^{20}_D 1.49704, acid number 1.8, ester number 5.1, after acetylation 46.7 (*Pharm. Zentralh.*, 1908, 49, 974). Two samples of *Myrtle oil* from Corsica have been examined: D^{15}_D 0.8828 and 0.8868, α_D 26.75° and 23.25° , n^{20}_D 1.46644 and 1.46911, acid number 1.0 and 1.6, ester number 13.0 and 17.1, after acetylation 30.2 and 38.5. Two samples from *Syria* had D^{15}_D 0.8930 and 0.8985, $\alpha_D + 14.5^\circ$ and $+11^\circ$, n^{20}_D — and 1.46417, acid number 1.9 and —, ester number 20.3 and 26.6, after acetylation 72.0 and 70.7. One sample from *Asia Minor* had D^{15}_D 0.9138, $\alpha_D + 10.7^\circ$, n^{20}_D 1.46704, acid number 1.5, ester number 39.4, after acetylation, 94.9. Two samples of *Sage oil* from Corfu were found to have a different odour from the oil obtained from *Salvia officinalis* (this vol., i, 39); they were almost colourless, and had respectively D^{15}_D 0.9153 and 0.9132, $\alpha_D - 15.25^\circ$ and -15.08° , acid number 0.5 and 0.5, ester number 9.0 and 10.6. *Mexican Schinus oil*, differing from that previously described (Abstr., 1908, i, 666), has been studied; it was pale yellow, having D^{15}_D 0.8492, $\alpha_D + 56.45^\circ$, n^{20}_D 1.47616, and contained a considerable quantity of phellandrene. *Canadian Snake root oil*, from *Asarum canadense* (compare Abstr., 1908, i, 666), had the following constants: (I) Roots with fibre, D^{15}_D 0.9519, $\alpha_D - 10.5^\circ$, n^{20}_D 1.49987, acid number 4.7, ester number 74.7, after acetylation 125.0. (II) Roots without fibre, D^{15}_D 0.9520, $\alpha_D - 10.7^\circ$, n^{20}_D 1.48863, acid number 3.1, ester number 86.1, after acetylation 125.8. Flowers of *Tagetes patula* (*loc. cit.*) when fresh yield 0.08%, when dried 0.57%, of a brownish-yellow oil having D^{15}_D 0.8925, $\alpha_D - 9^\circ$, n^{20}_D 1.49938, acid number 6.4, ester number 10.6. The stalks and leaves when fresh or dry give 0.07% or 0.218% of a similar oil, having D^{15}_D 0.9034, $\alpha_D + 1.25^\circ$, n^{20}_D 1.49938, acid number 14, ester number 12.4. Further data for *Tetranthera oil* are given: (I) from the bark, D^{15}_D 0.9062, $\alpha_D + 14^\circ$, n^{20}_D 1.46595, ester number after acetylation 230.2; (II) from the leaves, D^{15}_D 0.8990, $\alpha_D - 12^\circ$, n^{20}_D 1.46426; (III) from the fruit, D^{15}_D 0.8932, $\alpha_D + 6.13^\circ$, n^{20}_D 1.48141, and an aldehyde content of 85%. *Red cedar oil*, from dried leaves of *Thuja plicata* (*loc. cit.*), yield 1.32%, is pale yellow with a pungent thujone odour, D^{15}_D 0.9056, $\alpha_D + 5.07^\circ$, n^{20}_D 1.45721, acid number 0.8, ester number 16.9.

The following are described for the first time. *Oil of Barosma pulchellum*, obtained from the leaves, yield 3% of a golden-yellow oil with a decided unpleasant odour. It had D^{15}_D 0.8830, $\alpha_D + 8.51^\circ$, n^{20}_D 1.45771, acid number 18.5, ester number 27.2, after acetylation 237.0. The unpleasant smelling constituent is a pungent narcotic base, which has b. p. $130-140^\circ/5$ mm., and in addition this oil contains citronellal and methylheptenone. *Oil from Satureja macrostema* is a pale yellow substance having an odour resembling mint, and D^{15}_D 0.9182, $\alpha_D + 6.85^\circ$, n^{20}_D 1.46852, acid number 15.6, ester number 10.3, after acetylation 37.9, soluble in all proportions of 90% alcohol. *Oil from Mexican Marsh Cypress (Taxodium mexicanum)* is light brown, odour resembling turpentine oil, D^{15}_D 0.8685, $\alpha_D - 10.33^\circ$,

n_D^{20} 1.46931, acid number 0.5, ester number 5.7. *Oil of Artemisia Herba-alba, var. densiflora* Bois (*Chieh Oil*) from Egypt.—The plant was steam distilled and gave 1.6% yield of a yellow oil possessing a decided thujone odour, D^{15} 0.9192, α_D -5.33° , n_D^{20} 1.45611, acid number 1.5, ester number 11.0, after acetylation 40.7 (compare Abstr., 1904, i, 605). J. V. E.

Solubility of Kauri Copal. CHARLES COFFIGNIER (*Bull. Soc. chim.*, 1909, [iv], 5, 289—296).—Four grades of Kauri copal are recognised commercially, for which the author gives the following data :

	Kauri blonde.	Kauri brune.	Kauri busch.	Kauri busch récolté.
D	1.036/17°	1.053/9°	1.030/17°	1.038/15°
M. p.	165° (softening at 175°)	183° (softening at 90°)	150° (softening at 60°)	125° (softening at 50°)
Acid number	70.9	78.8	83.1	81.8
Kottstorfer's index ...	73.0	89.7	78.5	87.0

The following table gives the % of matter insoluble in the boiling solvent :

Ethyl alcohol	6.60	35.80	12.30	4.20
Methyl „	46.90	61.90	47.30	34.20
Amyl „	0.0	0.0	0.0	0.0
Ether	61.80	60.70	55.10	51.10
Chloroform	54.40	58.70	50.70	43.40
Benzene	66.70	70.60	61.70	57.60
Acetone	8.90	38.70	20.70	11.30
Turpentine	77.50	73.60	72.90	63.0
Benzaldehyde.....	0.0	0.0	0.0	0.0
Aniline	0.0	0.0	0.0	0.0
Amyl acetate	0.0	2.0	0.0	0.0
Carbon tetrachloride...	81.10	77.3	71.90	63.0

C. S.

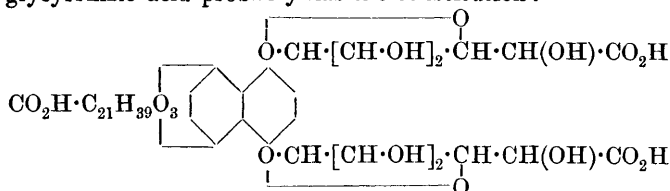
A Liquid Resin. WILHELM FAHRION (*Zeitsch. angew. Chem.*, 1909, 22, 582—583).—A liquid resin, *Tall oil*, has been obtained by Larsson as a by-product in the preparation of cellulose from Swedish pine wood by the soda process (*Svensk. Kem. Tidskr.*, 1905, 148). It is a dark brown, limpid liquid, and does not solidify at -20° . It has b. p. $270^\circ/40$ mm., D^{15} 0.997, acid number 163, iodine number 118, and hydrolysis number 179. The oil contains neutral substances, and when its alcoholic solution is neutralised, a precipitate is formed. These neutral substances are removed when the solution in 50% aqueous alcohol is shaken with light petroleum. The amount of such neutral substance is 9.4%, and on treatment with alcoholic potassium hydroxide a portion is hydrolysed to acids, but the greater portion cannot be hydrolysed. The composition of the resin is :—resin acids 85.2, oxy-acids 4.6, hydrolysable neutral compounds 2.9, non-hydrolysable 6.5%.

Whereas the abietic acids of ordinary colophony cannot be esterified by means of alcohol and sulphuric acid, it is shown that certain of the acids of tall oil are readily esterified. A liquid *ester*, $C_{19}H_{29} \cdot CO_2Et$,

has been obtained with a hydrolytic number 186·7, instead of 169·7. The resin acid obtained from this ester is also liquid, and has a molecular weight 312·5. The acids which are not esterified are solid; they correspond exactly with a pale colophony, and give the Storch-Morawski reaction.

J. J. S.

Glycyrrhizin. ALEXANDER TSCHIRCH and S. GAUCHMANN (*Arch. Pharm.*, 1909, 247, 121—123. Compare Abstr., 1908, i, 898; Tschirch and Cederberg, Abstr., 1907, i, 545).—The formation of naphthalene when glycyrrhizic acid is distilled with zinc dust has been proved definitely. It is also found that phthalic acid is produced when glycyrrhizic acid is oxidised with potassium permanganate. From these results, and those obtained previously, the conclusion is drawn that glycyrrhizic acid probably has the constitution:



W. H. G.

Sicilian Aloes. G. CONDÒ-VISSICCHIO (*Arch. Pharm.*, 1909, 247, 81—95).—The native aloes of Sicily belong to the species *Aloe vulgaris*, and contain a hitherto unknown aloin, which it is proposed to designate *sicaloin*. It is considered probable, therefore, that the different properties of many of the aloins are due, not only to the different methods of preparation of the drug, but also to the conditions under which the plant grows. The sap of the Sicilian aloes does not contain emodin, but this substance is formed slowly when the sap is exposed to the air; the change is probably brought about by the action of oxydases.

Sicaloin, $\text{C}_{15}\text{H}_{20}\text{O}_7 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, crystallises in white prisms; it loses $1\text{H}_2\text{O}$ over sulphuric acid, decomposes slowly at 110° , and does not give Schonteten's or Bornträger's reaction. Estimations by Zeisel's method show that the molecule of sicaloin contains one methoxy-group.

W. H. G.

Picrotoxin. FRANCESCO ANGELICO (*Gazzetta*, 1909, 39, i, 296—303. Compare Abstr., 1907, i, 332).—Bromopicrotoxinin and the corresponding acid are stable towards permanganate, whilst picrotoxinin yields a complex mixture.

The oxidation of the acid obtained by oxidising bromopicrotoxin with permanganate with a boiling solution of chromic acid leads to the formation of *bromopicrotoxic acid*, $\text{C}_{15}\text{H}_{15}\text{O}_7\text{Br} \cdot \frac{1}{2}\text{H}_2\text{O}$, m. p. 180° (decomp.), $[\alpha]_D^{25} - 96\cdot38^\circ$. Alkalis convert it into a mixture of products, a solution of which gives the reactions of an aromatic *o*-dihydroxy-derivative. When baryta water is used, two substances may be isolated. One of these crystallises from water in small, white

needles, m. p. 250° , and has the composition $C_{14}H_{15}O_7Br$. It may be called *bromopicrotoxinic acid*. The second product is *hydroxypicrotoxinic acid*, $C_{14}H_5O_7 \cdot OH$, forming large, white prisms, m. p. 270° (decomp.).

Cold saturated barium hydroxide solution converts picrotoxinin into a *barium salt*, $C_{18}H_{16}O_7Ba$, the acid from which has only been obtained in an oily form.

The oxidation products of picrotin contain two acids, α -*picrotinic*, m. p. 245° (decomp.), not yet analysed, and β -*picrotinic*, $C_{11}H_{14}O_5$, white leaflets, m. p. 254° , subliming unchanged at 330° . The *acetyl* derivative forms white crystals, m. p. 220° . C. H. D.

Bile Pigments: Bilirubin, Biliverdin, and their Fission Products. WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1909, 59, 63—95).—Bilirubin has the formula $C_{32}H_{36}O_6N_4$. Under certain definite conditions it is transformed into a green colouring matter of the composition $(C_{16}H_{18}O_4N_2)_x$, soluble in alcohol (biliverdin), but in the presence of excess of an alkali carbonate and atmospheric oxygen it is, in part, decomposed further, even at 10° , and ether-soluble acids, including hæmatic acid, are formed. By warming with sodium hydroxide, especially when a little oxygen (one atomic proportion) is supplied by an oxidising agent, 40% of the pigment is transformed into ether-soluble acids, half being hæmatic acid; this behaviour is very different from that of hæmatin, which is stable under the conditions mentioned. A relationship between bilirubin and the indigoid colouring matters prepared by Friedländer, is suggested. G. B.

Studies in the Coumaran Group. II. STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1909, 42, 901—910. Compare Abstr., 1908, i, 442).—Ethyl chloroacetate reacts as easily with orcinol as with resorcinol (compare Hantzsch, Abstr., 1887, 282) in the presence of sodium ethoxide to form *ethyl 5-hydroxy-2:3-dimethylcoumarilate*, $OH \cdot C_6H_2Me \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CMe \end{smallmatrix} \geq C \cdot CO_2Et$, which crystallises in white needles, m. p. 212° . This constitution is held to be the more probable, although it might be the 2:5-dimethylcoumarilate. This ester, on methylation with methyl sulphate and potassium hydroxide, yields *ethyl 5-methoxy-2:3-dimethylcoumarilate*, $C_{14}H_{16}O_4$, which crystallises from alcohol in needles, m. p. 115 — 116° , and, on hydrolysis with potassium hydroxide, yields *5-methoxy-2:3-dimethylcoumarilic acid*, $C_{12}H_{12}O_4$, forming white needles, m. p. 215° (decomp.); its *potassium salt* is difficultly soluble.

When the acid is heated in a retort, there is a vigorous evolution of carbon dioxide, and the corresponding coumarone distils over; it can be freed from any unchanged acid by distillation in a current of steam.

5-Methoxy-2:3-dimethylcoumarone, $OMe \cdot C_6H_2Me \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CMe \end{smallmatrix} \geq CH$, crystallises from dilute alcohol in glistening, white leaflets, m. p. 61 — 62° .

Pæonol and ethyl bromoacetate in the presence of sodium ethoxide condense after twelve hours' heating at 100° to form *ethyl 2-acetyl-5-methoxyphenoxyacetate*, $OMe \cdot C_6H_3Ac \cdot O \cdot CH_2 \cdot CO_2Et$, which forms leaflets, m. p. 78° . The *acid*, $C_{11}H_{12}O_5 \cdot H_2O$, prepared by hydrolysing the

mixture from the phenol and ethyl bromoacetate reaction, forms stout crystals, m. p. 132°. On digestion of this acid with acetic anhydride and sodium acetate, a good yield of 5-methoxy-2-methylcoumarone (*loc. cit.*) is obtained. This method, due to Rössing (Abstr., 1885, 388), is a general one, and has been used frequently in this work.

2-Acetyl-5-ethoxyphenoxyacetic acid, $C_{12}H_{14}O_5$, prepared from ethyl ether of resacetophenone and ethyl bromoacetate, forms crystals, m. p. 150°, and the 5-ethoxy-2-methylcoumarone, $C_{11}H_{12}O_3$, prepared from it by the acetic anhydride method forms leaflets, m. p. 51–52°, b. p. 255°/719 mm.

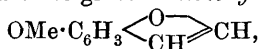
2-Propionyl-5-ethoxyphenoxyacetic acid, $C_{13}H_{16}O_5$, from the ethyl ether of propionylresorcinol, forms white needles, m. p. 125–126°, and the 5-ethoxy-2-ethylcoumarone, $C_{12}H_{14}O_3$, derived from it crystallises in white leaflets, m. p. 66–67°.

Condensation of ethyl bromoacetate and 2-acetyl-1-naphthol leads to the formation of 2-acetyl-1-naphthoxyacetic acid, $C_{14}H_{12}O_4$, which separates from alcohol in leaflets, m. p. 130°. The acetic anhydride method is a particularly good one for the preparation of 2-methyl- α -naphthafuran (compare Stoermer, Abstr., 1900, i, 654).

Condensation of ethyl chloroacetate and phloroglucinol and subsequent methylation gives a poor yield of ethyl 3:5-dimethoxy-2-methylcoumarilate, $C_6H_2(OMe)_2 \begin{smallmatrix} \diagup O \diagdown \\ CMe_6 \end{smallmatrix} C \cdot CO_2Et$. It is much better to use the dimethyl ether of phloroacetophenone and ethyl bromoacetate. It crystallises in white needles, m. p. 133–134°. The acid, $C_{12}H_{12}O_5$, obtained by the hydrolysis of the ester by alcoholic potassium hydroxide forms rosettes of needles from alcohol, m. p. 242° (decomp.). 3:5-Dimethoxy-2-methylcoumarone, $C_{11}H_{12}O_3$, forms prisms, m. p. 39°, b. p. 283°/714 mm. Unlike 5-methoxy-2-methylcoumarone, it is odourless; successful reduction to the corresponding coumaran has not yet been accomplished.

W. R.

Coumarone Group. H. DUMONT and STANISLAUS VON KOSTANECKI (*Ber.*, 1909, 42, 911–915. Compare preceding abstract).—Condensation of *p*-methoxysalicylaldehyde and ethyl bromoacetate in the presence of sodium ethoxide gives ethyl 5-methoxy-2-aldehydophenoxyacetate, $OMe \cdot C_6H_3(CHO) \cdot O \cdot CH_2 \cdot CO_2Et$, which crystallises from dilute alcohol in silky needles, m. p. 68–69°. The free acid, $C_{10}H_{10}O_5$, crystallises in needles, m. p. 144°, and on treatment with acetic anhydride and sodium acetate gives 5-methoxycoumarone,



in good yield. It is a colourless oil, b. p. 226°/706 mm., and has an odour resembling *o*-hydroxyacetophenone.

p-Ethoxysalicylaldehyde, $C_9H_{10}O_3$, prepared from resorcyaldehyde, potassium hydroxide, and ethyl iodide, forms long, white needles, m. p. 35°. It yields the following compounds: 5-ethoxy-2-aldehydophenoxyacetic acid, $C_{11}H_{12}O_5$, crystallising in needles from alcohol, m. p. 189°; its ethyl ester, $C_{13}H_{16}O_5$, glistening leaflets, m. p. 90°; and 5-ethoxycoumarone, $C_{10}H_{10}O_3$, leaflets, m. p. 10°, b. p. 238°/700 mm.

W. R.

Action of Aluminium Chloride on Diphenyl Disulphide and the Thiocresols, and the Action of Sulphuric Acid on Thianthren. J. J. B. DEUSS (*Rec. trav. chim.*, 1909, 28, 136—141).—When diphenyl disulphide dissolved in dry light petroleum is treated with aluminium chloride and the product heated to boiling for several hours, hydrogen chloride and sulphide are evolved, and about 50% of the theoretical quantity of thianthren together with some thiophenol are formed. Thus a better yield of thianthren is obtained than when thiophenol is used (compare Abstr., 1908, i, 530). On similarly treating light petroleum solutions of *o*- and *p*-thiocresols, prepared from the toluidines by Bourgeois' method (Abstr., 1900, i, 163), with aluminium chloride, hydrogen sulphide is evolved and the corresponding ditolyl sulphides are produced. *m*-Thiocresol is not attacked, and in no case could a methylthianthren be obtained. The difference in the behaviour of *m*-thiocresol from that of the ortho- and para-compounds is probably to be explained by the formation of an additive compound of aluminium chloride with the former compound (compare Boeseken, Abstr., 1905, i, 424). In fact, when finely powdered aluminium chloride is added to a solution of *o*- or *p*-thiocresol in carbon disulphide, the thiocresol is recovered unchanged on evaporation of the solvent, whilst with *m*-thiocresol a homogeneous, black residue is obtained, having the composition $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SH} \cdot \text{AlCl}_3$.

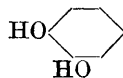
Genvresse (Abstr., 1897, i, 240, 514), by treating thianthren with sulphuric acid containing 30% of sulphur trioxide, obtained a red colouring matter. The latter is better prepared by heating thianthren on a water-bath for eight days (and nights) with ordinary sulphuric acid. The colouring matter is soluble in dilute sulphuric acid, but precipitated by barium carbonate. A small quantity of *thianthren-disulphonic acid*, $\text{C}_{12}\text{H}_6\text{S}_2(\text{SO}_3\text{H})_2$, is also formed, of which the *potassium* salt forms white, crystalline crusts. The latter when treated with phosphorus pentachloride gives an insoluble product.

During the course of the sulphonation, a sublimate of Krafft and Lyons' thianthren disulphoxide is produced on the neck of the flask.

E. H.

Syntheses in the Adrenaline Series. CARL MANNICH and JACOB SOHN (*Chem. Zentr.*, 1909, i, 923—924; from *Apoth. Zeit.*, 1909, 24, 60—61).—By manipulative improvements on the method employed by Barger and Jowett (*Trans.*, 1905, 87, 967) and by Pauly and Neukam (this vol., i, 96), the authors have obtained the pure methylene ether of adrenaline, m. p. 81°, b. p. 189—192°/14 mm., and also *adrenaline dimethyl ether*, m. p. 64—65°; the *hydrochloride* of the latter base has m. p. 178—179°. By the addition of two bromine atoms to methylisoeugenole and subsequent replacement of one bromine atom, the bromohydrin, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CH}(\text{OH}) \cdot \text{CHMeBr}$, m. p. 78°, is

obtained, which, with methylamine, yields *β -methyladrenaline dimethyl ether*, m. p. 63°. By boiling with hydriodic acid, this was converted into *β -methyladrenaline* (annexed formula), of which the



hydriodide has m. p. 160° . According to Kobert the last-named base has not the physiological action of adrenaline (compare Böttcher, this vol., i, 152). G. B.

Ephedrine and ψ -Ephedrine. ERNST SCHMIDT (*Arch. Pharm.*, 1909, 247, 141—149. Compare Abstr., 1908, i, 452).—An investigation on the preparation and properties of substances of the types: $\text{OH}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{NMe}_3\text{Cl}$ and $\text{NMe}_3\text{Cl}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{OH}$; the two compounds formulated should yield ephedrine and ψ -ephedrine on the elimination of methyl chloride.

[With A. GOEHRING.]— β -Bromopropiophenone unites with pyridine, forming an *additive* product, $\text{COPh}\cdot\text{CHMe}\cdot\text{C}_5\text{NH}_5\text{Br}$, which crystallises in colourless prisms, m. p. 130 — 131° ; the *platinichloride*, $(\text{C}_{14}\text{H}_{14}\text{ON})_2\text{PtCl}_6$, forms yellowish-red needles, m. p. 222 — 223° ; the *aurichloride*, $(\text{C}_{14}\text{H}_{14}\text{ON})\text{AuCl}_4$, forms stellate groups of yellow needles, m. p. 134 — 136° ; the *picrate* crystallises in yellow needles, m. p. 134 — 136° .

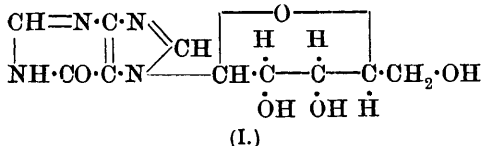
Trimethylamine and β -bromopropiophenone combine to form the *additive* product, $\text{COPh}\cdot\text{CHMe}\cdot\text{NMe}_3\text{Br}\cdot\text{H}_2\text{O}$, crystallising in colourless prisms, m. p. 206 — 208° (dried in a desiccator), 212 — 213° (dried in a steam-oven); the *platinichloride*, $(\text{C}_{12}\text{H}_{18}\text{ON})_2\text{PtCl}_6$, forms reddish-yellow needles, m. p. 231° ; the *aurichloride* crystallises in yellow leaflets, m. p. 156° . The additive product when reduced with sodium amalgam does not yield the corresponding secondary alcohol, but a *substance*, which crystallises in slender, white needles, m. p. 150 — 151° .

Phenylethylcarbinol, when acted on by bromine in acetic acid, yields a *dibromo-derivative*, $\text{C}_9\text{H}_{10}\text{OBr}_2$, which crystallises in aggregates of colourless needles, m. p. 68 — 69° . The *oily product*, obtained at the same time as the dibromo-derivative, is converted by trimethylamine into an *additive* product, which, after treatment with silver chloride, yields the *platinichloride*, $[\text{OH}\cdot\text{CHPh}\cdot\text{C}_2\text{H}_4\cdot\text{NMe}_3]_2\text{PtCl}_6$, opaque, nodular crystals, m. p. 215° , and transparent, hexagonal prisms, m. p. 218° ; the *aurichloride*, $(\text{C}_{12}\text{H}_{20}\text{ON})\text{AuCl}_4$, forms glistening leaflets and slender needles.

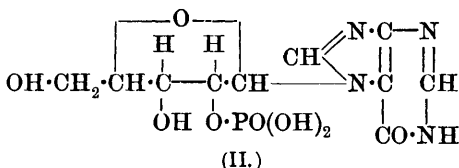
[With G. BÜMMING.]—Both ephedrine hydrochloride and ψ -ephedrine hydrochloride, when distilled in a stream of carbon dioxide, yield methylamine hydrochloride and propiophenone, and in the latter case also ammonium chloride. It is therefore probable that the hydroxyl group in ephedrine and ψ -ephedrine is connected with a carbon atom adjoining a phenyl group. W. H. G.

Carnine and Inosic Acid. II. FRANZ HAISER and FRANZ WENZEL (*Monatsh.*, 1909, 30, 147—164. Compare Abstr., 1908, i, 561; Neuberg and Brahn, Abstr., 1907, i, 1097; 1908, i, 1029; Bauer, Abstr., 1907, i, 1098; Levene and Jacobs, Abstr., 1908, i, 931).—Attempts to crystallise the pentose obtained from inosine have been unsuccessful; the syrup has $[\alpha]_D^{17} - 19.6^{\circ}$ in aqueous solution. It is considered probable that the sugar is *d*-lyxose, although con-

firmation of this is still lacking. Assuming *d*-lyxose to be present in inosine, then the latter substance probably has formula (I).



following reasons: (1) a pentose-phosphoric acid resulting from the combination of phosphoric acid with a sugar through the aldehyde group would not reduce Fehling's solution; (2) the formation of a reducing pentose-phosphoric acid from the non-reducing inosic acid by the elimination of hypoxanthine shows that the

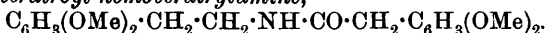


xanthine base is not joined directly with the phosphoric acid.

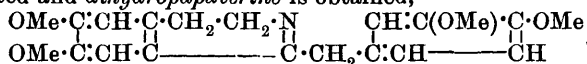
On the assumption that inosic acid contains *d*-lyxose, it is probable that inosic acid has the constitution represented by formula (II).

W. H. G.

Complete Synthesis of Laudanosine. AMÉ PICTET and Mlle. M. FINKELSTEIN (*Compt. rend.*, 1909, 148, 925—927. Compare *Abstr.*, 1900, i, 685).—The first complete synthesis of an opium alkaloid has been effected by the following operations: (1) Methylvanillin is converted into dimethylhydrocaffeic acid (Tiemann, *Abstr.*, 1878, 580); the amide of this acid on treatment with sodium hypobromite yields *homoveratrylamine*, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$. (2) *Homoveratroyl chloride*, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}_2\cdot\text{COCl}$, is prepared from Tiemann's homoveratric acid (*Abstr.*, 1878, 503). (3) In the presence of sodium hydroxide, homoveratrylamine and homoveratroyl chloride react to give *homoveratroyl homoveratrylamine*,



(4) When this is treated with phosphoric oxide, 1 mol. H_2O is eliminated and *dihydropapaverine* is obtained,

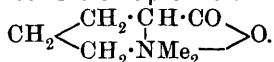


(5) Reduction of the *methochloride* of this base leads to the formation of racemic *N*-methyltetrahydropapaverine, from which laudanosine is prepared by the method described in a previous communication.

W. O. W.

Stachydrine. ERNST SCHULZE and G. TRIER (*Zeitsch. physiol. Chem.*, 1909, 59, 233—235).—Stachydrine, $\text{C}_7\text{H}_{12}\text{O}_2\text{N}$, discovered by von Planta and Schulze in the tubers of *Stachys*, does not contain a double linking; on treatment with concentrated potassium hydroxide, dimethylamine is evolved. A carboxyl group is present. There appears to be a pyrrolidine ring, which is in agreement with the fact that on destructive distillation the vapours of stachydrine give the

pine-wood reaction for pyrrole. It is therefore suggested that the substance is a dimethylbetaine of α -proline of the following structure :



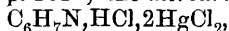
G. B.

Bases Contained in the Tar from Otto-Hilgenstock Coke-Ovens. FREDERICK GEORGE TROBRIDGE (*J. Soc. Chem. Ind.*, 1909, 28, 230—232).—Coke-oven tar yields a basic oil volatile in steam, 24% of which distils over below 170°, from which the following bases have been isolated: pyridine, 2-methylpyridine, 4-methylpyridine, and 2:4-dimethylpyridine.

Great discrepancies appear in the values recorded by various authors for the m. p.'s of the platinichlorides of these bases. It is found, as a general rule, that the platinichlorides, prepared by adding a solution of platinic chloride to an acidified aqueous solution of the hydrochloride of the base and evaporating, are darker in colour and have higher m. p.'s than those prepared in absolute alcoholic solution and crystallised by spontaneous evaporation. The compounds do not differ in chemical composition, and although they differ in crystalline habit, they nevertheless belong to the same crystallographic system. In some cases it is possible to convert one form into the other by recrystallisation from the different solvents. Pyridine aurichloride behaves in the same way, but the aurichlorides of the other bases give only slight indications of anything similar.

Pyridine platinichloride forms red crystals, m. p. 241—242°, and golden scales, m. p. 228°; the aurichloride forms golden-yellow crystals, m. p. 323°, and lemon-yellow crystals, m. p. 329°; the *picrate* forms canary-yellow needles, m. p. 163°.

2-Methylpyridine platinichloride crystallises in orange-red prisms, m. p. 194° (decomp.), and yellow scales, m. p. 178° (decomp.); the aurichloride forms bright yellow crystals, m. p. 175°; the *picrate* forms lemon-yellow needles, m. p. 161°; the *mercurichloride*,



crystallises in small plates or stout prisms, m. p. 151°.

4-Methylpyridine platinichloride forms red, rhombic crystals, m. p. 208°, and golden scales of the rhombic system, m. p. 208° (decomp.); the aurichloride crystallises from alcohol in bright yellow needles, m. p. 203°, and from water in bright yellow needles, m. p. 205°; the *picrate* forms small, pale lemon-yellow needles, m. p. 160°; the *mercurichloride* crystallises in slender needles, m. p. 121°. 2:4-Dimethylpyridine platinichloride forms orange-red, monoclinic crystals, m. p. 216° (decomp.), and minute prisms with pyramidal ends belonging to the monoclinic system, m. p. 209° (decomp.); the aurichloride forms yellow crystals, m. p. 77°; the *picrate* forms yellow crystals, m. p. 178°; the *mercurichloride*, $\text{C}_8\text{H}_9\text{N}, \text{HCl}, 2\text{HgCl}_2$, crystallises in white, hair-like needles, m. p. 128.5°.

W. H. G.

Constitution of Conhydrine (Optically Active α -Ethylpiperidylalkine). KARL LÖFFLER and REINHOLD TSCHUNKE (*Ber.*, 1909, 42, 929—948).—The relationships of conhydrine to β -coniceine (*l*-2-allylpiperidine, this vol., i, 180) indicate that the former compound

must be either α - or β -hydroxypropylpiperidine. It has been synthesised by the addition of hydrogen iodide to β -coniceine, replacement of the iodine by the acetoxy-group, and replacement of this latter by hydroxyl. Two active compounds are thus obtained, which can be separated by crystallisation from light petroleum, but neither is identical with conhydrine. This latter compound must therefore be α -hydroxypropylpiperidine, as suggested by Engler and Bauer (Abstr., 1891, 1504; 1894, i, 471). This is confirmed by the fact that when water is eliminated from conhydrine by heating with fuming hydrochloric acid, the products include γ -coniceine, in addition to α - and β -coniceines and *iso*allylpiperidine. The γ -coniceine is the product which forms a deliquescent hydrochloride; it has the constitutional formula $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{C} \begin{smallmatrix} \text{CH}\cdot\text{CH}_2 \\ \text{NH}\cdot\text{CH}_2 \end{smallmatrix} > \text{CH}_2$, and is also formed in small quantity by the action of phosphoric oxide on conhydrine. Engler and Bauer's inactive α -hydroxypropylpiperidine also yields γ -coniceine when heated with phosphoric anhydride, whereas β -hydroxypropylpiperidine yields no trace of the γ -base. The formation of γ -coniceine from α -hydroxypropylpiperidine can readily be explained by the formation of $\text{C}_5\text{NH}_3\cdot\text{CH}\cdot\text{CH}_2\text{Me}$, which undergoes molecular rearrangement by the shifting of the double linking.

The conclusion is drawn that β -coniceine and 2-*iso*allylpiperidine are *cis* or *trans* stereoisomerides, but that conhydrine and ψ -conhydrine are structurally different and not stereoisomeric, since the latter yields neither β - nor γ -coniceine when treated with phosphoric oxide.

Details for the separation of β -coniceine and the isomeric liquid base (*l*-2-*iso*allylpiperidine) (Abstr., 1905, i, 917) are given. The latter can be obtained pure by some twelve recrystallisations of the hydrochloride from acetone; it has the same m. p. as the dextro-compound obtained by resolving inactive *iso*-2-allylpiperidine with *d*-tartaric acid (this vol., i, 180). The base has D_4^{15} 0.8672 and $[\alpha]_D^{15} - 29.02^\circ$.

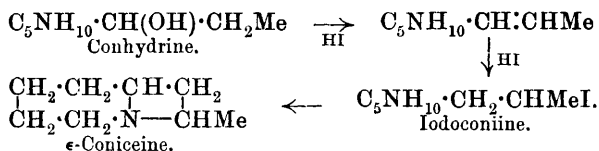
Both β -coniceine and its isomeride combine with hydrogen iodide when heated at 100° with fuming hydriodic acid and red phosphorus, yielding *iodoconiine hydriodide*, $\text{C}_8\text{H}_{16}\text{NI}\cdot\text{HI}$, in the form of compact needles, m. p. $195\text{--}198^\circ$. The same product is also formed by the action of hydriodic acid and red phosphorus on conhydrine at $140\text{--}145^\circ$.

Alkalis and moist silver oxide react with this iodine derivative, yielding the dicyclic conidine, but with silver acetate it yields an acetate from which 2- β -hydroxypropylpiperidine is obtained by hydrolysis with potassium hydroxide solution. When this hydroxy-derivative is crystallised from light petroleum, it yields a pure product crystallising in large refracting plates, m. p. $84\text{--}86^\circ$, and with $n_D + 22.5^\circ$ in a 5-dcm. tube. The *hydrochloride* forms long needles, m. p. $141\text{--}142^\circ$; the *aurichloride*, large plates, m. p. 99° , and the *platinichloride*, hyacinth-red prisms, m. p. 111° . The light petroleum mother liquors yield an isomeride which is *lævorotatory*, but which has not been obtained pure.

Hydrogen chloride also combines with β -conceine at 100° , yielding *chloroconine hydrochloride*, $C_5H_{10}N \cdot CH_2 \cdot CHMeCl \cdot HCl$, which crystallises in brilliant needles, m. p. 199° ; the *platinichloride* forms long needles, m. p. 210 — 211° , but the *aurichloride* is an oil. The chloro-derivative reacts with alkalis in much the same manner as the iodo-derivative. When the acetate is boiled with potassium carbonate solution it yields a product melting at 93 — 94° , but its composition does not correspond with that of a mono- or di-acetyl derivative. Hydrolysis with potassium hydroxide solution gives rise to the hydroxy-compound, m. p. 84 — 86° , together with a considerable amount of the *lævorotatory isomeride*.

It has been found possible by the addition to, and subsequent removal of hydrogen chloride from, β -conceine, or its stereoisomeride, partly to transform each into the other. A considerable amount of γ -conceine is formed by the elimination of water from conhydrine by means of fuming hydrochloric acid at 200 — 220° . It can be isolated in the form of the *cadmium salt*, $C_8H_{15}N, HI, CdI_2$, which crystallises from hot water in long needles, m. p. 146 — 147° . The *platinichloride* has m. p. 192° . J. J. S.

Constitution and Synthesis of ϵ -Conceine (2-Methylconidine and *iso*-2-Methylconidine). KARL LÖFFLER (*Ber.*, 1909, 42, 948—960).—The ϵ -conceine obtained by Lellmann (*Abstr.*, 1890, 1328) by the action of alkali on Hofmann's iodoconine is shown to be a mixture of two stereoisomeric tertiary bases. The formation of these bases is represented by the following scheme:



The base contains two asymmetric carbon atoms, and the two isomerides isolated correspond with the (— —) and (— +) compounds.

The same stereoisomerides are formed by the action of hydrobromic or hydriodic acid on α -pipercolymethylalkine (2- β -hydroxypropyl-piperidine). The dicyclic ring system shown above has been previously termed *conidine* (*Abstr.*, 1907, i, 437), and the two bases of which ϵ -conceine is composed are called *2-methylconidine* and *iso-2-methylconidine* respectively.

ϵ -Conceine is most readily obtained by the action of concentrated potassium hydroxide solution on bromoconine (Löffler and Kirschner, *Abstr.*, 1905, i, 938). The yield is only some 20—25%, as considerable amounts of tarry matter are formed; the crude base is best isolated in the form of its picrate (m. p. 220 — 221°). The base distils at 150 — $153^\circ/748$ mm., and has D^{15}_D 0.8836 and $\alpha + 42.34^\circ$. It can be resolved into two components, 2-methylconidine and *iso*-2-methylconidine, by fractional crystallisation of the acid *d*-tartrate from water.

After repeated crystallisation, the *d*-tartrate of the *iso*-base, which is

sparingly soluble in water, is obtained as long, well-developed needles, containing $2\text{H}_2\text{O}$, and having m. p. $91-92^\circ$. *iso*-2-Methylconidine is a clear, strongly refracting liquid, b. p. $143-145^\circ$, $D_{15}^{25} 0.8624$, and $[\alpha]_D^{15} -87.34^\circ$. It is a strong base absorbing carbon dioxide, and is stable towards permanganate. The *hydrochloride* is deliquescent; the *aurichloride*, $\text{C}_8\text{H}_{15}\text{N}, \text{HAuCl}_4$, crystallises in yellow, feathery needles, m. p. $198-199^\circ$. The *platinichloride* forms similar needles, m. p. 185° . The *ethiodide*, $\text{C}_8\text{H}_{15}\text{N}, \text{EtI}$, forms a snow-white powder, m. p. $180-181^\circ$. It also forms a sparingly soluble *picrate* and *mercurichloride*.

2-Methylconidine d-tartrate is more readily soluble in water, and crystallises in long, slender needles containing $2\text{H}_2\text{O}$, and has m. p. $72-73^\circ$. The base has b. p. $151-154^\circ$, $D_{15}^{25} 0.8856$, and $[\alpha]_D^{15} +67.4^\circ$. The *platinichloride*, $(\text{C}_8\text{H}_{15}\text{N})_2, \text{H}_2\text{PtCl}_6$, forms nodular crystals, m. p. $184-185^\circ$. The *aurichloride* has m. p. $167-168^\circ$, and the *ethiodide* has m. p. 165° (decomp.). J. J. S.

b- ψ -Conhydrine. KARL LÖFFLER (*Ber.*, 1909, 42, 960-962).—*b* ψ -Conhydrine (compare this vol., i, 181) is merely a monohydrate of ψ -conhydrine, and has the formula $\text{C}_8\text{H}_{17}\text{ON}, \text{H}_2\text{O}$. When exposed to the air for some time, or over sulphuric acid, it loses its water and then has the m. p. of conhydrine (106°). The hydrate when plunged in a bath at 58° melts at $58-60^\circ$. J. J. S.

Derivatives of Piperazine. WILLEM A. VAN DORP, jun. (*Rec. trav. chim.*, 1909, 28, 68-91. Compare Franchimont, *Abstr.*, 1907, i, 395).—When piperazyldicarbamide dinitrate, prepared by mixing a hydrochloric acid solution of piperazine with a concentrated aqueous solution of potassium isocyanate and treating the aqueous solution of the resulting carbamide with nitric acid, is acted on with absolute nitric acid, almost equal volumes of carbon dioxide and nitrous oxide are evolved, the amino-groups being attacked and *piperazine dinitrate*, small, limpid, prismatic crystals, together with a small quantity of a second substance, possibly nitropiperazine, being formed. Dibenzene-sulphonpiperazide, obtained by the action of benzenesulphonyl chloride on piperazine, reacts with absolute nitric acid, giving *dinitropiperazine*, $\text{CH}_2 \cdot \text{N}(\text{NO}_2) \cdot \text{CH}_2$, which forms fine colourless needles, m. p. 215° , and on reduction gives Schmidt and Wichmann's piperazyldihydrazine (*Abstr.*, 1892, 210). Dinitropiperazine is not attacked by absolute nitric acid, consequently the formation of nitrous oxide by the action of nitric acid on piperazyldicarbamide dinitrate is not due to the decomposition of the former compound. The reaction is thus completely distinguished from the action of absolute nitric acid on piperyl-carbamide, which gives nitropiperidine.

Ethyl piperazine-1 : 4-dicarboxylate, prepared by the action of ethyl chloroformate on piperazine in the presence of alkali, has m. p. 45° (Rosdalsky, *Abstr.*, 1896, i, 257, gives 42°).

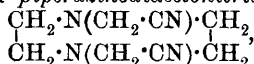
Methyl 1 : 4-piperazinedicarboxylate, $\begin{array}{c} \text{CH}_2 \cdot \text{N}(\text{CO}_2\text{Me}) \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{N}(\text{CO}_2\text{Me}) \cdot \text{CH}_2 \end{array}$, obtained

similarly, forms large, colourless, transparent, cuspidated crystals, m. p. 81°. When either of these urethanes is dissolved in absolute nitric acid, oxidation occurs, giving very fine white needles of a substance, which was not further examined.

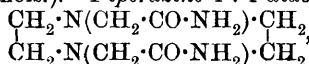
Dipicrylpiperazine, $\begin{array}{c} \text{CH}_2 \cdot \text{N}[\text{C}_6\text{H}_2(\text{NO}_2)_3] \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{N}[\text{C}_6\text{H}_2(\text{NO}_2)_3] \cdot \text{CH}_2 \end{array}$, resulting when piperazine is treated with picryl chloride, forms small, orange-yellow crystals, decomposing at about 287°. It dissolves in absolute nitric acid, undergoing slight oxidation, and gives an insoluble, amorphous, red substance.

According to Rosdalsky (*loc. cit.*), the action of formaldehyde on a slight excess of piperazine gives methylenepiperazine (annexed formula), whilst Herz (Abstr., 1897, i, 488), using excess of formaldehyde, obtained the compound $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_2$. Ladenburg and Herz, moreover, showed (Abstr., 1898, i, 209) that the product methylenepiperazine is decomposed by phenol, thus invalidating Rosdalsky's molecular-weight determinations. The author, repeating Rosdalsky's experiments, obtained a compound with the empirical formula, $\text{C}_5\text{H}_{10}\text{N}_2$, in the presence of even a slight excess of aldehyde, however, the product seems to be identical with Herz's substance. Eschweiler having shown (Abstr., 1894, i, 267) that hydrogen cyanide acts on hexamethylenetetramine, rupturing the $\begin{array}{c} \cdot \text{CH}_2 \\ \cdot \text{NH} \end{array}$ groups, the

action of this reagent on methylene-piperazine, $\text{C}_5\text{H}_{10}\text{N}_2$, was studied. The reaction of methylene piperazine with hydrogen cyanide gives small, limpid crystals of *piperazinodiacetonitrile*,



m. p. 165°, of which a better yield is obtained by treating piperazine (1 mol.) in aqueous solution with formaldehyde (2 mols.) and then with hydrogen cyanide (2 mols.). *Piperazine-1 : 4-diacetamide*,



prepared by hydrolysing the nitrile with sulphuric acid, forms small crystals decomposing above 250°; the *dihydrochloride* is formed by hydrolysis with hydrochloric acid. When the nitrile is boiled for a prolonged period with barium hydroxide solution, *piperazine-1 : 4-di-*

acetic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{N}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{N}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \cdot \text{CH}_2 \end{array} + 2\text{H}_2\text{O}$, is formed in magnificent,

colourless, transparent crystals, which effloresce in the air; the *barium*,

silver, *sodium*, and *potassium* salts were prepared. The acid forms an additive compound, $\text{C}_5\text{H}_{14}\text{O}_4\text{N}_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{HCl}$, with hydrogen chloride, which, when heated at 100°, loses water, but not hydrogen chloride; it is not decomposed by boiling water, from which it crystallises in brilliant, limpid crystals. An analogous compound is formed with nitric acid.

All attempts to esterify the acid failed. When an absolute alcoholic solution of piperazine (1 mol.) is treated with ethyl chloroacetate

(1 mol.), the product must contain ethyl piperazine-1:4-diacetate, since on saponification with baryta the acid is formed, but the ester could not be obtained pure.

It is suggested, in conclusion, that the product of the action of formaldehyde on piperazine is dimethylene-dipiperazine (annexed formula). This would explain the action of hydrogen cyanide.

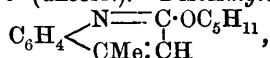
E. H.

Quinazolines. XXI. Certain Quinazoline Oxygen Ethers of the Type $\cdot\text{N}:\text{C}(\text{OR})\cdot$ and the Isomeric $\cdot\text{NR}\cdot\text{CO}\cdot$ Compounds.

MARSTON T. BOGERT and CLARENCE EARL MAY (*J. Amer. Chem. Soc.*, 1909, 31, 507—513).—In an earlier paper (Bogert and Seil, *Abstr.*, 1907, i, 560) an account was given of the formation and properties of two series of quinazoline derivatives, namely, the *O*-derivatives, $\cdot\text{C}(\text{OR})\cdot\text{N}\cdot$, and *N*-derivatives, $\cdot\text{CO}\cdot\text{NR}\cdot$. In continuing the study of these compounds, *O*-ethers have been prepared by the action of alkyl oxides on the chloroquinazolines, and *N*-ethers by direct alkylation of the 4-quinazolones (4-hydroxyquinazolines) with alkyl halides, as well as by other methods described in previous papers. When 4-quinazolones are treated with alkyl iodides in presence of sodium ethoxide, a mixture of the *O*- and *N*-ethers is produced, but in the case of methyl, ethyl, *n*-propyl, and *n*-butyl iodides, the proportion of the *O*-ether formed is exceedingly small. The *N*-compounds are colourless, odourless solids, soluble in water, difficultly volatile with steam, of higher m. p. than the *O*-isomerides, and are not hydrolysed by strong hydrochloric acid. The *O*-compounds are oily liquids or solids of low m. p., usually of pleasant odour, readily volatile with steam, less soluble in water than the *N*-isomerides, and are readily hydrolysed by hydrochloric acid with formation of the corresponding hydroxyquinazolines (quinazolones). The following compounds are described.

The mercuric chloride compound of 2-ethoxyquinoline melts at 136—138°. 2-isoAmyloxyquinoline, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N}=\text{C}\cdot\text{OC}_5\text{H}_{11} \\ \text{CH}:\text{CH} \end{array}$, is readily hydrolysed by hydrochloric acid with formation of carbostyryl.

1-isoAmyl-2-quinolone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N}(\text{C}_5\text{H}_{11})\cdot\text{CO} \\ \text{CH}=\text{CH} \end{array}$, forms a mercuric chloride compound, m. p. 89—90° (uncorr.). 2-isoAmyloxyepidine,



has m. p. 120—140°, and b. p. above 360°.

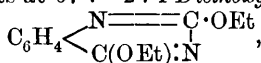
4-Methoxyquinazoline, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N}=\text{CH} \\ \text{C}(\text{OMe})\cdot\text{N} \end{array}$, m. p. 35·4°, and 4-ethoxyquinazoline, m. p. 42—44°, form colourless crystals. 4-*n*-Propoxyquinazoline and 4-*n*-butoxyquinazoline are colourless oils, which boil at 257—260° and 263—265° respectively. 3-*n*-Propyl-4-quinazolone,

$\text{C}_6\text{H}_4 \begin{array}{c} \text{N}=\text{CH} \\ \text{CO}\cdot\text{NPr}^a \end{array}$, m. p. 82—83°, and the corresponding *n*-butyl compound, m. p. 73°, crystallise in needles.

When tetrachloro-2-methylquinazoline, $\text{C}_6\text{HCl}_3 \begin{array}{c} \text{N}=\text{CMe} \\ \text{CCl}:\text{N} \end{array}$ (Dehoff,

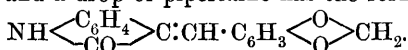
Abstr., 1891, 84), is treated with sodium methoxide, *trichloro-4-methoxy-2-methylquinazoline*, $\text{C}_6\text{HCl}_3 \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{C(OMe):N} \end{smallmatrix}$, m. p. 87—88°, is obtained in colourless, silky needles. *Tetrachloro-2-ethylquinazoline*, $\text{C}_6\text{HCl}_3 \begin{smallmatrix} \text{N}=\text{CEt} \\ \text{CCl:N} \end{smallmatrix}$, m. p. 80°, obtained by heating 2-ethyl-4-quinazoline with phosphorus pentachloride and oxychloride, forms minute, colourless needles. Trichloro-4-ethoxy-2-methylquinazoline has the properties ascribed to it by Dehoff (*loc. cit.*).

2-Methoxyquinazoline, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}=\text{C}\cdot\text{OMe} \\ \text{CH:N} \end{smallmatrix}$, m. p. 55—56°, crystallises in needles. *2-Ethoxyquinazoline* was obtained as a yellow oil, which, on cooling, forms cubical crystals. *2:4-Dimethoxyquinazoline* (Abt, Abstr., 1889, 610) melts at 67°. *2:4-Diethoxyquinazoline*,



m. p. 50—51°, forms silky needles. *2:4-Di-n-propoxyquinazoline*, m. p. 40—41°, crystallises in long needles. *1:3-Dimethylbenzoylenecarbamide* (Abt, *loc. cit.*) melts at 163—165°. *2:4-Diketo-1:3-diethylquinazoline*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NEt}\cdot\text{CO} \\ \text{CO-NEt} \end{smallmatrix}$, m. p. 105—106°, forms minute, colourless needles. By the action of *n*-propyl iodide on benzoylenecarbamide in presence of alcoholic sodium hydroxide, *2:4-diketo-1-(or 3)-n-propylquinazoline*, m. p. 171°, is produced, but a dipropyl derivative could not be obtained. E. G.

A New Isomeride of Indigo. ANDRÉ WAHL and P. BAYARD (*Compt. rend.*, 1909, 148, 716—719).—Oxindole condenses with aromatic aldehydes, giving coloured, crystalline compounds, which are isomeric with the indogenides (Baeyer, Abstr., 1884, 73). The compound obtained by boiling an alcoholic solution of oxindole with piperonaldehyde and a drop of piperidine has the formula



This crystallises in bright yellow, silky needles, m. p. 228—229°. The name *isoidogenides* is proposed for compounds of this type.

3:3-Bisindole, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{NH}$, is prepared by heating on a water-bath oxindole and isatin in acetic acid containing a little hydrogen chloride.

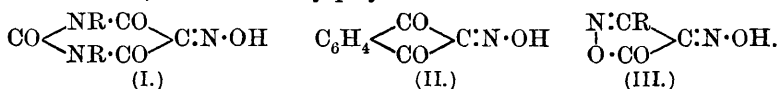
The substance is sparingly soluble in ether, alcohol, and acetic acid, but crystallises from absolute methyl alcohol in garnet-red, acicular plates. When heated on platinum it melts above 350°, evolving yellow vapours. It is conveniently purified by sublimation in a vacuum.

The existence of this new isomeride of indigotin affords conclusive proof of the correctness of the generally-accepted formula for indigored. The latter has been prepared by a new synthesis, which consists in condensing oxindole with isatin chloride under the same conditions as described in connexion with the preparation of the phenylisoxazolones (this vol., i, 261). W. O. W.

Pantochromism and Chromoisomerism of Violurates and Allied Oximinoketone Salts. ARTHUR HANTZSCH (*Ber.*, 1909, 42, 966—985).—A theoretical paper, in which the results obtained by the author and his co-workers (see following abstracts) during their investigations on the colour of the salts of violuric acid and of closely-related compounds are discussed. An explanation of many of the facts observed cannot yet be given, and although investigations on this subject are still in progress, these results are now published owing to the appearance of a paper by Dimroth (this vol., i, 62).

It has already been shown that the production of coloured salts from colourless acids and colourless metals must be accompanied by a constitutional rearrangement, namely, an alteration of the manner in which the atoms are linked together; this change may occur without rearrangement of the atoms themselves within the molecule. Further, when a hydrogen compound in the solid state or in solution differs optically from its alkyl derivatives, it points to a constitutional change; for example, the esters of the so-called violuric acids having the formula $\text{CO} \begin{smallmatrix} \text{NR} \cdot \text{CO} \\ \text{NR} \cdot \text{CO} \end{smallmatrix} \text{C} : \text{NOR}$ are esters of ψ -violuric acid (*leucoluric acid*), since they are quite colourless, and correspond, chemically, with the colourless salts, but not with the ordinary chromo-salts of these acids.

Many of the open-chain monoximes of diketones, particularly the colourless compounds, yield only colourless salts; apparently, polychromatic salts are only obtained from cyclic oximinoketones. Nevertheless, there are certain oximinoketones which yield salts with colourless metals having the same colour as the parent substance and its true oxime-ethers; thus, the ethers and salts of isatoxime have the same yellow colour as the parent substance. The salts of violuric acid, methylvioluric acid, dimethylvioluric acid, diphenylvioluric acid (I), oximinodiketohydrindene (II), and the oximino-oxazolones (III) are, however, extraordinarily polychromatic:



The preparation and analysis of several hundreds of salts of these compounds has led to the establishment of the following tenet: colourless or faintly-coloured cyclic oximinoketones yield salts with colourless metallic and ammonium ions which are red, orange, yellow, green, blue, violet, sometimes brown, olive-green, greenish-violet, flesh-coloured, and occasionally colourless. In other words, the

complex $\text{X} \begin{smallmatrix} \text{C} \cdot \text{O} \\ \text{C} \cdot \text{N} \cdot \text{O} \end{smallmatrix} \} \text{M}_1, \text{M}_2, \dots, \text{M}_n$, where X represents a cyclic nucleus and M a metal, is *pantochromatic*, depending on the nature of the colourless or faintly-coloured anion and the colourless cation. As a general rule, a salt of one colour only is obtained with each individual colourless metallic or ammonium ion; particularly is this true when the same method of preparation is employed. Sometimes, however, the colour of the salt as initially precipitated changes; this change of colour is effected more frequently by altering the tempera-

ture or the solvent. It is proposed to distinguish this variation of colour of one and the same salt by the word *chromotropy*, and to designate salts which exist in differently-coloured modifications as *variochromatic*. As examples of chromotropes of variochromatic salts may be cited the blue potassium, rubidium, and caesium violurates, which change into red salts without loss of weight when heated under moist benzene at 140—150°; the rubidium salt of oximino-*p*-bromophenyloxazolone is pink (labile), bluish-violet (labile), or violet (stable), whilst the corresponding caesium salt is pink (stable), bluish-violet (labile), or violet (labile). The stability of the different modifications of a variochromatic salt is extremely variable; generally, the velocity of transformation of the dry, solid salt is very small. Definite relationships between the nature of the colourless metal and the stability and colour of the salt have not yet been established. As a rule, the lithium salts are yellow, orange, or red; blue and violet salts have hitherto not been isolated; only the orange and red sodium salts are stable; occasionally labile blue and violet sodium salts are obtained; the stable potassium, rubidium, and caesium salts are usually blue, bluish-green, or violet, whilst the labile salts are red; orange salts of these metals have not been obtained.

In many cases, combination of the solvent with the salt alters the colour; thus, the silver salt of oximinomethyloxazolone is red; the compound with $\frac{1}{2}\text{C}_5\text{NH}_5$ is pink, that with 2NH_3 is violet, and that with $\text{C}_5\text{H}_{11}\text{N}$ is violet. The change of colour is not directly due to the combination of the salt with the solvent, since the potassium, rubidium, and caesium salts of oximino-*p*-bromophenyloxazolone with and without ethyl alcohol are pink, but is produced indirectly, in that the solvent renders stable an otherwise labile chromotrope. Sometimes the additive compounds themselves are variochromatic; thus, silver dimethylviolurate with C_5NH_5 exists in a stable, bluish-violet form and a labile, green form.

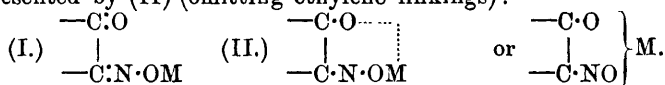
Solutions of the variochromatic modifications of one and the same salt in the same solvent are identical.

Strong solutions of the same salt in different solvents, however, have different colours. The colour of the solutions of the salts with various alkali-metals becomes deeper as the atomic weight of the metal increases; thus, in acetone, the solution of the lithium salt of oximino-*p*-bromophenyloxazolone is carmine, the sodium salt is violet, the potassium salt is violet-blue, the rubidium salt is bluish-violet, and the caesium salt is blue. The colour of the same salt in non-dissociating solvents is weakened by "negative" solvents (phenol, etc.) and strengthened by "positive" solvents (ammonia, amines, etc.); thus, the solutions of the potassium, rubidium, and caesium salts of oximino-*p*-bromophenyloxazolone in phenol are red, in acetone bluish-violet, and in pyridine, blue.

Mol.-wt. determinations show that the polychromatic salts are unimolecular, consequently the various polychromatic salts are constitutively different, and the variochromatic salts are true isomeric salts. All attempts to obtain isomeric alkyl and acyl derivatives from the variously-coloured salts have been unsuccessful; in some cases, however, differences in the reaction-velocities were observed;

for example, the blue silver salt of oximino-*p*-bromophenyloxazolone explodes when treated with methyl iodide, whilst the red silver salt when similarly treated merely reacts with a great development of heat.

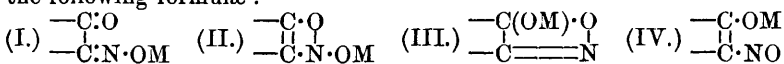
Since salts of simple oximes, $>\text{C}:\text{N}\cdot\text{OM}$, are colourless, whereas the oximinoketone salts are coloured, it follows that the production of colour is due to the presence of the carbonyl group; consequently, if the *leuco*-salts have the formula (I), the *chromo*-salts may be represented by (II) (omitting ethylene linkings):



It is possible to account for the production of colour in this way, but not the occurrence of pantochromatic salts. The possibility that pantochromism may be produced by the various metals occupying different positions relative to the carbonyl oxygen atom and the oxime oxygen atom, such positions depending on the different affinities of the various metals for one or other oxygen atom, is considered improbable.

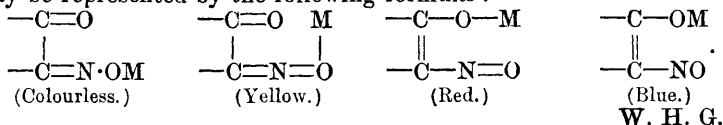
Notwithstanding the extraordinary diversity of colour of the salts of the violuric acids, it is found that about one-half are carmine, whilst the members of a smaller group comprising the potassium, rubidium, cesium, and ammonium salts are bluish-violet to blue, and those of a third group of about equal numbers containing several lithium salts and the acid salts of dimethylvioluric acid are yellow. The same applies to the salts of the oximino-oxazolones; in fact, the primary colours of the salts of oximinoketones are yellow, red, and blue; the other coloured salts are mixed salts, for example, the violet salts are mixtures of blue with red salts.

The existence of the colourless, yellow, red, and blue isomerides may be explained by assuming that they are structural isomerides having the following formulæ:



Since the *chromo*-salts are so similar in their chemical behaviour, it is very improbable, however, that they are structural isomerides.

A third explanation, depending on the presence and varied distribution of the partial valencies of the atoms of the unsaturated chromophoric complex and the partial valencies of the metallic atoms, may also be given. The four primary forms of the salts of oximinoketones may be represented by the following formulæ:



Salts and Esters of the Violuric Acid Group. ARTHUR HANTZSCH and P. C. C. ISHERWOOD (*Ber.*, 1909, 42, 986—1000. Compare preceding abstract; Wagner, *Abstr.*, 1894, ii, 8; Guinchard, *Abstr.*, 1899, i, 779).—A large number of salts of colourless metals

with violuric acid, methylvioluric acid, and dimethylvioluric acid have been prepared, and the majority analysed. Contrary to the statement of Andreasch (Abstr., 1895, i, 336), acid salts are also formed; the first two acids also yield dimetallic derivatives. The colourless methyl and benzyl esters of the three acids have also been prepared. The esters of violuric acid yield colourless mono- and di-metallic salts; the esters of methylvioluric acid yield colourless mono-metallic salts. Since these esters and salts are colourless, they must be regarded as derivatives of ψ -violuric acid or *leucoluric* acid.

About 100 violurates have been prepared, of which 73 are red, 10 bluish-violet, 10 yellow, 5 green, and the others colourless; 22 of the 31 dimetallic salts are red.

Benzyl violurate, $C_4H_2O_3N_3 \cdot C_7H_7$, prepared by the action of α -benzylhydroxylamine on alloxan, crystallises in colourless leaflets, decomposing at 222° ; the *sodium*, *potassium*, *ammonium*, *silver*, *disodium*, and *dipotassium* salts are colourless; the *disilver* salt is slightly yellow.

Benzyl dimethylviolurate, $C_{13}H_{13}O_4N_3$, has m. p. 164° .

Salts of Violuric Acid.—The *lithium* salt, $C_4H_2O_4N_3Li$, is a carmine-red powder; the *sodium* salt forms red needles; the *potassium* salt ($2H_2O$) crystallises in bluish-violet needles; the *rubidium* salt from water is bluish-violet, and from alcohol is pure blue; the *caesium* salt is blue; the *ammonium* salt from water is bluish-violet, and from alcohol is pure blue; the *glucinium* salt crystallises in dark red prisms; the *magnesium*, *calcium*, *strontium*, and *barium* salts form red needles; the *zinc* salt ($2H_2O$) forms reddish-brown needles; the *anhydrous* salt is carmine; the *cadmium* salt is brownish-red; the *thallium* salt forms red leaflets; the *lead* salt crystallises in dark red needles; the *silver* salt is practically colourless when first precipitated at -15° , and becomes grey, violet, or green when dry; it passes into small, heavy, dark green crystals when kept for some time under the liquid; the *dilithium* salt, $C_4HO_4N_3Li_2$, is pure yellow; the *disodium*, *dipotassium*, *dirubidium*, and *dicaesium* salts are dark red; the *diammonium* salt is light red; the *dibarium*, *distrontium*, *dimagnesium*, and *dilead* salts are red powders; the *disilver* salt is dark green; the *hydrogen potassium*, *hydrogen rubidium*, and *hydrogen caesium* salts are obtained as dark red crystals; the *hydrogen thallium* salt forms pale green leaflets; the *hydrogen silver* salt, $(C_4H_2O_4N_3)_2HAg \cdot 3H_2O$, crystallises in red, hexagonal plates.

Salts of Dimethylvioluric Acid.—The *lithium* salt, $C_6H_6O_4N_3Li$, crystallises in pale carmine needles; the *sodium* salt is also pale carmine; the *rubidium* and *caesium* salts are bluish-violet; the *glucinium* salt forms brownish-red plates; the *thallium* salt is dark red; the *silver* salt is reddish-brown; the blue silver salt described by Andreasch (*loc. cit.*) is a *potassium silver* salt, $(C_6H_6O_4N_3)_2KAg$; the *hydrogen rubidium*, *hydrogen caesium*, *hydrogen ammonium*, and *hydrogen thallium* salts are orange-yellow; the *hydrogen silver* salt forms red, transparent needles.

Chromotropy of Solid Violurates.—The blue potassium, rubidium, and caesium violurates when heated with moist benzene under pressure at 140° pass into red modifications; the red sodium salt when

similarly treated becomes slightly lighter; the *carmine* lithium salt when heated with moist benzene at 170° passes into a *brownish-yellow* modification; the *bluish-violet* potassium methylviolurate when treated in the same manner yields a *dark red* variety. The dimethylviolurates do not change colour when similarly treated.

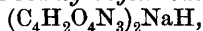
W. H. G.

Polychromatic and Chromotropic Violurates. ARTHUR HANTZSCH and BASILE ISSAIAS (*Ber.*, 1909, 42, 1000—1007. Compare preceding abstract).—An investigation on the formation and properties of several chromotropes of violurates and dimethylviolurates. It is found that the salts of these acids with the alkali metals exist in at least three differently coloured forms: yellow, red, and blue, or the corresponding mixed colours. Each alkali salt can exist in at least two modifications, either yellow and red or red and blue, one of which is always stable; thus, the red salts of lithium and sodium, and the blue salts of potassium, rubidium, and caesium, are stable; yellow salts are obtained only with lithium and are labile.

Silver violurates in combination with colourless components, such as pyridine, silver nitrate, and alkali violurates, exist in colourless, yellow, red, blue, and green forms.

The labile violurates described below are obtained usually by one of the following methods: (1) heating the stable variety with moist benzene under pressure at 140 — 150° ; (2) heating the stable variety with water vapour at a temperature slightly above 100° ; (3) precipitation from alcoholic solution with ether; (4) preparation of the salt in absolute alcoholic solution. In some cases, the formation of the labile modification is dependent on the presence of catalysts, the nature of which is sometimes unknown.

Potassium violurate may be obtained as small *red* crystals, and also as a *pale pink* precipitate by precipitation in absolute alcohol at -70° . The red sodium salt becomes *bluish-violet* at 150° . A *yellow* lithium salt is obtained by evaporating a methyl-alcoholic solution in a desiccator. *Silver dipyridine violurate*, $C_4H_2O_4N_3Ag, 2C_5H_5N$, is obtained as microscopic, colourless needles by adding ether to a solution of silver violurate in pyridine; it becomes blue when kept. A stable red *sodium silver violurate* is prepared by treating a solution of sodium violurate with silver nitrate. A stable blue *potassium silver violurate* is obtained by similar means; a labile red potassium silver salt is formed by treating dipotassium violurate with strong aqueous silver nitrate. A red *hydrogen sodium violurate*,



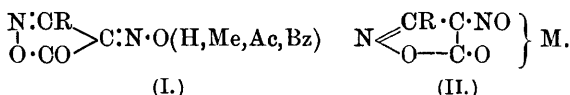
and orange-yellow *hydrogen potassium* salt have also been prepared.

Various coloured dimetallic salts have also been prepared, for example, a yellow *lithium silver* salt. The labile lithium dimethylviolurate crystallises in *yellow* needles; the ordinary red sodium salt ($3H_2O$), when heated at 150° , becomes *violet*, and then contains about 1% of water; it becomes again red at the ordinary temperature; a stable *blue* potassium dimethylviolurate may be obtained by boiling the violet salt ($\frac{1}{2}H_2O$) with methyl alcohol; the violet salt becomes *red* at about -70° .

W. H. G.

Polychromatic Salts from Oximino-oxazolones. ARTHUR HANTZSCH and W. KEMMERICH (*Ber.*, 1909, 42, 1007—1015. Compare preceding abstracts).—The salts of the colourless or faintly

yellow oximino-oxazolones, $\begin{matrix} \text{N:CR} \\ | \\ \text{O} \cdot \text{CO} \end{matrix} > \text{C:N} \cdot \text{OH}$, with colourless metals, like the violurates, exist in yellow, red, and blue modifications; occasionally, orange, violet, and green salts are obtained. From this it follows that pantochromism is not dependent on the presence of the complex $\cdot \text{CO} \cdot \text{C}(\text{NOH}) \cdot \text{CO} \cdot$, and that two, and only two, negative, unsaturated groups are necessary for the production of the chromophore in the salt formation. The alkyl and acyl derivatives, unlike the polychromatic salts, are colourless or but faintly yellow, consequently they must have the formula I, whilst the salts have the general formula II.



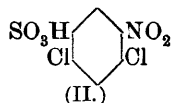
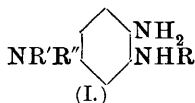
Derivatives of Oximinophenylloxazolone.—The salts of oximinophenyl-oxazolone are stable in the dry state and in indifferent solvents; they explode when heated, even below 100°. The *lithium* and *sodium* salts are vermilion; the *potassium* salt, $\text{C}_9\text{H}_5\text{O}_3\text{N}_2\text{K}$, crystallises in small, violet needles, which become blue when kept; the *hydrate* ($1\text{H}_2\text{O}$) forms red needles; the violet *rubidium* salt also becomes blue when kept; the *caesium* salt is bluish-violet and deliquescent; the *ammonium* salt forms garnet-red needles; the *tetramethylammonium* salt is deep blue; the *barium* salt is pink; the *calcium* salt is orange-red; the *acid potassium*, *rubidium*, and *caesium* salts are yellow; the *hydrogen sodium* salt is pink; an apparently colourless *silver* salt is obtained by precipitating the ammonium salt in alcoholic solution with silver nitrate at -30° ; by varying the method of preparation, a pink, vermilion, carmine, or blue silver salt may be obtained; the *hydrogen silver* salt, $(\text{C}_9\text{H}_5\text{O}_3\text{N}_2)_2\text{HAg}$, exists in a yellow and orange form; the *potassium silver* salt, $(\text{C}_9\text{H}_5\text{O}_3\text{N}_2)_2\text{AgK}$, is blue; the salt, $\text{C}_9\text{H}_5\text{O}_3\text{N}_2\text{Ag}, \text{AgNO}_3$, is olive-green; the *silver dipyridine* salt,

$\text{C}_9\text{H}_5\text{O}_3\text{N}_2\text{Ag}, 2\text{C}_5\text{H}_5\text{N}$, forms violet crystals; the *silver diammonia* salt, $\text{C}_9\text{H}_5\text{O}_3\text{N}_2\text{Ag}, 2\text{NH}_3$, is blue; the *thallium* salt is red; the *pyridine* salt is brick-red; the *piperidine* salt is scarlet; the *ethyl* ester, $\text{C}_{11}\text{H}_{10}\text{O}_3\text{N}_2$, is pale yellow, and has m. p. 113° (decomp.); the *acetate*, $\text{C}_{11}\text{H}_9\text{O}_4\text{N}_2$, is slightly yellow, and has m. p. 155° ; the *benzoate*, $\text{C}_{16}\text{H}_{10}\text{O}_4\text{N}_2$, is quite colourless.

Salts of Oximinomethylloxazolone.—The *sodium* salt is light red; the *potassium* salt is violet; the *potassium hydrogen* salt is yellow; the *barium* salt is pink; the *silver pyridine* salt, $\text{C}_4\text{H}_8\text{O}_3\text{N}_2\text{Ag}, \frac{1}{2}\text{C}_5\text{H}_5\text{N}$, is pink; the *silver ammonia* salt, $\text{C}_4\text{H}_8\text{O}_3\text{N}_2\text{Ag}, 2\text{NH}_3$, is reddish-violet; the *piperidine* salt is orange; the *pyridine* salt is lemon-yellow.

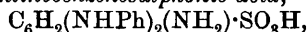
W. H. G.

[Preparation of Derivatives of Triaminobenzene.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 205358).—Derivatives of 1:2:4-triaminobenzene, having the general formula (I), are readily



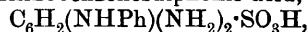
obtained from 2:4-dichloro-5-nitrobenzenesulphonic acid by successively condensing with organic bases and reducing the nitro-group.

5-Amino-2:4-dianilinobenzenesulphonic acid,



a colourless, sparingly soluble powder, is thus obtained by heating 2:4-dichloro-5-nitrobenzenesulphonic acid (II) with aqueous aniline at 120—150° in the presence of some substance, such as chalk, sodium carbonate, or sodium acetate, for neutralising the hydrogen chloride liberated. The intermediate nitrodianilinobenzenesulphonic acid is then reduced with iron and acetic acid, or with alkaline sodium hyposulphite.

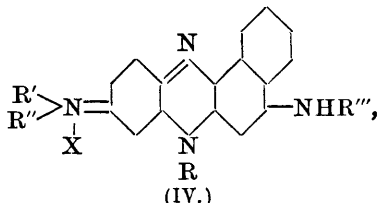
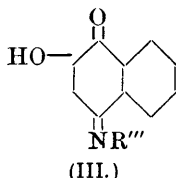
2:5-Diamino-4-anilinobenzenesulphonic acid,



colourless, lustrous, sparingly soluble leaflets, was obtained by the following series of operations.

Sodium 2-chloro-5-nitro-4-anilinobenzenesulphonate, yellow crystals, soluble in hot water, was produced by heating together 2:4-dichloro-5-nitrobenzenesulphonic acid (1 mol.), aniline (1 mol.), and aqueous sodium acetate. This product, on heating with 20% ammonium hydroxide at 150°, gives sodium 5-nitro-2-amino-4-anilinobenzenesulphonate, lustrous, yellow leaflets, which on reduction yields the foregoing diamine.

These triaminobenzene derivatives when condensed with the β -hydroxynaphthaquinoneimides (III), or their sulphonic acids, give rise to naphthasafranines having the general formula (IV):



where R is an alkyl or aryl group, and R', R'', and R''' are hydrogen, alkyl, or aryl radicles.

These dyes furnish red to greenish-blue shades, suitable either for wool or silk.

F. M. G. M.

Derivatives of Osotetrazines and Osotriazoles. ROBERT STOLLÉ (Ber., 1909, 42, 1047. Compare Pechmann and Bauer, this vol., i, 270; Stollé, this vol., i, 123).—Polemic. Stollé was the first to

ascribe to diphenylosotetrazine the constitution of a 1-amino-3:4-diphenyl-1 : 2 : 5-triazole.
E. F. A.

Behaviour of a Diazo-salt towards Organic Solvents. GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1909, 44, 232—243).—Under the influence of various organic solvents, the *p*-bromodiazobenzene derivative of ω -dinitrotoluene, $\text{CPh}(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Br}$, undergoes two distinct intramolecular transformations, yielding: (1) α -nitro- β -nitroso- α -benzoyl- β -*p*-bromophenylhydrazine, which may then, by losing two atoms of nitrogen and three of oxygen in the form of nitrous compounds, become converted into benzoylazo-*p*-bromobenzene, and (2) ω -*p*-bromobenzeneazo- ω -dinitrotoluene.

The *p*-bromodiazobenzene salt of ω -dinitrotoluene,
 $\text{CPh}(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Br}$,
prepared by the action of *p*-bromodiazobenzene acetate on the potassium derivative of ω -dinitrotoluene, separates as a golden-yellow powder, m. p. 98° (decomp.).

α -Nitro- β -nitroso- α -benzoyl- β -*p*-bromophenylhydrazine,
 $\text{NO}_2 \cdot \text{NBz} \cdot \text{N}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{NO}$,

obtained by maintaining an anhydrous benzene solution of the above salt at 0°, separates in pale straw-yellow laminae, m. p. 121—122° (decomp.), gives Liebermann's reaction, and decomposes in moist air with evolution of nitrous vapours. Towards water, it behaves like other nitronitrosohydrazines previously described (compare Abstr., 1908, i, 482; Ponzio and Charrier, Abstr., 1908, i, 582), the nitro-group being readily replaced by an atom of hydrogen, yielding β -nitroso- α -benzoyl- β -*p*-bromophenylhydrazine, $\text{NHBz} \cdot \text{N}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{NO}$, which separates in pale straw-yellow laminae, m. p. 123° (decomp.), gives Liebermann's reaction, and dissolves in concentrated sulphuric acid, yielding a wine-red solution; with alkalis, this compound forms salts, such as

$\text{NNaBz} \cdot \text{N}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{NO}$,

soluble in water to reddish-yellow solutions, whilst with hot water it behaves like other nitrosohydrazines (*loc. cit.*), losing the nitroso-group for a hydrogen atom and yielding α -benzoyl- β -*p*-bromophenylhydrazine. The latter compound can be readily converted back into its nitroso-derivative by the action of nitrous acid.

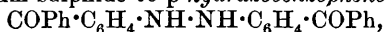
The transformation of the *p*-bromodiazobenzene salt of ω -dinitrotoluene into benzoylazo-*p*-bromobenzene, m. p. 71° (Freer, Abstr., 1899, i, 357, gave 69°), takes place readily in presence of an organic solvent, such as benzene, ether, carbon disulphide, or chloroform, containing a small proportion of water.

ω -*p*-Bromobenzeneazo- ω -dinitrotoluene, $\text{CPh}(\text{NO}_2)_2 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$, obtained in small proportion by the action of cold absolute alcohol on the *p*-bromodiazobenzene salt of ω -dinitrotoluene, or by leaving the latter in a desiccator for eight to ten days, crystallises from chloroform in orange-red laminae, m. p. 162—163° (decomp.).

All the results obtained confirm the structure of α -nitro- β -nitroso- α -benzoyl- β -*p*-bromophenylhydrazine, and also support the constitution, $\text{NO}_2 \cdot \text{CPh}(\text{NO}) \cdot \text{O} \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$, for the compound obtained by the action of *p*-bromodiazobenzene acetate on the potassium derivative of ω -dinitrotoluene.
T. H. P.

Alkaline Reduction of the Three Nitrobenzophenones.

PAUL CARRÉ (*Bull. Soc. chim.*, 1909, [iv], 5, 277—283. Compare *Abstr.*, 1907, i, 142).—When a boiling alcoholic solution of *o*-nitrobenzophenone is rapidly reduced by sodium hydroxide and zinc dust, the main product is *o*-aminobenzophenone; a small quantity of an inseparable mixture of *o*-hydrazodiphenylmethane and diphenylmethane-*o*-hydrazobenzhydrol is also obtained, which by treatment with concentrated hydrochloric acid yields from the former substance, 4:4'-diamino-3:3'-dibenzylidiphenyl, and from the latter, benzaldehyde and 4:4'-diamino-3-benzylidiphenyl, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{CH}_2\text{Ph}$, m. p. 209°, the salts of which are extensively dissociated in water. The reduction of *p*-nitrobenzophenone in a similar manner yields a mixture of *p*-azobenzophenone and *p*-azoxybenzophenone, which is reduced by boiling alcoholic ammonium sulphide to *p*-hydrazobenzophenone,



which separates from alcohol in white needles containing 1 mol. H_2O , m. p. 130° (162° when anhydrous); in boiling alcoholic solution the hydrazo-compound is oxidised by mercuric oxide to *p*-azobenzophenone, m. p. 219°, which separates from toluene in red leaflets and yields a phenylhydrazone, $\text{C}_{38}\text{H}_{30}\text{N}_6$, m. p. 130°.

m-Nitrobenzophenone, reduced in a similar manner, yields Elbs and Wogrintz's *m*-azoxybenzophenone. C. S.

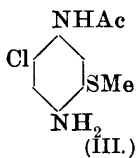
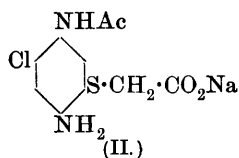
Preparation of *O*-Acetyl Derivatives of the Aminophenols and Aminonaphthols.

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 206455).—Excepting when the two substituents are in contiguous ortho-positions, the diazophenols and diazonaphthols can be readily acetylated with acetic anhydride in aqueous solutions containing only organic acids. The *O*-acetyl derivatives thus produced, although not isolated from solution, couple more readily with β -naphthol than the diazophenols themselves, giving azo-derivatives having distinctive colours. Solutions of 4-diazophenol and 8-diazo- α -naphthol-3:6-disulphonic acid were thus acetylated and the products coupled with alkaline β -naphthol. F. M. G. M.

[Preparation of Alkylthiol Derivatives of Primary Aromatic Amines.]

KALLE & Co. (D.R.-P. 205421).—Amines having the general formula (I), when diazotised and combined with heteronuclear α -naphthylaminesulphonic acids (such as the 1:6-sulphonic acid) and then hydrolysed to remove the acyl group, give rise to substantive bisazo-dyes, which when again diazotised on the cotton fibre can be coupled with β -naphthol to produce indigo shades of great fastness.

(I.) In the foregoing formula, Y may be an alkyl, acyl, or $\text{CH}_2 \cdot \text{CO}_2\text{H}$ radicle,



whilst X may be alkyl, alkyloxy, or halogen. Dyes from the bases (II) and (III) are described in the patent. F. M. G. M.

Hydrolysis of Egg-albumin by Sodium Hydroxide. ZDENKO H. SKRAUP and F. HUMMELBURGER (*Monatsh.*, 1909, 30, 125—145).—An investigation on protalbic acid and lysalbic acid (compare Paal, *Abstr.*, 1902, i, 653). It is found that lysalbic acid is not a simple substance, but consists of a substance precipitated by ammonium sulphate, which it is proposed to name *egg-lysalbic acid*, and another substance, not precipitated by this reagent, which is designated *lysalbin-peptone*. Protalbic acid, when treated with sodium hydroxide, yields egg-lysalbic acid and lysalbin-peptone, whilst egg-lysalbic acid under similar conditions yields ammonia, hydrogen sulphide, and a small quantity of a substance soluble with difficulty in water. It is shown, however, that when egg-albumin is hydrolysed by sodium hydroxide, one part of the molecule yields protalbic acid, whilst the other part gives rise to egg-lysalbic acid and lysalbin-peptone. In order to obtain further information on the relationship existing between protalbic acid, egg-lysalbic acid, lysalbin-peptone, and egg-albumin, the hydrolysis of these substances by sulphuric acid was investigated quantitatively. The following table gives the results obtained, in parts %:

	Egg- albumin.	Protalbic acid.	Egg- lysalbic acid.	Lysalbin- peptone.
Histidine	1·5	2·3	0·3	0·6
Arginine	2·9	0·4	0·2	0·3
Lysine	3·9	3·3	5·3	4·0
Tyrosine	2·4	3·4	2·6	1·1
Phenylalanine	5·8	12·0	5·2	2·4
Proline	1·5	2·0	1·0	0·3
Amino-acids	7·9	14·7	7·0	3·2
Glutamic acids.....	3·2	1·8	1·0	1·6

Egg-lysalbic acid and lysalbin-peptone give with α -naphthol and thymol the reactions which are characteristic of carbohydrate residues, whilst protalbic acid does not give these reactions.

It is therefore evident that the more stable part of the egg-albumin molecule which passes into protalbic acid consists chiefly of the aromatic components, whilst the so-called carbohydrate residue is present in the other part of the molecule, which breaks down into the albumose and peptone.

W. H. G.

The Serum Proteins of Different Animals. EMIL ABDERHALDEN and SLAVU (*Zeitsch. physiol. Chem.*, 1909, 59, 247—248).—Serum-albumin and serum-globulin were prepared by the ammonium sulphate method from goose's blood. Their yield of certain amino-acids was then determined, and the results compared with those from horse's blood may be given as follows in parts %.

		Tyrosine.	Glutamic acid.	Glycine.
Serum-albumin	horse	2·1	7·7	0·0
„ „	goose	1·95	8·1	0·0
Serum-globulin	horse	2·5	8·5	3·5
„ „	goose	2·45	9·1	3·62

W. D. H.

Hydrolysis of Vitellin from the Hen's Egg. THOMAS B. OSBORNE and D. BREESE JONES (*Amer. J. Physiol.*, 1909, **24**, 153—160).—The amounts of amino-acids obtained are very similar to those previously given by Abderhalden and Hunter; glycine, however, was not found. W. D. H.

Some Picryl Derivatives of Protein Fission Products. K. HIRAYAMA (*Zeitsch. physiol. Chem.*, 1909, **59**, 290—292).—Picryl chloride, dissolved in toluene, is shaken with one equivalent proportion of the amino-acid dissolved in an equivalent of alkali hydroxide. The *picryl* derivatives of *glycine*, $C_8H_6O_8N_4$, m. p. 161°, *valine*, $C_{11}H_{12}O_8N_4$, m. p. 171°, and of *aspartic acid*, $C_{10}H_8O_{10}N_4$, m. p. 137°, are well crystallised and very sparingly soluble in cold water. *Dipicryl-arginine* and *dipicrylhistidine* were also prepared, but are not so readily obtained pure. G. B.

Electrolytes and Colloids. The Physical State of Gluten. THOMAS B. WOOD and WILLIAM B. HARDY (*Proc. Roy. Soc.*, 1909, **B**, **81**, 38—43).—Gliadin (from wheat) is not soluble in distilled water or in acids of more than a certain critical concentration. Dilute acids, however, destroy the cohesion and form a hydrosol. Salt solutions in the presence of acids restore the cohesion. The effect of alkalis is similar to that of acids. The phenomena are in agreement with the hypothesis that the gluten hydrosol is a pseudo-solution in virtue of the existence of an electrical double layer round the gluten particles; this hypothesis receives support from the measurement of the potential difference between the two faces of the double layer by means of the electrical conductivity of the solutions of gluten in acids, and the rate of transport of the particles in a uniform electric field. G. B.

Action of Sulphur Dioxide on Flour and Cereals. M. CARTERET and GEORGES CARTERET (*Bull. Soc. chim.*, 1909, [iv], **5**, 270—272).—Flour or grain submitted to the action of sulphur dioxide for six hours suffers serious deterioration. The grain loses its germinating power, and both grain and flour, in consequence of some action of the sulphur dioxide on the gluten, yield a dough which can be kneaded only with difficulty and does not ferment with yeast; bread made from it is heavy and unfit for consumption. C. S.

Bleaching of Flour. E. F. LADD and H. P. BASSETT (*J. Biol. Chem.*, 1909, **6**, 75—86).—The modern process of bleaching or ageing flour by means of nitrogen peroxide is regarded as injurious. The bleached flour and the bread made from it are less susceptible to the action of digestive and other enzymes. It is suggested that the action on the gluten is a diazo-reaction, for nitrogen is evolved when the flour is treated with an acid. In extreme cases, the xanthoproteic reaction may be produced. The iodine absorption of the oil separated from patent flour is lessened by bleaching; the oil also contains nitrogen. W. D. H.

Oxyhæmoglobin of Different Animals. I. EMIL ABDERHALDEN and FLORENTIN MEDIGRECEANU (*Zeitsch. physiol. Chem.*, 1909, 59, 165—169).—The oxyhæmoglobin of mammals yields a high percentage of histidine; the relationship of this substance to the purine group suggests that in non-nucleated corpuscles it may play the part of a nuclear material; but this hypothesis was negatived by the finding that the hæmoglobin from the nucleated corpuscles of birds contains also a high percentage of the same base. The hæmoglobin of birds' corpuscles was prepared in crystalline form, and the purer the crystals the less phosphorus do they contain, which confirms the view so generally held, that phosphorus is due to admixture with nuclein.

W. D. H.

A New Hæmatin. FRANCESCO DE GRAZIA (*Biochem. Zeitsch.*, 1909, 16, 277—293).—In gastric digestion of blood in the presence of mineral or organic acids, or a mixture of both, a hæmatin is formed which resembles acid-hæmatin spectroscopically, but contains less nitrogen. The formula given is $C_{32}H_{38}O_7N_2Fe$.

W. D. H.

Synthesis of Paranuclein through the Agency of Pepsin and the Chemical Mechanics of the Hydrolysis and Synthesis of Proteins through the Agency of Enzymes. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1909, 5, 493—523. Compare Armstrong, *Abstr.*, 1906, i, 217; Neuberg, 1907, i, 808).—The synthesis of protein as effected by large quantities of trypsin or pepsin is not in agreement with the hypothetical reaction of pure catalysts in accelerating both forward and reverse reactions. Experiments with paranuclein and pepsin indicate that the velocity constant of hydrolysis diminishes with increasing substrate concentration; the velocity of synthesis falls off abruptly when the pepsin concentration falls below a certain value. Excess of pepsin shifts the equilibrium between paranuclein and its products. Synthesis occurs at a temperature 10° to 15° above the "death-point" of pepsin; the conclusion is drawn that the synthetic agent is not identical with the hydrolytic enzyme.

The relation between protein and enzyme is assumed to be reciprocal. The enzyme carries water into the protein molecule and, parting with it, recoups itself from the medium, while the protein splits up into the products of hydrolysis. The products of protein hydrolysis are assumed to part with water to the anhydrous form of the enzyme, whereby protein is regenerated and the hydrated form of the enzyme set free. A definite ratio between the velocities of these two reciprocal processes exists; this determines the final equilibrium of the system both as regards the relative proportions of protein and the products of its hydrolysis, and also the relative proportions of anhydrous (synthetic) and hydrated (hydrolytic) enzyme.

The relation between the anhydrous and hydrated forms of the enzyme may be similar to that between the internal salt and the hydrated forms of an amino-acid.

E. F. A.

Reducing Component of Nucleic Acid from Yeast. WILLIAM F. BOOS (*J. Biol. Chem.*, 1909, 5, 469—476).—The reducing substance obtained from yeast nucleic acid cannot be a pentose. Its simplest empirical formula is C_7H_8O . It is not yet identified.

W. D. H.

Alteration of Gelatin Solutions. Determination of their Gold Numbers and Ultra-microscopic Observations. W. MENZ (*Zeitsch. physikal. Chem.*, 1909, 66, 129—137).—In order to test the widely held view, recently disputed by Pauli, that the gelatinisation of gelatin solutions on cooling is attended by the separation of a new phase, the author has examined gelatin solutions of varying concentrations with the ultra-microscope and has determined their gold number according to Zsigmondy; the results show that not only the solidified mixtures, but even fairly weak solutions of gelatin, are heterogeneous.

According to Zsigmondy, the gold number of a protective colloid is the number of mgs. which is just insufficient to prevent a definite change of colour (in the present case from red to purple) in a dilute solution of colloidal gold on the addition of 1 c.c. of a 10% solution of sodium chloride. The preparation of a gold solution suitable for the experiments is fully described. It has been found that the gold numbers of solutions one day old of concentrations from 0.001% to 1% are the greater the more concentrated the solution. The numbers in the case of the concentrated solutions remain fairly constant on keeping, but those of the weakest solutions increase rapidly at first and then become constant. In the ultra-microscope, the solutions from 0.1% to 1% show a heterogeneous cone of light; the less concentrated solutions (from 0.01%) also show a light cone, which, however, is no longer resolvable, and in the weakest solution (0.001%) is only just noticeable.

From these observations the conclusions are drawn (1) that the protective action of the gelatin is due to the amicroscopic particles, or, perhaps, to the smallest particles visible in the ultra-microscope; the larger particles have little or no protective action; (2) the state of the gelatin in aqueous solution depends essentially on its concentration after the latest warming; it is not greatly altered by dilution with cold water.

Some experiments on the precipitation of colloidal gold by gelatin alone are described. Further, the phenomena observed when a gelatin solution solidifies under the ultra-microscope are described and figured.

G. S.

Comparative Investigation of the Composition and Structure of Various Kinds of Silk. II. The Mono-amino-acids of Canton Silk. EMIL ABDERHALDEN and LOTTE BEHREND (*Zeitsch. physiol. Chem.*, 1909, 59, 236—238).—The results are in close agreement with those obtained by Fischer and Skita for (Italian) silk-fibroin (*Abstr.*, 1901, i, 783). In the hydrolysis only traces of melanins remained undissolved. The phenylalanine is best purified as hydrochloride.

G. B.

Physical Constants of Peptones. L. LEMATTE and A. SAVÈS (*Compt. rend.*, 1909, 148, 553—554).—The densities, refractive indices, and freezing points of aqueous solutions of trypsinic peptones have been determined. Analysis of the peptones gave 16.8% nitrogen and 0.756% chlorine. If P is the number of grams of peptone contained in 100 c.c. of solution, the density at 15° is given by $D = 1 + P \times 0.003637$; the difference between the refractive index and that of water at 17.5° by $n = P \times 0.001869$, and the lowering of the freezing point by $\Delta = P \times 0.119$.
H. M. D.

Clupeone. ALBRECHT KOSSEL and FR. WEISS (*Zeitsch. physiol. Chem.*, 1909, 59, 281—284. Compare Abstr., 1907, i, 266).—This protone, obtained by boiling clupeine for three hours with 10% sulphuric acid, yields a crystalline picrolonate. After removal of the picrolonic acid, the regenerated base contains the same percentage of arginine-nitrogen, namely, 88%, as that found by Pringle in clupeone.
G. B.

Action of Some Acid Chlorides on Protamines. K. HIRAYAMA (*Zeitsch. physiol. Chem.*, 1909, 59, 285—289).— β -Naphthalenesulphonylclupeine and benzenesulphonylclupeine have respectively about half and the whole of the basic hydrogen replaced; both are amorphous. β -Naphthalenesulphonylclupeone, prepared from the crystalline picrolonate (compare preceding abstract), is crystalline, and has a composition corresponding with that of a diarginylmonoamino-acid, as supposed by Kóssel and Pringle (Abstr., 1907, i, 226); thus the sulphur and nitrogen content agree with that of a tetranaphthalenesulphonyl derivative of diarginylvaline, $C_{57}H_{63}O_{23}N_9S_4$. The benzenesulphonyl and β -naphthalenesulphonyl derivatives of sturine are amorphous.
G. B.

Composition and Derivation of Protamine. ALONZO E. TAYLOR (*J. Biol. Chem.*, 1909, 5, 389—398).—Salmine (the protamine of the salmon) yields on hydrolysis arginine, an aminovaleric acid, serine, and proline (Kossel and Dakin); Abderhalden adds leucine, alanine, and probably phenylalanine and aspartic acid to the list. With purified salmine, Abderhalden's results are not confirmed; he was possibly dealing with an impure product, such as is obtained from the unripe roe. A theory that the protamine is derived from the muscle-proteins is put forward; these are believed to be converted into the blood-proteins for transport, and these into protamines by the testis through the intermediate stage of histone.
W. D. H.

Synthesis of Protamine through Ferment Action. ALONZO E. TAYLOR (*J. Biol. Chem.*, 1909, 5, 381—388. Compare Abstr., 1907, i, 665).—Another successful experiment is recorded on the synthesis of a small amount of a protamine by means of tryptic action on the purified amino-acids separated from salmine.
W. D. H.

Electrical Migration of Enzymes. VICTOR HENRI (*Biochem. Zeitsch.*, 1909, 16, 473—474).—Polemical (compare Michaelis, this

vol., i, 277). The author has previously described an apparatus for the investigation of the electric migration of a number of enzymes. Stress is laid on the importance of first dialysing the enzyme solutions and controlling the freedom from electrolytes by conductivity measurements. Pancreas amylase alone migrates to the cathode; all other enzymes go to the anode. E. F. A.

Electrical Migration of Enzymes. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1909, 16, 475).—Polemical. A reply to Henri (see preceding abstract.) E. F. A.

Electrical Migration of Enzymes. II. Trypsin and Pepsin. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1909, 16, 486—488. Compare preceding abstracts).—Trypsin, in $\frac{1}{2}\%$ solution, after dialysis for twenty-four hours, was placed as the middle element of a cell having silver in sodium chloride as anode and zinc in zinc sulphate as cathode, and the current passed for twenty-four hours. In this time the enzyme migrates almost entirely to the anode. It behaves similarly in weak alkaline solution, but when the solution is made distinctly acid, the enzyme migrates to the cathode. The addition of sodium chloride to the neutral solution does not disturb the normal anode migration. The undialysed enzyme migrates mainly to the anode, but at the same time, to a slight extent, towards the cathode. These observations are in agreement with the amphoteric character of trypsin, in which, further, the electro-negative properties preponderate. Pepsin, either in neutral or acid solution, migrates to the anode. This, also, is in agreement with its strongly electro-negative character. E. F. A.

Are Pepsin and Rennin Identical? ALONZO E. TAYLOR (*J. Biol. Chem.*, 1909, 5, 399—404).—The theory that these two enzymes are identical cannot be proved by quoting Ehrlich's side-chain theory; its application to enzyme action is regarded as arbitrary and devoid of experimental basis.

It is possible to prepare a pepsin which has no rennetic properties, and to prepare a rennin without peptic properties. The data are best interpreted as indicating that the two enzymes are different substances.

In cancer of the stomach in man, rennet disappears at an early stage, but the gastric juice still digests protein. W. D. H.

Fermentative Cleavage of Polypeptides. VII. EMIL ABDERHALDEN, G. CAEMMERER, and LUDWIG PINCUSOHN (*Zeitsch. physiol. Chem.*, 1909, 59, 293—319. Compare Abstr., this vol., i, 275).—The present paper records a number of experiments on the influence of certain salts on the activity of peptolytic enzymes. Potassium cyanide, 1 in 50,000, has no effect; greater concentrations accelerate the cleavage until the concentration of 1% inhibits the action. Sodium fluoride has also an inhibiting effect, but in low concentrations accelerates. Magnesium sulphate has little or no effect, but magnesium chloride in high concentration is inhibitory; calcium chloride accelerates, but

strontium chloride is indifferent. The addition of glycerol or of *d*-, *l*-, and *dl*-alanine is inhibitory to the fermentation cleavage of *dl*-leucyl-glycine and of glycyl *l*-tyrosine by yeast juice; *d*-alanine is most active in this direction, especially at the temperature of 45°.

W. D. H.

Animal Invertins and Lactases. Their Specific Action. H. BIERRY (*Compt. rend.*, 1909, 148, 949—952).—A discussion of the results of work published elsewhere (*Compt. rend. Soc. Biol.*, 1906, 1908). Experiments have been carried out on the hydrolytic action of certain animal ferments on sucrose, raffinose, gentianose, stachyose, lactose, lactobionic acid, lactosazone, and lactose-carbamide. The ferments employed were obtained by extraction of the small intestine of dogs or foetal calves and the gastro-intestinal sac of the lobster and *Aplysia punctata*.

It is probable that the invertin obtained from the intestine of dogs is different from that secreted by the gastro-intestinal sac of molluscs. For invertins of this type, which bring about the separation of lævulose from sugars, the author proposes the name "lævulo-polyase." The gastro-intestinal sac of snails is capable of hydrolysing lactose, lactosazone, and lactobionic acid with formation of galactose. For diastases of this type, the name "lacto-bionase" is suggested. There are probably several species of diastases.

W. O. W.

The Influence of Magnesia on the Inversion of Sucrose [by Invertase] at Different Temperatures. J. TRIBOT (*Compt. rend.*, 1909, 148, 788—790. Compare this vol., i, 73).—Experiments were made with impure invertase with and without the addition of magnesia, and with invertase purified by twelve successive precipitations and leaving no perceptible residue on ignition. At temperatures above 30°, the action was somewhat accelerated by the presence of magnesia, and was much more rapid where impure invertase was used than where the invertase had been purified.

E. J. R.

Inversion of Sucrose and Maltose by Ferments. ALONZO E. TAYLOR (*J. Biol. Chem.*, 1909, 5, 405—408).—The results given confirm those of Hudson, that the inversion of sucrose, and probably of maltose, follows the course of a unimolecular reaction. This is contradictory to the statements of Mlle. Piloche (*J. Chim. Phys.*, 1908, 6, 229), but a recalculation of her results show they are not always regular; the reasons for the variations are not at present clear.

W. D. H.

Critical Hydroxyl Ion Concentrations in Diastatic Hydrolysis. CLARENCE QUINAN (*J. Biol. Chem.*, 1909, 6, 53—63).—Diastase obtained from three different sources maintains a constant relation to equivalent solutions of sodium carbonate and hydroxide. Evidence is adduced which makes it probable that the diastase concentration of the pancreatic juice very greatly exceeds that of saliva. Diastase is shown to be a very delicate indicator of the presence of free hydroxyl ions. It is possible to make a sharp quantitative distinction between various fluids containing diastase in terms of decinormal sodium hydroxide.

W. D. H.

Ionic Potentials of Salts and their Power of Inhibiting Lipolysis. R. H. NICHOLL (*J. Biol. Chem.*, 1909, 5, 453—468).—The power of the nitrates of various metals to inhibit the action of lipase on ethyl butyrate is a function chiefly of the energy content or ionic potential of the cations. This confirms Mathew's hypothesis on the subject.

W. D. H.

New Analogies between Natural and Artificial Oxydases. JULES WOLFF (*Compt. rend.*, 1909, 148, 946—949. Compare this vol., i, 279).—The paper contains details of experiments on the action of easily hydrolysable salts, which, in the presence of natural or artificial oxydases, appear to behave as co-enzymes in promoting the oxidation of certain substances, such as quinol, catechol, cochineal, orcinol, and the sulphonic acids of alizarin and orcinol. The salts examined included manganous acetate and the phosphates and citrates of sodium. Colloidal ferrous ferrocyanide was employed as the artificial oxydase, and was found to behave in the same way as Bertrand's laccase extracted from lucerne. The following are the chief conclusions arrived at: (1) Traces of dibasic phosphates accelerate oxidation, whilst larger quantities retard it. (2) Monobasic phosphates have no action. (3) Neutralisation of the alkalinity in the case of the phosphate stops the oxidation, which re-commences on the addition of fresh dibasic phosphate. (4) There is an optimum concentration of phosphate corresponding with a definite amount of enzyme. (5) Tribasic citrates behave as dibasic phosphates, but the acid citrates exert a paralysing influence on the oxidation.

W. O. W.

Preparation of Arsenophenols. FARBERWERKE VORM. MEISTER LUCIUS & BRÜNING (D.R.-P. 206456).—Arsenophenol, $\text{As}_2(\text{C}_6\text{H}_4\cdot\text{OH})_2$, a yellowish-brown powder, decomposing above 200° , is obtained by reducing sodium hydroxyphenylarsinate with a solution of sodium hyposulphite, sodium hydroxide, and magnesium chloride; its alkali derivative is soluble in water, and is precipitated therefrom by alcohol.

Arseno-o-cresol, $\text{As}_2(\text{C}_6\text{H}_3\text{Me}\cdot\text{OH})_2$, is similarly prepared from 4-hydroxy-*m*-tolylarsinic acid.

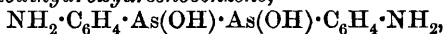
F. M. G. M.

Preparation of Derivatives of Phenylarsenious Oxide and Arsenobenzene. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 206057).—*p*-Aminophenylarsinic acid and its derivatives containing quinquivalent arsenic are reduced to derivatives containing this element in the trivalent condition, the products being far more toxic towards trypanosomes, either *in vitro* or *in vivo*, than are the organic derivatives of arsenic acid.

4-Aminophenylarsenious oxide, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}\cdot 2\text{H}_2\text{O}$, white needles or leaflets, evolving water at 80° and frothing at 100° , is produced by reducing 4-aminophenylarsinic acid with hydriodic and sulphurous acids, or with phenylhydrazine.

4:4'-Diaminoarsenobenzene, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{As}\cdot\text{As}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, pale yellow flakes, m. p. $139\text{--}140^\circ$, insoluble in water and the ordinary organic media, is produced by reducing atoxyl with stannous chloride.

4 : 4'-Diaminodihydroxyarsenobenzene,



pale yellow flakes, m. p. 227° , are obtained by reducing 4-amino-phenylarsenious oxide with sodium amalgam in methyl-alcoholic solution.

Phenylglycinearsinic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$, when reduced with alkaline sodium hyposulphite, gives rise to *arsenophenylglycine*, $\text{As}_2(\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, reddish-brown powder, soluble in aqueous sodium carbonate, but insoluble in dilute mineral acids and the ordinary organic media.

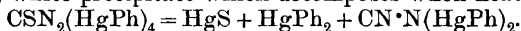
Oxalyl-p-aminophenylarsinic acid, white, crystalline powder, melting above 360° , is prepared by heating atoxyl with oxalic acid; when reduced with sodium hyposulphite, it yields *arseno-oxanilic acid*, $\text{As}_2(\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{H})_2$, a pale yellow precipitate, insoluble in organic solvents, but dissolving in aqueous alkalis. F. M. G. M.

New Organic Mercury Compounds. LEONE PESCI (*Gazzetta*, 1909, 39, i, 147—154).—Salts of mercuriphenyl react with ammonia to form compounds of phenylmercuriammine, $[(\text{HgPh})_2\text{NH}_2]$. Alkalis or silver oxide do not yield the hydroxide, but decompose the salts with evolution of ammonia.

Phenylmercuriammine acetate crystallises from methyl alcohol in needles, m. p. 179° ; it dissolves readily in alcohol, but sparingly in water. The *nitrate* crystallises from alcohol in brilliant scales, m. p. 230 — 235° (decomp.); the *sulphate* forms a crystalline, infusible precipitate, which forms a compound with ammonium sulphate,

$[(\text{HgPh})_2\text{NH}_2]_2\text{SO}_4\cdot(\text{NH}_4)_2\text{SO}_4$, crystallising in rectangular tablets. The *chloride* separates from water in microscopic prisms, m. p. 184° (decomp.).

The acetate reacts with carbon disulphide in alcoholic solution, forming mercury diphenyl: $(\text{HgPh})_2\text{NH}_2\cdot\text{C}_2\text{H}_3\text{O}_2 + \text{CS}_2 = \text{HgPh}_2 + \text{HgS} + \text{C}_2\text{H}_4\text{O}_2 + \text{CNSH}$. Thiocarbamide forms a white, amorphous compound, $\text{CSN}_2(\text{HgPh})_4$, darkening at 104 — 105° , insoluble in ordinary solvents: $(\text{HgPh})_2\text{NH}_2\cdot\text{C}_2\text{H}_3\text{O}_2 + \text{CS}(\text{NH}_2)_2 = \text{CSN}_2(\text{HgPh})_4 + 2\text{NH}_4\cdot\text{C}_2\text{H}_3\text{O}_2$. Boiling alcohol decomposes this compound, yielding mercuric sulphide, mercury diphenyl, and *mercuriphenylcyanamide*, an amorphous, white precipitate which decomposes when heated:



Diphenylthiocarbamide and phenylmercuriammine acetate yield mercuric sulphide, mercury diphenyl, and diphenylguanidine. *p*-Ditolylthiocarbamide reacts similarly. C. H. D.

Organic Chemistry.

Electron Conception of Valency in Organic Chemistry. JOHN M. NELSON and K. GEORGE FALK (*School of Mines Quart.*, 1909, 30, 179—198).—J. J. Thomson (*Corpuscular Theory of Matter*, 1907) has suggested that the valency of an element depends on the number of electrons which can be transferred to or from an atom of the element by the action of the atoms of other elements. On this view the valency lines, being tubes of electric force, are supposed to have direction, the direction of transfer of the (negative) electron being indicated by an arrow. In methane, for example, the four lines are directed towards the carbon, in carbon tetrachloride away from the carbon, the difference between the two extreme states of carbon being eight electrons. The authors have extended these considerations to a number of organic compounds, and explain the existence of a number of geometrical isomerides without taking into account spatial relations.

In the case of ethane, one carbon atom has a charge of four, the other of two, negative electrons, so that one methyl group is regarded as being positively charged compared with the other. The behaviour of triphenylmethyl as an electrolyte may be accounted for on similar lines in solution $C(C_6H_5)_3$ ions, positive and negative, being present.

For compounds containing double or triple linkings, the direction of the valencies may, to some extent, be deduced from the behaviour of the compound. From the additive reactions of propylene the conclusion is drawn that compounds of the type $R_2C:CR_2$ exist in the form $R_2C \equiv CR_2$. Of the isomeric substances of type $RR'C:CRR'$, the stable have the formula $RR'C \rightleftharpoons CRR'$; the unstable, $RR'C \rightleftharpoons CRR'$. In the case of cinnamic acid, there are three possibilities, $PhCH \rightleftharpoons CH \cdot CO_2H$, $PhCH \rightleftharpoons CH \cdot CO_2H$, and $PhCH \rightleftharpoons CH \cdot CO_2H$, which may correspond with the three known isomerides. The formula for benzene and the representation of compounds with triple linkings are also considered.

The difference between the two extreme states of nitrogen (from ammonia to nitric acid) is eight electrons; between that in ammonia, $N \equiv H_3$, and nitrous acid, $O \rightleftharpoons N \rightarrow O \leftarrow H$, six electrons. Hydrazine is thus represented $H_2 \rightleftharpoons N \rightarrow N \rightleftharpoons H_2$, which accounts for the apparent difference in the behaviour of the nitrogens. As regards the diazo-compounds, reasons are given for the assignation of the following

$$R-N \equiv N$$

formulæ: \downarrow for diazonium salts, $R-N \rightleftharpoons N \cdot X$ for *syn*-compounds, and $R \cdot N \rightleftharpoons N \cdot X$ for *anti*-compounds.

The representation of isomeric ketones and oximes is also discussed.
G. S.

γ -Methylheptane. LATHAM CLARKE (*J. Amer. Chem. Soc.*, 1909, 31, 558—561).—In continuation of a study of the octanes (this vol., i, 125,

and earlier abstracts), γ -methylheptane has been prepared. This hydrocarbon has previously been obtained in an impure state by Welt (Abstr., 1895, ii, 97) by treating a mixture of amyl and ethyl iodides with sodium.

When methyl *n*-butyl ketone, obtained by the hydrolysis of ethyl *n*-propylacetoacetate, is treated with magnesium ethyl bromide, γ -methyl- γ -heptanol, $\text{CH}_2\text{Me}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\text{Pr}^a$, b. p. 161—162°/763 mm., is produced as a colourless liquid with a eucalyptus-like odour. On converting this compound into the corresponding iodide and reducing the latter, γ -methylheptane, $\text{CH}_2\text{Me}\cdot\text{CHMe}\cdot\text{CH}_2\text{Pr}^a$, b. p. 117·6°/760 mm., is obtained as a colourless, mobile liquid, which has D_{15}^{25} 0·7167 and n_D^{25} 1·4022. The hydrocarbon attacks mercury with formation of a black substance. E. G.

Diisobutyl or β -Dimethylhexane. LATHAM CLARKE (*J. Amer. Chem. Soc.*, 1909, 31, 585—590).—The values assigned to the physical constants of β -dimethylhexane by different observers show considerable variation. The synthesis of the hydrocarbon has therefore been carried out by two distinct methods, and the product carefully purified.

The first method consists in treating isobutyl iodide with sodium, whilst the second is as follows. Methyl isoamyl ketone, prepared by the hydrolysis of ethyl isobutylacetoacetate, is treated with magnesium methyl iodide, and β -dimethyl- β -hexanol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Pr}^b$, b. p. 152—154°/760 mm., is thus obtained. This compound is converted into the corresponding iodide, which, on reduction, yields β -dimethylhexane as a colourless, mobile liquid with a pleasant odour. The hydrocarbon obtained by the first method had b. p. 108—108·3°/760 mm., D_{15}^{25} 0·6989, and n_D^{25} 1·3926, whilst that obtained by the second method had b. p. 108·3—108·5°, D_{15}^{25} 0·6993, and n_D^{25} 1·3935. The first method is the quicker and simpler, but the second yields a purer product. E. G.

Preparation of Pure Ethyl Alcohol. W. PLÜCKER (*Zeitsch. Nahr. Genussm.*, 1909, 17, 454—458).—Of the many methods which have been proposed for the preparation of pure ethyl alcohol, the one which yields the best results consists in boiling the alcohol under a reflux apparatus for about ten hours after the addition of about 7% of sodium hydroxide; the alcohol is then distilled from the alkali. Metallic calcium affords the best means of dehydrating alcohol.

W. P. S.

Derivatives of the Amyl Alcohols from Fusel Oil. V. WILLY MARCKWALD and ERNST NOLDA (*Ber.*, 1909, 42, 1583—1594. Compare Abstr., 1904, i, 362).—The tendency to the formation of mixed crystals, which is shown by mixtures of derivatives of *d*-amyl alcohol and isoamyl alcohol (*loc. cit.*), is still more pronounced in the case of derivatives of *d*- and of *l*-amyl alcohols. Since the latter is unknown, the experiments have been performed with derivatives of the purest obtainable commercial (95%) *d*-amyl alcohol and of *r*-amyl alcohol prepared from formaldehyde and magnesium *sec*-butyl bromide.

The freezing-point curve of a ψ -racemic mixture is generally a

horizontal straight line. This is shown to be the case with *d*- and *r*-1-amy1 3-nitrophthalates, the m. p. of the esters and of their mixtures being 116°; with *d*- and *r*-2-amy1 3-nitrophthalates, m. p. 155°, and with *d*- and *r*-amy1 phenylcarbamates, m. p. 31°. The solubility curve of aqueous solutions of the barium salts of *d*- and *r*-amy1-sulphuric acids is also rectilinear. The freezing-point curve of a ψ -racemic mixture may, however, show a maximum or a minimum. The only recorded case of the first kind is Adriani's carboximes (Abstr., 1900, ii, 462). The authors have discovered the first instance of the second type in the amy1 carbamates. Mixtures of *d*-amy1 carbamate, m. p. 62·2° (not 61°: *loc. cit.*) and *r*-amy1 carbamate, m. p. 51·3°, form an unbroken series of mixed crystals, and the m. p. curve, which is neither parabolic nor hyperbolic, shows a minimum. *d*- and *r*- β -Methylvaleramides, $\text{CHMeEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, which contain an atom of oxygen less than the preceding carbamates, do not exhibit the same behaviour; the amides and also their mixtures have the same m. p., 126°. The active amide is obtained by converting *d*-amy1 iodide into the nitrile, $\text{C}_5\text{H}_{11}\cdot\text{CN}$, b. p. 152°, D_4^{25} 0·8077, $[\alpha]_D + 7\cdot62^\circ$, which is changed by concentrated hydrochloric acid into the amide. *r*- β -Methylvaleramide and the isomeric *isohexoamide*, $\text{CH}_2\text{Pr}^\beta\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, m. p. 119°, form a series of mixed crystals, and the m. p. curve is parabolic. The preceding active amide yields on hydrolysis by 70% sulphuric acid at 110° *d*- β -methylvaleric acid, identical with Neuberg and Rewald's *d*-hexoic acid (Abstr., 1908, i, 310; compare also Hardin and Sikorsky, *ibid.*, ii, 470).

The problem of racemisation during chemical transformations has been attacked. Pure *d*-amy1 alcohol and hydrogen bromide yield *d*-amy1 bromide, $[\alpha]_D + 3\cdot68^\circ$. Commercial 95% *d*-amy1 alcohol and phosphorus tribromide yield *d*-amy1 bromide, $[\alpha]_D + 4\cdot05^\circ$, or $4\cdot25^\circ$ allowing for the presence of 5% of *isoamy1* bromide. *d*-Amy1 alcohol, having $\alpha_D - 2\cdot29^\circ$ in a 0·5 dm. tube, is converted into *d*-amy1 bromide, which is changed by silver acetate at 150° into *d*-amy1 acetate, the hydrolysis of which by 22% sodium hydroxide for twenty-two hours yields *d*-amy1 alcohol having α_D only $-1\cdot08^\circ$. The racemisation is not due to the hydrolysis of the acetate, because *d*-amy1 acetate, prepared from the alcohol and acetic acid, regenerates by hydrolysis under the same conditions *d*-amy1 alcohol of unchanged rotation $-2\cdot29^\circ$. The proof that the racemisation occurs during the action of the silver acetate on the bromide is furnished by converting the bromide by alcoholic sodium iodide into the more reactive iodide, and converting the latter by alcoholic potassium acetate into *d*-amy1 acetate, which by hydrolysis yields *d*-amy1 alcohol, $\alpha_D - 2\cdot13^\circ$ (0·5-dm. tube). When the iodide is treated with silver acetate, the *d*-amy1 alcohol finally obtained has $\alpha_D - 1\cdot53^\circ$, whilst the alcohol obtained directly from the iodide by moist silver oxide has $\alpha_D - 1\cdot49^\circ$.

C. S.

Reductions with Sodium Amyloxide. OTTO DIELS and RICHARD RHODRUS (*Ber.*, 1909, 42, 1072—1076).—Sodium amyloxide acts as an active reducing agent, being itself converted into *isovaleric* acid and other compounds. Benzylideneaniline is easily converted into benzyl-aniline. Azobenzene is reduced within a few minutes to hydrazo-

benzene, *iso*amylaniline being also formed, possibly owing to the condensation of *isovaleraldehyde* to a Schiff's base, which is subsequently hydrated. When the reduction is prolonged, *iso*amylaniline is the sole product. Cinnamic acid is reduced to phenylpropionic acid.

Indigotin is instantly converted into a yellow product; anthraquinone yields oxanthranol, which is reconverted into indigotin on exposure to air; benzophenone forms benzhydrol.

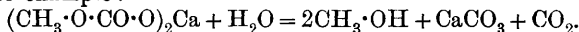
The superior reducing activity of a mixture of sodium and amyl alcohol to one of sodium and ethyl alcohol is usually attributed to the higher reaction temperature in the former case. That this is not the case is indicated by the fact that benzophenone is not reduced by sodium ethoxide at 140°, but easily reduced by sodium amyloxide at 90°.

E. F. A.

The Scission of Sugars. IV. The Electrolysis of Glycerol and Glycol. WALTHER LÖB and GEORG PULVERMACHER (*Biochem. Zeitsch.*, 1909, 17, 343—355).—Glycerol, on subjection to electrolysis in 5% sulphuric acid with cooled lead anodes, yielded formaldehyde, formic acid, non-volatile acids, of which the calcium salts contained from 19—26% calcium, and a pentose. Similar results were obtained by direct oxidation of glycerol with lead peroxide. Glycol, under similar conditions of electrolysis, yielded formaldehyde, formic and carbonic acids, and non-volatile acids, which have not been identified.

S. B. S.

Union of Carbon Dioxide with Alcohols, Sugars, and Hydroxy-acids. MAX SIEGFRIED and S. HOWWJANZ (*Zeitsch. physiol. Chem.*, 1909, 59, 376—404).—Experiments have shown that when carbon dioxide is led at 0° into milk of lime containing aliphatic hydroxy-derivatives, a certain amount of the dioxide combines with the hydroxy-compound. This is proved by the fact that the filtrate when kept, or when warmed, deposits calcium carbonate, and that the amount of this carbonate is constant within certain limits for each hydroxy-compound. The phenomena are not due to the formation of a colloidal solution of calcium carbonate, since in the presence of an excess of calcium hydroxide the solution is first alkaline, but, on standing, becomes distinctly acid. The hydroxy-derivatives combine with the carbon dioxide, yielding acids, for example: $\text{CH}_3\cdot\text{OH} \rightarrow \text{CH}_3\cdot\text{O}\cdot\text{CO}\cdot\text{OH}$, which are converted into calcium salts. These salts are soluble, but when their solutions are kept or heated, decomposition occurs, for example:



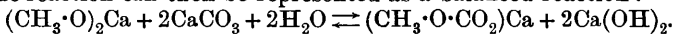
The calcium salts of *glycerolcarbonic acid* and of *ethyleneglycolcarbonic acid* have been prepared. The analytical data for the former agree fairly well with the formula $\text{OH}\cdot\text{CH}_2\cdot\text{CH} \begin{array}{c} \text{O}\cdot\text{CO} \text{---} \text{O} \\ \text{CH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{O} \end{array} \text{Ca}$, and

for the latter with the formula $\begin{array}{c} \text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{O} \\ | \\ \text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{O} \end{array} \text{Ca}$.

Precipitated calcium carbonate does not react with hydroxy-derivatives, except in the presence of the calcium hydroxide, and it is possible that the hydroxyl derivative reacts with the calcium

hydroxide, forming a compound of the type $(\text{CH}_3\cdot\text{O})_2\text{Ca}$, the hydrolysis of which is prevented to a large extent by the excess of alkali present.

The reaction can then be represented as a balanced reaction :



The reaction $2\text{CH}_3\cdot\text{OH} + \text{Ca}(\text{OH})_2 + 2\text{CO}_2 = (\text{CH}_3\cdot\text{O}\cdot\text{CO}_2)\text{Ca} + 2\text{H}_2\text{O}$ also takes place to a certain extent.

The following compounds combine with carbon dioxide : methyl, ethyl, propyl, butyl, *isobutyl*, *tert.*-butyl, and benzyl alcohols. Ethylene glycol, glycerol, erythritol, quercitol, mannitol, dulcitol, *l*-arabinose, xylose, dextrose, *l*-xylulose, *d*-galactose, sucrose, lactose, maltose, hydroxyacetic acid, α -lactic acid, paralactic acid, hydroxy-*iso*-butyric acid. The ratio $\text{CO}_2/\text{substance}$ has been determined in each case. The value is less than unity in the case of monohydroxy-derivatives, owing to the reversible nature of the reaction. J. J. S.

Oxonium Dibromides of Simple Ethers and their Constitution. WLADIMIR W. TSCHELINZEFF and W. K. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 131—145 ; *Ber.*, 1909, 42, 1531—1540).—The authors have investigated the properties and transformations of the compounds formed by bromine with ethyl and *isoamyl* ethers.

The former compound has in freezing acetic acid a molecular weight corresponding with the composition, Et_2OBr_2 , McIntosh's views (*Trans.*, 1905, 87, 784) concerning the constitution of this compound hence being inaccurate. The compound has D_4^{25} 1.7647, D_4^{25} 1.7168, D_4^{25} 1.6644, n_D 1.496. Taking for the oxygen atom of the compound the same atomic refraction as is possessed by hydroxyl oxygen, the molecular refraction is calculated to be 39.80, the actual value being 41.07 ; the difference is accounted for by oxonium oxygen having a different atomic refraction from hydroxyl oxygen, and by the influence exerted on the refraction by the bromine atoms in the dibromide. With magnesium ethyl iodide, the compound gives butane: $\text{Et}_2\text{O}\cdot\text{Br}_2 + 2\text{MgEtI} = \text{Et}_2\text{O} + 2\text{MgBrI} + \text{C}_4\text{H}_{10}$, the compound $\text{Et}_2\text{O}\cdot\text{Et}_2$ being probably an intermediate product. Similarly, with magnesium propyl iodide, hexane is obtained.

The heat of formation of Et_2OBr_2 from its constituents at 20° is 9.13 cal., and that of the corresponding compound of *isoamyl* ether, $(\text{C}_5\text{H}_{11})_2\text{OBr}_2$, 8.75 cal. The velocities of formation and of decomposition by water have been measured.

Of the various structural formulæ possible for these compounds, the authors give preference to $\begin{array}{c} \text{R} > \text{O} < \text{Br} \\ \text{R} > \text{O} < \text{Br} \end{array}$ or $\begin{array}{c} \text{R} > \text{O} < \text{Br} \\ \text{R} > \text{O} < \text{Br} \end{array}$. T. H. P.

Derivatives of Monohalogenated Ethers. D. GAUTHIER (*Ann. Chim. Phys.*, 1909, [viii], 16, 289—358).—In a preliminary paper (*Abstr.*, 1907, i, 20) the author has described the method of preparation of alkyloxy-nitriles of the type $\text{RO}\cdot\text{CH}_2\cdot\text{CN}$ (compare also Sommelet, *Abstr.*, 1907, i, 21) by the action of cuprous cyanide and Henry's chloromethyl alkyl ethers, $\text{RO}\cdot\text{CH}_2\text{Cl}$; the investigation has been extended to alkyloxy-nitriles of the type $\text{RO}\cdot\text{CHMe}\cdot\text{CN}$, and the extensive series of derivatives described in the original may be conveniently considered under the following headings : (i) alkyloxy-nitriles of the type

$\text{RO}\cdot\text{CH}_2\cdot\text{CN}$, and the corresponding amides, acids, and esters; (ii) chloroethyl alkyl ethers of the type $\text{RO}\cdot\text{CHMeCl}$, and the corresponding nitriles, amides, acids, and esters; (iii) alkyloxyketones of the type $\text{RO}\cdot\text{CHR}'\cdot\text{CO}\cdot\text{R}''$, obtained from the nitriles by means of the Grignard reaction; (iv) imino-ketones of the type $\text{RO}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{R}'$, obtained by the condensation of the nitriles with methyl ketones in the presence of sodium; (v) ethers of acetylenic glycols of the type $\text{RO}\cdot\text{CHR}'\cdot\text{C}\equiv\text{C}\cdot\text{CHR}'\cdot\text{OR}$, obtained from the chloro-alkyl ethers by condensation with acetylenic organomagnesium compounds; and the products derived from these compounds by the action of bromine, hydrogen, or sodium alkyl oxides.

A list of the compounds described under these several headings is appended.

(i) Ethoxyacetone nitrile (compare Sommelet, Abstr., 1907, i, 21), b. p. $131-132^\circ/732$ mm., D_4^{20} 0.9077, n_D^{20} 1.388; methoxyacetone nitrile (*loc. cit.*) has D_4^{20} 0.9373, n_D^{20} 1.380: the *amide* has m. p. 92° ; propoxyacetone nitrile (*loc. cit.*) has D_4^{20} 0.896, n_D^{20} 1.401: the *amide* has m. p. 63° ; isobutoxyacetone nitrile has D_4^{20} 0.873, n_D^{20} 1.404; isobutoxyacetic acid, $\text{C}_4\text{H}_9\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, has b. p. $216^\circ/730$ mm.: the *amide* has m. p. 76° ; isoamyl oxyacetone nitrile (*loc. cit.*) has D_4^{20} 0.877, n_D^{20} 1.414.

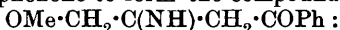
(ii) The following chloroethyl alkyl ethers were prepared by the action of hydrochloric acid on a mixture of the alcohol and paraldehyde: β -Chloroethyl propyl ether, $\text{C}_3\text{H}_7\text{O}\cdot\text{CHClMe}$, b. p. $112-115^\circ/731$ mm.; β -chloroethyl isobutyl ether, $\text{C}_4\text{H}_9\text{O}\cdot\text{CHClMe}$, b. p. $132-138^\circ/731$ mm.; β -chloroethyl isoamyl ether, $\text{C}_5\text{H}_{11}\text{O}\cdot\text{CHClMe}$, b. p. $162-165^\circ/721$ mm.; these ethers react with cuprous cyanide to yield the corresponding nitrile, and the following compounds were thus prepared: α -ethoxypropionitrile (compare Colson, Abstr., 1899, i, 251), b. p. $129-130^\circ/730$ mm., D_4^{16} 0.878, n_D^{16} 1.390; α -methoxypropionitrile, $\text{OMe}\cdot\text{CHMe}\cdot\text{CN}$, b. p. $118^\circ/729$ mm., D_4^{20} 0.893, n_D^{20} 1.382: the *amide*, m. p. 81° ; α -propoxypropionitrile, $\text{C}_3\text{H}_7\text{O}\cdot\text{CHMe}\cdot\text{CN}$, b. p. $150^\circ/727$ mm., D_4^{20} 0.866, n_D^{20} 1.398; α -isobutoxypropionitrile, $\text{C}_4\text{H}_9\text{O}\cdot\text{CHMe}\cdot\text{CN}$, b. p. $155-158^\circ/721$ mm., D_4^{20} 0.848, n_D^{20} 1.402.

(iii) isobutoxypropanone, $\text{C}_4\text{H}_9\text{O}\cdot\text{CH}_2\cdot\text{COMe}$, b. p. $157^\circ/730$ mm.; isoamyl oxypropanone, $\text{C}_5\text{H}_{11}\text{O}\cdot\text{CH}_2\cdot\text{COMe}$, b. p. $179-181^\circ/730$ mm.; α -methoxybutan- β -one, $\text{OMe}\cdot\text{CH}_2\cdot\text{COEt}$, b. p. $130-131^\circ/729$ mm.: the phenylhydrazone has b. p. $170^\circ/18$ mm.; α -methoxypentan- β -one, $\text{OMe}\cdot\text{CH}_2\cdot\text{COPr}^a$, b. p. $142-150^\circ/730$ mm.; β -methoxybutan- γ -one, $\text{OMe}\cdot\text{CHMe}\cdot\text{COMe}$, b. p. $114^\circ/727$ mm.: the phenylhydrazone forms yellow crystals, m. p. 57° ; β -ethoxybutan- γ -one, $\text{OEt}\cdot\text{CHMe}\cdot\text{COMe}$, has b. p. $128^\circ/727$ mm.; β -propoxybutan- γ -one, $\text{C}_3\text{H}_7\text{O}\cdot\text{CHMe}\cdot\text{COMe}$, b. p. $148-149^\circ/727$ mm.; β -methoxypentan- γ -one, $\text{OMe}\cdot\text{CHMe}\cdot\text{COEt}$, b. p. $133^\circ/729$ mm.; β -ethoxypentan- γ -one, $\text{OEt}\cdot\text{CHMe}\cdot\text{COEt}$, b. p. $145^\circ/727$ mm.

(iv) The imino-ketones prepared by the condensation of the alkyloxyacetone nitriles in the presence of sodium were isolated in the form of their copper salts; the ketones themselves were not obtained in a state of purity; ethoxyacetone nitrile condenses with (a) acetone to form the imino-ketone, $\text{OEt}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CH}_2\cdot\text{COMe}$, of which the copper salt has m. p. 158° : the copper salt of the methyl derivative, $\text{OEt}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CHMe}\cdot\text{COMe}$, is also described; with (b) methyl ethyl ketone to form the imino-ketone, $\text{OEt}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CH}_2\cdot\text{COEt}$,

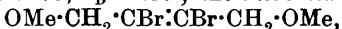
the *copper* salt of which has m. p. 135° ; with (c) acetophenone to form the imino-ketone, $\text{OEt}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CH}_2\cdot\text{COPh}$, of which the *copper* salt is described.

Methoxyacetoneitrile condenses with (a) acetone to form the compound $\text{OMe}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CH}_2\cdot\text{COMe}$, isolated in the form of its *copper* salt; with (b) acetophenone to form the compound

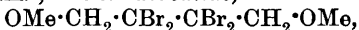


the *copper* salt has m. p. 190° .

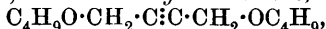
(v) $\alpha\delta$ -*Dimethoxy* - Δ^{β} -*butinene*, $\text{OMe}\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{OMe}$, b. p. $158^{\circ}/730$ mm., D_4^{22} 0.9575, n_D^{22} 1.437; the *dibromide*,



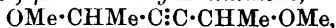
has b. p. $120^{\circ}/16$ mm.; the *tetrabromide*,



b. p. $162^{\circ}/17$ mm.; $\alpha\delta$ -*diethoxy* - Δ^{β} -*butinene*, $\text{OEt}\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{OEt}$, has b. p. 179 — $180^{\circ}/730$ mm., D_4^{22} 0.9156, n_D^{22} 1.435; $\alpha\delta$ -*dipropoxy* - Δ^{β} -*butinene*, $\text{C}_3\text{H}_7\text{O}\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{OC}_3\text{H}_7$, b. p. $150^{\circ}/20$ mm., D_4^{20} 0.8916, n_D^{20} 1.434; $\alpha\delta$ -*diisobutoxy* - Δ^{β} -*butinene*,



b. p. 159 — $160^{\circ}/20$ mm., D_4^{19} 0.8739, n_D^{19} 1.433; $\alpha\delta$ -*diisomamloxy* - Δ^{β} -*butinene*, $\text{C}_5\text{H}_{11}\text{O}\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{OC}_5\text{H}_{11}$, b. p. 190 — $192^{\circ}/15$ mm., D_4^{18} 0.8834, n_D^{18} 1.445; $\beta\epsilon$ -*dimethoxy* - $\Delta\gamma$ -*hexinene*,



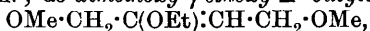
b. p. $160^{\circ}/730$ mm., D_4^{19} 0.8995, n_D^{19} 1.428; $\beta\epsilon$ -*diethoxy* - $\Delta\gamma$ -*hexinene*, $\text{OEt}\cdot\text{CHMe}\cdot\text{C}:\text{C}\cdot\text{CHMe}\cdot\text{OEt}$, b. p. 178 — $180^{\circ}/730$ mm., D_4^{19} 0.8944, n_D^{19} 1.435.

On direct hydrogenation in the presence of reduced nickel, the above acetylenic ethers yield the corresponding saturated derivative; in order to obtain as large a surface of nickel as possible, the author adopted the expedient of coating glass beads, 2 mm. diameter, with nickel by shaking the slightly moist beads with nickel oxide, which was then reduced at 330° . $\alpha\delta$ -*Dimethoxybutane*, b. p. 132 — $134^{\circ}/733$ mm. (compare Hamonet, Abstr., 1905, i, 403), obtained by reducing the corresponding butinene, was, at Bouveault's suggestion, converted into adipic acid by the successive action of carbon dioxide and water on the organomagnesium derivative,

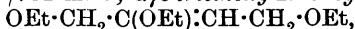


obtained from the $\alpha\delta$ -*dibromobutane* prepared by the action of hydrobromic acid on the ether; sebacic acid was also obtained in the course of this reaction. $\alpha\delta$ -*Diethoxybutane*, $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{OEt}$, has b. p. 155 — $157^{\circ}/730$ mm.

By the action of sodium alkylloxides on the ethers of acetylenic glycols, ethylenic ethers of the type $\text{OR}\cdot\text{CH}_2\cdot\text{C}(\text{OR}')\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OR}$ were obtained, which on hydrolysis furnish diketones; $\alpha\gamma\delta$ -*trimethoxy* - Δ^{β} -*butylene*, $\text{OMe}\cdot\text{CH}_2\cdot\text{C}(\text{OMe})\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OMe}$, has b. p. 179 — $180^{\circ}/730$ mm.; $\alpha\delta$ -*dimethoxy* - γ -*ethoxy* - Δ^{β} -*butylene*,



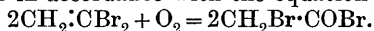
has b. p. 185 — $187^{\circ}/732$ mm.; $\alpha\gamma\delta$ -*triethoxy* - Δ^{β} -*butylene*,



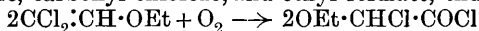
has b. p. 198 — $200^{\circ}/729$ mm.; $\beta\epsilon$ -*dimethoxy* - δ -*ethoxy* - $\Delta\gamma$ -*hexylene*, $\text{OMe}\cdot\text{CHMe}\cdot\text{C}(\text{OEt})\cdot\text{CH}\cdot\text{CHMe}\cdot\text{OMe}$, has b. p. 175 — $177^{\circ}/730$ mm.

M. A. W.

Slow Oxidation of *as*-Dichlorovinyl Ethyl Ether. WILLIAM FOSTER (*J. Amer. Chem. Soc.*, 1909, 31, 596—602).—Halogen derivatives of ethylene are capable of direct combination with oxygen with formation of acyl halides. Demole (Abstr., 1878, 401, 847) has shown, for example, that *as*-dibromoethylene undergoes oxidation on exposure to the air in accordance with the equation



A study of the action of dry oxygen on *as*-dichlorovinyl ethyl ether, prepared by Neher and Foster's method (this vol., i, 202), has shown that this compound is slowly oxidised with formation of ethoxychloroacetyl chloride, carbonyl chloride, and ethyl formate, thus:



and $\text{CCl}_2\text{:CH}\cdot\text{OEt} + \text{O}_2 \rightarrow \text{COCl}_2 + \text{H}\cdot\text{CO}_2\text{Et}$. Small quantities of ethyl chloride also seem to be produced. The mechanism of the reaction is discussed.

Ethoxychloroacetyl chloride, $\text{OEt}\cdot\text{CHCl}\cdot\text{COCl}$, b. p. about 150° under ordinary atmospheric pressure, and $53\text{--}54^\circ/11\text{ mm.}$, is a clear, colourless, fuming liquid, which has $D_4^{25} 1.2639$. When treated with sodium ethoxide, it is converted into ethyl diethoxyacetate. E. G.

Spontaneous Crystallisation of Chloroacetic Acid and its Mixtures with Naphthalene. HENRY A. MIERS and FLORENCE ISAAC (*Proc. Roy. Soc.*, 1909, 82, A, 184—187*).—Microscopic examination of crystals of chloroacetic acid obtained from fusion or solution has shown that there are three modifications, α , β , and γ , which melt respectively at 61.5° , 55° , and 50° . The α -form is the most stable, and the γ -form the least stable. The more stable modification crystallises with sharp edges in the solid mass of the less stable substance as if it were growing in a liquid.

The solubility and supersolubility curves of the three forms in water have been determined; the supersolubility curves are separated from each other by intervals of 5° to 6° .

Experiments with mixtures of chloroacetic acid and naphthalene have given no indication of the formation of mixed crystals, a result which is opposed to that obtained by Cady (Abstr., 1899, ii, 405). The four curves representing the solubility of naphthalene in liquid chloroacetic acid and of α -, β -, and γ -chloroacetic acids in liquid naphthalene, as well as the corresponding supersolubility curves, have been determined. The diagrammatic representation of these curves shows that no less than eight freezing points may be exhibited by the fused mixture of the two substances. Each modification of a polymorphous substance possesses therefore a definite temperature of spontaneous crystallisation in its mixtures with another substance which is not polymorphous. H. M. D.

Solidification of Mixtures of Water and *n*-Butyric Acid. M. H. FAUCON (*Compt. rend.*, 1909, 148, 1189—1192. Compare this vol., i, 130).—The freezing-point curve of the system water-butyric acid has been studied. The eutectic mixture, separating at -13.4° , has the molar composition $\text{C}_4\text{H}_8\text{O}_2 + 0.70\text{H}_2\text{O}$. No evidence has been obtained of the existence of definite hydrates. Above -3.8° , butyric

* and *Phil. Trans.*, 1909, A, 209, 337—377.

acid and water are miscible in all proportions ; below this temperature, mixtures containing 25—60% of acid are not homogeneous.

W. O. W.

Theory of Hydrolysis of Fats and Oils. J. KELLNER (*Chem. Zeit.*, 1909, 33, 453. Compare Balbiano, *Abstr.*, 1902, i, 450 ; 1903, i, 547 ; 1904, i, 216, 798 ; Lewkowitsch, *Proc.*, 1899, 15, 190, *Abstr.*, 1903, i, 225 ; and Marcusson, *Abstr.*, 1906, i, 924).—It is shown that when palm kernel oil is hydrolysed by an alkali hydroxide under atmospheric pressure, the reaction is quadrimolecular, and no mono- or di-glyceride is formed as an intermediate product. When the hydrolysis is accomplished in an autoclave in presence of zinc oxide, the reaction tends to become bi- and ter-molecular by the formation of lower glycerides as intermediate products.

T. A. H.

Oleic Acid. WILHELM FAHRION (*Chem. Zeit.*, 1909, 33, 429).—The author calls attention to the occasional presence of unsaponifiable matters, saturated fatty acids (palmitic acid), and linoleic acid in commercial "Acid Oleic puriss."

L. DE K.

Linolenic Acid of Linseed Oil. ERNST ERDMANN and FRED BEDFORD (*Ber.*, 1909, 42, 1324—1333).—The results of the investigation show that linseed oil contains α -linolenic acid, and that the solid hexabromide of this, on debromination, yields a mixture of α - and β -linolenic acids, the second isomeride being characterised by yielding a liquid tetrabromide.

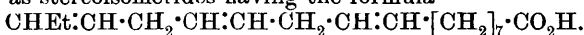
The mixed fatty acids of linseed oil, after removal of saturated acids by cooling to 0° and filtering, were found to distil for the most part unchanged at constant temperature under reduced pressure, and this method could not be used for their separation. The oleic acid was eliminated by converting the acids into their barium salts and treating these with a mixture of benzene, alcohol, and water, in which barium oleate is sparingly soluble. The mixture of acids, recovered from the barium salts, and now free from oleic acid, was esterified, and the quantity of hydrogen required for the complete reduction of the mixed esters by Sabatier and Senderens' catalytic process determined in a specially devised apparatus, described elsewhere (Bedford, *Inaug. Diss. Halle*, 1906). The sole product of the reduction was ethyl stearate, and the quantity of hydrogen absorbed indicated that in the mixture of esters used about 22% was ethyl α -linolenate, $C_{20}H_{34}O_2$, and the rest ethyl linoleate, $C_{20}H_{36}O_2$. α -Linolenic acid hexabromide, m. p. 179° (hexabromostearic acid), is readily prepared by adding bromine in small quantities to a well-cooled solution of the distilled, mixed fatty acids of linseed oil, separating the crystals, which form after twelve hours, and washing with ethyl acetate. The *ethyl* ester of the hexabromide, m. p. 151.5—152.5°, is crystalline, as is also the *methyl* ester, m. p. 157—158°.

When dissolved in alcohol and heated with zinc filings, the hexabromide is reduced, yielding a mixture of α - and β -linolenic acids, b. p. 157—158°/0.001—0.002 mm. The ethyl ester of the hexabromide is reduced under similar conditions, yielding a mixture of the *ethyl* esters of α - and β -linolenic acids, b. p. 132—133°/0.001 mm.

pressure, D_4^{20} 0.8919, n_D^{20} 1.46753, n_a^{20} 1.46458, n_β^{20} 1.47489. On reduction by Sabatier and Senderens' process, both the mixture of acids and the mixture of esters absorb the equivalent of six atoms of hydrogen, but on re-bromination, only a small proportion of the solid hexabromide (the additive product of the α -acid or its ester) is formed, the residue in the product of the reaction being a liquid tetrabromide (the additive product of the β -acid or its ester) in each case.

T. A. H.

Constitution of Linolenic Acid. ERNST ERDMANN, FRED BEDFORD, and FRITZ RASPE (*Ber.*, 1909, 42, 1334—1346. Compare preceding abstract).—Investigation of the decomposition products of the ozonide peroxides of α - and β -linolenic acids shows that the two acids must be regarded as stereoisomerides having the formula



The mixture of α - and β -linolenic acids, obtained by the reduction of the hexabromide of the α -acid (*loc. cit.*), when dissolved in hexahydro-toluene and treated with ozone at -20° , yields an *ozonide*, $\text{C}_{18}\text{H}_{30}\text{O}_{11}$, in the form of a colourless, viscous oil. If chloroform be used as a solvent, an *ozonide peroxide*, $\text{C}_{18}\text{H}_{30}\text{O}_{12}$, of gummy consistence is formed. The ethyl ester prepared from the mixed acids also yields an *ozonide peroxide* under similar conditions (compare Harries and Thieme, *Abstr.*, 1906, i, 226, 793).

The ozonide peroxide of the ethyl esters, when treated with cold water, is decomposed readily to the extent of about one-third, and this portion is regarded as derived from α -linolenic acid, whilst the residue, which decomposes when heated with water, is regarded as derived from the β -acid. The decomposition products in both cases are the same, namely, propaldehyde (*p*-nitrophenylhydrazone, m. p. 124 — 124.5°), malonic acid and the dialdehyde and semialdehyde corresponding to this, and ethyl hydrogen azelate with the corresponding semialdehyde. The carbon dioxide and acetaldehyde also formed are shown to be due to the decomposition of the malonic acid semialdehyde on heating.

T. A. H.

Catalytic Actions of Colloidal Metals of the Platinum Group. V. Reduction of Fats. CARL PAAL and KARL ROTH (*Ber.*, 1909, 42, 1541—1553. Compare *Abstr.*, 1908, i, 599).—It has been found possible completely to reduce castor oil, croton oil, olive oil, cotton seed oil, linseed oil, butter, and lard by repeating the treatment with palladium hydrosol and hydrogen a second time; sesamé oil and oleomargarin were not reduced completely. In all cases the volume of hydrogen required to effect complete reduction was greatly in excess of that calculated from the iodine values.

The product obtained from castor oil is a hard, white, crystalline mass, softening at 78° , m. p. 81° , which does not taste like the parent substance.

That derived from croton oil is a reddish-brown, hard fat, m. p. 49 — 51° , which does not possess the characteristic physiological properties of croton oil. Olive oil yields a hard, white, crystalline mass, which softens at 61° , m. p. 68.5° . A white, brittle substance, m. p.

65—69°, having an iodine value 2, was obtained by reducing sesame oil. Cotton seed oil yields an almost colourless and tasteless, hard, brittle substance, m. p. 56—60°. The product derived from linseed oil is a hard, white substance, m. p. 61—65°. Butter, when reduced completely, is converted into a white, fairly hard, brittle substance, which softens at 36°, m. p. 44°, tastes somewhat like cacao fat, and remains unaltered for several months. Lard is converted into an almost tasteless, hard, white tallow, m. p. 56—60°. The product (iodine value 1·2) obtained from oleomargarin is a white, brittle, crystalline, almost tasteless substance, which softens at 47°, m. p. 55°.

W. H. G.

Preparation of Ether Esters. M. H. PALOMAA (*Ber.*, 1909, 42, 1299—1302).—The methyl, ethyl, and propyl esters of methoxyacetic acid, when prepared by the action of the corresponding alkyl iodides on silver methoxyacetate, have b. p. 131·06—131·12°/763·1 mm., 143·9°/747·5 mm., and 165·2—165·4°/759·5 mm. respectively; these boiling points are in every case higher than those quoted by previous authors for samples prepared by the interaction of the sodium alkoxide with the esters of the chloro-substituted acids.

P. H.

The Walden Inversion. IV. EMIL FISCHER and HELMUTH SCHEIBLER (*Ber.*, 1909, 42, 1219—1228. Compare *Abstr.*, 1908, i, 857).—The object of this investigation was to ascertain whether the Walden-inversion is conditioned by the direct union of the carboxyl group with the asymmetric carbon atom. *l*- β -Hydroxybutyric acid yields a dextrorotatory β -chlorobutyric acid, which, when treated with silver oxide and water, is reconverted into the original *l*- β -hydroxybutyric acid. In this case, therefore, a Walden inversion does not take place, although it is possible, but very improbable, that a double inversion occurs.

Methyl l- β -hydroxybutyrate, $C_5H_{10}O_3$, is a colourless oil, b. p. 67—68·5°/13 mm.; the corresponding *inactive* ester has b. p. 67—68°/12—13 mm. The active ester, when hydrolysed, yields *l*- β -hydroxybutyric acid, $[\alpha]_D^{20} - 14·1^\circ (\pm 0·1^\circ)$ in water (compare Magnus-Levy, *Arch. expt. Path. Pharm.*, 1901, 45, 390; McKenzie, *Trans.*, 1902, 81, 1411), and when treated with phosphorus pentachloride yields dextrorotatory *methyl* β -chlorobutyrate, $C_5H_9O_2Cl$, a colourless oil, b. p. 48—51°/13 mm., $[\alpha]_D^{20} + 21·96^\circ$ to $+23·89^\circ$. The latter substance, when hydrolysed with alkalis, is converted chiefly into crotonic acid, whilst with acids, it yields dextrorotatory β -chlorobutyric acid, $C_4H_7O_2Cl$, a white, crystalline solid, b. p. 99—100°/13 mm., $[\alpha]_D^{20} + 27·1^\circ$ in water containing an equivalent amount of sodium hydroxide, $[\alpha]_D^{20}$ about $+42^\circ$ in water. The active methyl β -chlorobutyrate, when boiled with water for about forty hours, is converted into *l*- β -hydroxybutyric acid, although racemisation takes place to some extent during the reaction. The active β -chlorobutyric acid behaves in an analogous manner when treated with water and silver oxide at 37°.

W. H. G.

Oxidation of Ethyl Glycollate by Mercuric Oxide. HERMANN FINGER (*J. pr. Chem.*, 1909, [ii], 79, 368).—Warm solutions of the hydrochloride of ethyl glycollate in water, alcohol, pyridine, and

other solvents are oxidised by yellow mercuric oxide, forming a red syrup which does not contain mercury and forms a red potassium salt. The investigation of the substance is being continued. C. S.

Solubilities of the Oxalates of the Rare Earths. II. Solubility of Manganous Oxalate in Water, Ammonium Oxalate, Sulphuric or Oxalic Acid, and their Mixtures. OTTO HAUSER and FRITZ WIRTH (*J. pr. Chem.*, 1909, [ii], 79, 358—368. Compare Abstr., 1908, ii, 778).—Fractional crystallisation of the double manganese nitrates affords a rapid method for the separation of the metals of the cerium group, but it is essential that the double salt and the solution should be free from the simple manganese salt. Contrary to statements in the literature, manganous oxalate is not easily soluble in dilute acids; the precipitate obtained by the addition of oxalic acid to an acid solution of salts of manganese and the metals of the cerium group always contains manganese. To find an explanation of this fact, the solubility of manganous oxalate at 25° in water, oxalic acid, ammonium oxalate, sulphuric acid, and mixtures of sulphuric and oxalic acids has been determined.

Manganous oxalate occurs as a pink trihydrate, which changes at the ordinary temperature to a colourless, stable dihydrate; the anhydrous salt is pink. The solubility of the dihydrate in water at 25° is 0.00218 gram-mol. per litre. In oxalic acid or ammonium oxalate the solubility is greater, probably owing to the formation of a mangano-oxalic acid, $Mn(HC_2O_4)_2$; in accordance with this supposition, it is found that the solubility in sulphuric acid is greater than that in water, and is only slightly diminished by the addition of oxalic acid.

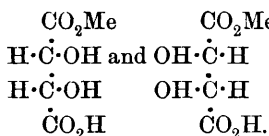
The most favourable condition for the separation of manganese from metals of the cerium group is the addition of a large excess of a concentrated solution of oxalic acid to a solution of the oxalates in an acid of 2.5 normality; the precipitate, however, even after a repetition of the process still contains manganese. C. S.

Velocities of Addition of Bromine to Itaconic, Citraconic, and Mesaconic Acids. I. ARNALDO PIUTTI and G. CALCAGNI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], 15, 18—22).—The authors have measured the velocities of addition of bromine to itaconic, citraconic, and mesaconic acids in aqueous solution at 25°. The addition takes place very rapidly in all three cases, and is complete for the maleic forms, citraconic (910 seconds) and itaconic (967 seconds) acids, after about equal times; for mesaconic acid, which is fumaroid in structure, 2715 seconds are taken. These results are in agreement with the observation of Bauer (Abstr., 1904, i, 841), Bauer and Moser (Abstr., 1907, i, 307), and Abati (this vol., i, 104), that with *cis*-forms the addition of bromine is far more rapid than with the corresponding *trans*-modifications. With citraconic and itaconic acids the constants of the reaction undergo very great variations, at first oscillating about a certain value, and then increasing more and more rapidly until the reaction is complete. With mesaconic acid, these variations are small, the constant increasing somewhat only towards the end of the reaction.

T. H. P.

Optically Active Methyl Hydrogen Esters of the Tartaric Acids. WILLY MARCKWALD and L. KARZAG (*Ber.*, 1909, 42, 1518—1522).—In accordance with theory, it has been found possible to prepare from *i*-tartaric acid two optically active methyl hydrogen

esters, which may be represented by the annexed formulæ. It is not yet known which formula belongs to which acid.



Methyl hydrogen *d*-tartrate crystallises with $1\text{H}_2\text{O}$, the presence of which has hitherto been overlooked (compare Walden, *Abstr.*, 1898, ii, 149). The optical rotatory power of the aqueous solution is $[\alpha]_{\text{D}}^{16.5} + 14.56^\circ (c=35)$, $[\alpha]_{\text{D}}^{17.5} + 16.05^\circ (c=21)$, $[\alpha]_{\text{D}}^{15.5} + 18.41^\circ (c=10.5)$, $[\alpha]_{\text{D}}^{18} + 18.71^\circ (c=6.3)$; the crystalline calcium salt, $(\text{C}_5\text{H}_7\text{O}_6)_2\text{Ca}\cdot 5\text{H}_2\text{O}$, $[\alpha]_{\text{D}}^{20} + 17.80^\circ (c=22.5)$, $+ 18.56^\circ (c=10.1)$, $+ 17.32^\circ (c=5.06)$, was also prepared.

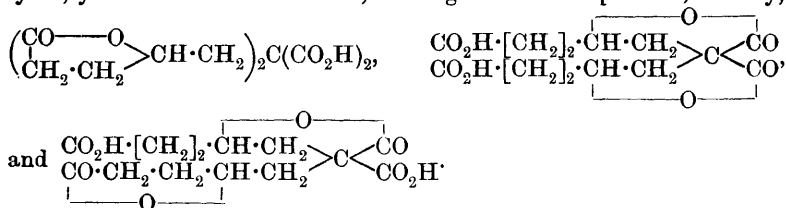
i-Tartaric acid, when boiled with an equal weight of methyl alcohol for six to seven hours, yields *r*-methyl hydrogen mesotartrate, $\text{C}_5\text{H}_8\text{O}_6$, a crystalline solid, m. p. 82° , and methyl mesotartrate, $\text{C}_6\text{H}_{10}\text{O}_6$, crystallising in glistening needles, m. p. 111° (compare Anschütz, *Abstr.*, 1888, 448). The calcium salt of the racemic hydrogen ester crystallises with $3\text{H}_2\text{O}$. The racemic compound is readily resolved through the strychnine salts. The strychnine salt of the levorotatory methyl hydrogen ester is soluble with difficulty in water, and has m. p. 118 — 119° ; the more soluble strychnine salt of the dextrorotatory ester has m. p. 97° . The dextrorotatory ammonium salt of the methyl hydrogen ester, $\text{C}_5\text{H}_7\text{O}_6\cdot\text{NH}_4$, forms colourless crystals, $[\alpha]_{\text{D}}^{21} + 13.28^\circ (c=30)$, $+ 17.08^\circ (c=12)$, $+ 18.09^\circ (c=6)$; the corresponding calcium salt, $(\text{C}_5\text{H}_7\text{O}_6)_2\text{Ca}\cdot 4\text{H}_2\text{O}$, forms white crystals, $[\alpha]_{\text{D}} + 6.7^\circ (c=6)$, and when decomposed with oxalic acid yields levorotatory methyl hydrogen mesotartrate, obtained as a syrup, $[\alpha]_{\text{D}}^{17} - 5.43^\circ (c=9.2)$.

The levorotatory ammonium salt has $[\alpha]_{\text{D}} - 20.83^\circ (c=6)$; the corresponding calcium salt has $[\alpha]_{\text{D}} - 7.3^\circ (c=5)$. W. H. G.

Application of δ -Chlorovalerolactone in the Preparation of Acids and Lactones. HERMANN LEUCHS and ERNESTO MOBIS (*Ber.*, 1909, 42, 1228—1238. Compare *Abstr.*, 1908, i, 510).— δ -Chlorovalerolactone may be employed with great advantage in the preparation of valerolactone and δ -hydroxyvalerolactone; in the first case the chloro-compound is treated with phosphorus and hydriodic acid, whilst in the second it is acted on by alkalis. δ -Chlorovalerolactone reacts with potassium cyanide in alcoholic solution, yielding δ -cyanovalerolactone, which is, however, almost entirely converted by the action of more potassium cyanide into $\delta\gamma$ -dicyanobutane- α -carboxylic acid. The latter substance when hydrolysed yields butane- α,β,δ -tricarboxylic acid, this being the best method of obtaining this acid. Ethyl sodiomalonate reacts with δ -chlorovalerolactone, yielding

two lactone esters, $\begin{array}{c} \text{CO} \text{---} \text{O} \\ | \quad \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2$ and $\begin{array}{c} \text{CO} \text{---} \text{O} \\ | \quad \diagup \\ (\text{CH}_2 \cdot \text{CH}_2) \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{Et})_2$. The latter substance, when hydro-

lysed, yields two isomeric acids, although three are possible, namely,



Ethyl αβ-dicyanobutane-δ-carboxylate, $\text{C}_9\text{H}_{12}\text{O}_2\text{N}_2$, prepared by acting on an alcoholic solution of δ-chlorovalerolactone with potassium cyanide and treating the product so formed with an alcoholic solution of hydrogen chloride, is a colourless, viscid oil, b. p. 198—200°/14 mm. (corr.); the corresponding *acid* was obtained as a viscous, non-crystalline mass; the *sodium* salt, $\text{C}_7\text{H}_7\text{O}_2\text{N}_2\text{Na}$, forms small needles; the *silver* salt, $\text{C}_7\text{H}_7\text{O}_2\text{N}_2\text{Ag}$, was prepared and analysed; the *amide*, $\text{C}_7\text{H}_9\text{ON}_3$, crystallises in large, hexagonal plates, m. p. 90—91° (corr.).

δ-Cyanovalerolactone was not isolated from the product obtained by the interaction of δ-chlorovalerolactone and potassium cyanide, but its presence was demonstrated by conversion into γ-hydroxyadipic acid

lactone, $\begin{array}{c} \text{CO} \text{---} \text{O} \\ | \quad \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, microscopic crystals, m. p. 201—202° (corr.). The latter substance is converted by alcoholic hydrogen chloride and subsequent treatment with alcoholic ammonia into *pyrrolidone-α-acetamide*, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad \diagup \\ \text{CO} \text{---} \text{NH} \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, crystallising in colourless needles and thin prisms, m. p. 149—150° (corr.).

The *lactone ester*, $\text{C}_{12}\text{H}_{18}\text{O}_6$, mentioned previously, is a heavy oil, b. p. 218—220°/14 mm.; the corresponding *acid* was obtained as a colourless syrup; the *silver* salt, $\text{C}_8\text{H}_9\text{O}_7\text{Ag}$, was prepared and analysed; the *amide*, $\text{NH}_2 \cdot \text{CO} \cdot \left[\text{CH}_2 \right]_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{CO} \cdot \text{NH}_2)_2$, crystallises in needles and small prisms, m. p. 154—155° (decomp., corr.).

The *lactone ester*, $\text{C}_{17}\text{H}_{24}\text{O}_8$, crystallises in tufts of colourless needles, m. p. 122—123° (corr.); the *amide*, $\text{C}_{13}\text{H}_{18}\text{O}_6\text{N}_2$, crystallises in four-sided plates, m. p. 239—240° (corr.).

The ester when hydrolysed yields a mixture of two isomeric *acids*, $\text{C}_{13}\text{H}_{16}\text{O}_8$; the one crystallises in colourless, iridescent, hexagonal leaflets or long needles, m. p. 235—236°, at which temperature it loses CO_2 ; the other crystallises in colourless, broad prisms or four-sided plates, m. p. 180—181°, and loses carbon dioxide above this temperature.

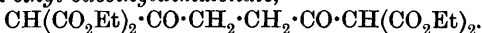
W. H. G.

Dibasic Ketonic Acids. II. Ethyl α-Oxalylglutarate. α-Keto-adipic Acid. HENRI GAULT (*Compt. rend.*, 1909, 148, 1113—1115. Compare Abstr., 1908, i, 713; this vol., i, 134).—Condensation of ethyl oxalate with ethyl glutarate is brought about by sodium ethoxide in ethereal solution with formation of a mixture of ethyl 4:5-diketocyclopentane-1:3-dicarboxylate (Dieckmann, Abstr., 1894, i, 324) and

ethyl α-oxalylglutarate, $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO} \cdot \text{CO}_2\text{Et}) \cdot \text{CO}_2\text{Et}_2$. Under certain conditions, only the latter is obtained. The new ester loses carbon monoxide when distilled in a vacuum, and forms ethyl α-carboxyglutarate (Emery, Abstr., 1891, i, 54). On hydrolysis, it yields α-ketoadipic acid, $\text{CO}_2\text{H} \cdot \text{CO} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2\text{H}$, m. p. 124°. W. O. W.

Action of Chlorides of Dibasic Acids on Ethyl Sodiomalonate. JOHANNES SCHEIBER (*Ber.*, 1909, 42, 1318—1323).—This work was undertaken with a view to the preparation of diketonic acids to be used in further syntheses.

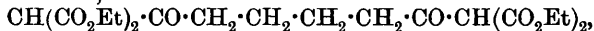
Succinyl chloride reacts with ethyl sodiomalonate to form a mixture of *ethyl 2:5-diketocyclopentane-1:1-dicarboxylate*, $\begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ | \\ \text{CH}_2 \cdot \text{CO} \end{array} > \text{C}(\text{CO}_2\text{Et})_2$, m. p. 68°, and *ethyl succinyldimalonate*,



The former dissolves in most organic solvents, but not in water or aqueous alkalis, and gives no coloration with ferric chloride. It reacts with phenylhydrazine in acetic acid to form a *pyrazolone* derivative, $\text{C}_{21}\text{H}_{20}\text{O}_3\text{N}_4$, m. p. 177°, which is crystalline and gives an intense violet coloration with ferric chloride. Ethyl succinyldimalonate was freed from the associated substance by treatment with a current of steam, and was then obtained as an oil. It dissolves unchanged in alkalis, gives a red coloration with ferric chloride, and yields a *dipyrzalone* derivative, $\text{C}_{26}\text{H}_{26}\text{O}_6\text{N}_4$, m. p. 188°, with phenylhydrazine in acetic acid.

Glutaric chloride reacts with ethyl sodiomalonate to form *ethyl glutaryldimalonate*, $\text{CH}(\text{CO}_2\text{Et})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}(\text{CO}_2\text{Et})_2$, which was obtained as a viscid oil. It gives a red coloration with ferric chloride, and with phenylhydrazine in acetic acid reacts to form a *dipyrzalone* derivative, $\text{C}_{27}\text{H}_{28}\text{O}_6\text{N}_4$, m. p. 118°, crystallising in pale yellow leaflets.

Adipic chloride condenses with ethyl sodiomalonate to give *ethyl adipyldimalonate*,



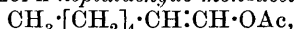
which was obtained as a viscous oil. It is hydrolysed readily by ammonia and by aniline, yielding respectively the amide and anilide of adipic acid. With phenylhydrazine in cold acetic acid it yields a *dipyrzalone* derivative, $\text{C}_{23}\text{H}_{30}\text{O}_6\text{N}_4$, m. p. 124°. T. A. H.

Acetalyl Sulphide. EMIL FISCHER (*Ber.*, 1909, 42, 1070—1071).—*Acetalyl sulphide*, $\text{S} \cdot [\text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_2$, is prepared by heating chloroacetal and potassium sulphide in concentrated aqueous-alcoholic solution in an autoclave at 130°. It is a colourless liquid, b. p. 143—147°/11 mm., or 280°/750 mm. (corr.; decomp.), easily soluble in organic solvents and distinctly so in water. E. F. A.

Preparation of Acraldehyde. GUSTAF FR. BERGH (*J. pr. Chem.*, 1909, [ii], 79, 351—357).—Five hundred grams of a mixture of 19 parts of glycerol, D 1.23, and one part of phosphoric acid, D 1.7, are placed in a metal still of 4 litres capacity, which is attached through a short condenser to a short-necked flask (750 c.c.) containing 100 grams

of sodium chloride immersed in a water-bath. The flask is attached through a long condenser to a receiver, consisting of an ordinary distilling bulb (300 c.c.) containing 15—20 grams of calcium chloride which has been treated with carbon dioxide. During the preparation, the water in the bath is kept boiling gently. The impurities are retained in the flask, and the acraldehyde which collects in the receiver is obtained pure by a single distillation. The yield is about 28%, the same as that obtained by Redtenbacher's potassium hydrogen sulphate method, but the author's process possesses the advantages that dehydrated materials need not be used, larger quantities can be employed, and the distillation can be commenced immediately after mixing. C. S.

Constituents of Ethereal Oils. *enol-n-Heptanal Acetate and enol-n-Octanal Acetate.* FRIEDRICH W. SEMMLER (*Ber.*, 1909, 42, 1161—1163. Compare this vol., i, 239).—When *n*-heptaldehyde is boiled with acetic anhydride and sodium acetate, the products are unaltered aldehyde, *enol-n-heptaldehyde monoacetate*,



and the *diacetate*, $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{OAc})_2$. The yield of enolic acetate is about 50%. It is a colourless oil, b. p. 76—79°/10 mm., D^{20}_D 0.888, n_D 1.43258. The diacetate has b. p. 122—124°/10 mm., D^{20}_D 0.963, n_D 1.427. When boiled for some time under atmospheric pressure, it yields acetic acid and the aldehyde or its monoacetate.

n-Heptaldehydesemicarbazone, $\text{C}_7\text{H}_{14} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, crystallises from methyl alcohol, and has m. p. 106—107°. *n-Octaldehyde* behaves in a similar manner with acetic anhydride and sodium acetate. *enol-n-Octaldehyde acetate*, $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH} : \text{CH} \cdot \text{OAc}$, has b. p. 90—94°/10 mm., D^{20}_D 0.88, and n_D 1.43256. The *diacetate* has b. p. 133—136°/10 mm.

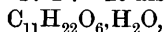
n-Octaldehydeoxime, $\text{CH}_3 \cdot [\text{CH}_2]_6 \cdot \text{CH} : \text{N} \cdot \text{OH}$, has b. p. 111—112°/9 mm. and m. p. 60°. The *semicarbazone*, $\text{C}_8\text{H}_{16} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, has m. p. 101°. J. J. S.

Semi-aldehyde of Succinic Acid. (A Correction.) ERNST ALEFELD (*Ber.*, 1909, 42, 1426. Compare this vol., i, 132).—The m. p. of the *p*-nitrophenylhydrazone of the semi-aldehyde is erroneously given as 158°; this substance has m. p. 175°. J. V. E.

Tautomerism of Aliphatic Ketones. V. H. HÂNCU (*Ber.*, 1909, 42, 1052—1055).—When heated in sealed tubes at above 200° with acetic anhydride and fused sodium acetate, the simple aliphatic ketones are converted into tautomeric enolic forms, with the exception of acetone, which instead yields a condensation product, mesityl oxide. The enolic form of diethyl ketone was obtained in the form of the *acetate*, $\text{CH}_2\text{Me} \cdot \text{C}(\text{OAc}) : \text{CHMe}$, a colourless liquid, b. p. 124—125°, which gives the ketonic form on hydrolysis with potassium hydroxide. The enolic *acetate* of dipropyl ketone is a colourless, pleasant smelling oil, b. p. 145—147°. The oximes of both these ketones are derivatives of the keto-forms. Mixed ketones, such as methyl ethyl ketone, methyl propyl ketone, or benzylideneacetone, could not be converted into enolic derivatives. E. F. A.

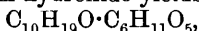
Syntheses of Glucosides. EMIL FISCHER and KARL RASKE (*Ber.*, 1909, 42, 1465—1476. Compare Abstr., 1894, i, 3; Königs and Knorr, *ibid.*, 1901, i, 369).—Glucosides have been obtained from *tert*-amyl alcohol, menthol, and borneol by condensing β -acetobromoglucose (Moll van Charante, Abstr., 1902, i, 426) with the alcohols in presence of freshly precipitated silver carbonate.

Tetra-acetyl- β -amylglucoside, $C_5H_{11} \cdot O \cdot C_6H_7O_5Ac_4$, crystallises from dilute alcohol in long, slender, glistening needles, m. p. 122—123° (corr.). When hydrolysed with cold barium hydroxide solution, it yields β -amylglucoside, $C_5H_{11}O \cdot C_6H_{11}O_5$, which crystallises from ethyl acetate in brilliant needles, m. p. 125—126° (corr.), after sintering at a lower temperature, and has $[\alpha]_D^{20} - 17.2^\circ$. It also forms a *hydrate*,



which crystallises from ether in needles, m. p. 113°.

Tetra-acetylmenthyl-d-glucoside, $C_{10}H_{19} \cdot O \cdot C_6H_7O_5Ac_4$, crystallises from 50% alcohol in long, colourless needles, m. p. 130° (corr.). It is fairly stable towards acid hydrolysing agents, but with an aqueous alcoholic solution of barium hydroxide yields *menthyl-d-glucoside*,



which crystallises from water in large, rectangular plates containing $1H_2O$, and melting at 77—79° (corr.). It has $[\alpha]_D^{20} - 93.0^\circ$ in alcoholic solution. When heated at 100° under 15 mm. it loses its water of hydration. It is more readily hydrolysed than the amylglucoside by emulsin or acids.

Tetra-acetylbornyl-d-glucoside, $C_{24}H_{36}O_{10}$, crystallises from dilute alcohol in slender needles, m. p. 119—120° (corr.). *d-Bornyl-d-glucoside*, $C_{16}H_{28}O_6$, crystallises from water in large needles containing $1H_2O$, which it loses when heated over phosphoric oxide at 122°/15 mm. It has m. p. 134—136° and $[\alpha]_D^{20} - 42.1^\circ$, is fairly readily hydrolysed by acids, but only slowly by emulsin.

Tetra-acetylglucovanillin, $C_8H_7O_2 \cdot O \cdot C_6H_7O_5Ac_4$, obtained by shaking for three days an aqueous solution of the sodium derivative of vanillin with an ethereal solution of acetobromoglucose, crystallises from dilute alcohol in thin, glistening prisms, m. p. 143—144° (corr.), and when hydrolysed with barium hydroxide yields glucovanillin (Tiemann, Abstr., 1885, 980). J. J. S.

Phenylthiolglucosides. EMIL FISCHER and KONRAD DELBRÜCK (*Ber.*, 1909, 42, 1476—1482).—Acetyl derivatives of phenylthiolglucosides have been prepared by shaking an ethereal solution of β -acetobromoglucose with an aqueous solution of the sodium derivative of a thiophenol for two days.

Tetra-acetylphenylthiolglucoside, $SPh \cdot C_6H_7O_5Ac_4$, crystallises from hot alcohol in small prisms, m. p. 118° (corr.), has $[\alpha]_D^{20} - 40.1^\circ$, is only sparingly soluble in water, and not readily hydrolysed by acids. *Phenylthiolglucoside*, $SPh \cdot C_6H_{11}O_5$, obtained by hydrolysing the acetyl derivative with barium hydroxide, crystallises from ethyl acetate in needles, m. p. 135° (corr.). It has $[\alpha]_D^{20} - 72.5^\circ$, is readily soluble in water, has a bitter taste, and is not hydrolysed readily by emulsin.

Hepta-acetylphenylthiol-lactoside, $SPh \cdot C_{12}H_{14}O_{10}Ac_7$, obtained from hepta-acetylborlactose (Ditmar, Abstr., 1902, i, 533) and sodium thio-

phenol, crystallises from alcohol in colourless prisms, m. p. 167° (corr.). It has $[\alpha]_D^{20} - 17.7^{\circ}$, and is only sparingly soluble in water. *Phenylthiol-lactoside*, $\text{SPh} \cdot \text{C}_{12}\text{H}_{21}\text{O}_{10}$, crystallises from hot alcohol in needles, m. p. 221° (corr.), has $[\alpha]_D^{20} - 40.1^{\circ}$, and is only sparingly soluble in water. When heated with *N*-sulphuric acid for one hour at 100° , it yields phenylthiolglucoside and galactose. It is also partly hydrolysed by emulsin, yielding phenylthiolglucoside. J. J. S.

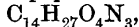
Formation of Hydrocelluloses by means of Sulphuric Acid. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1909, 22, 929—931. Compare this vol., i, 136).—Attention is again drawn to the fact that elementary analyses are of little use in the examination of hydrocelluloses. If the molecular weight of cellulose is very large, it is impossible to determine by elementary analysis whether water has entered the molecule or not, unless the amount of water introduced is large (compare Franchimont, *Rec. trav. Chim.*, 1883, 2, 244; Büttner and Neumann, this vol., i, 86). J. J. S.

Synthesis of Polypeptides. XXIX. Derivatives of *l*-Leucine, *d*-Alanine, and Glycine. EMIL FISCHER and JOSEPH STEINGROEVE (*Annalen*, 1909, 365, 167—180. Compare Abstr., 1908, i, 957).—The polypeptides glycyl-*l*-leucine, *l*-leucylglycyl-*d*-alanine, *l*-leucylglycyl-*l*-leucine, and *l*-leucyltriglycyl-*l*-leucine have been prepared in the usual manner. The first three were obtained in a crystalline state; the fourth, however, could not be crystallised. The first two substances were also obtained in an optically pure condition, since various preparations were found to have identical optical properties. This cannot be said of the other two compounds.

Chloroacetyl-l-leucine, $\text{C}_8\text{H}_{14}\text{O}_3\text{NCl}$, prepared from *l*-leucine and chloroacetyl chloride (compare Fischer and Warburg, Abstr., 1905, i, 690), crystallises in rectangular plates, m. p. 136° (corr.), $[\alpha]_D^{20} - 14.4^{\circ}$ ($\pm 0.2^{\circ}$) in alcohol. It is converted by ammonia into *glycyl-l-leucine*, $\text{C}_8\text{H}_{16}\text{O}_3\text{N}_2$, crystallising in small, long, thin plates, m. p. 242° (corr., decomp.), $[\alpha]_D^{20} - 34.9^{\circ}$ ($\pm 0.2^{\circ}$) in water. The latter substance yields *l*-leucylglycine anhydride identical with that prepared from *l*-leucylglycine (Abstr., 1906, i, 808).

d- α -Bromoisohexoylglycyl-d-alanine, $\text{C}_{11}\text{H}_{19}\text{O}_4\text{N}_2\text{Br}$, prepared from *d- α -bromoisohexoylglycine* (compare Abstr., 1905, i, 263) and *d*-alanine ethyl ester, forms colourless crystals, sinters at 112.5° (corr.), m. p. 118° (corr.), $[\alpha]_D^{20} + 20.4^{\circ}$ ($\pm 0.2^{\circ}$) in alcohol. It is converted by ammonia into *l-leucylglycyl-d-alanine*, $\text{C}_{11}\text{H}_{21}\text{O}_4\text{N}_3$, which forms tufts of slender needles, sinters at 238° (corr.), m. p. 249° (corr.), $[\alpha]_D^{20} + 20.3^{\circ}$ ($\pm 0.2^{\circ}$) in water.

d- α -Bromoisohexoylglycyl-l-leucine, $\text{C}_{14}\text{H}_{25}\text{O}_4\text{N}_2\text{Br}$, prepared either by the interaction of *d- α -bromoisohexoylglycyl chloride* and *l-leucine ester* or of *d- α -bromoisohexoyl chloride* and *glycyl-l-leucine*, crystallises in microscopic prisms, m. p. 100 — 101° (corr.), $[\alpha]_D^{20} + 29.1^{\circ}$ ($\pm 0.2^{\circ}$) in alcohol. The corresponding tripeptide, *l-leucylglycyl-l-leucine*,



is a colourless, crystalline powder; it is similar in m. p. and solubility to the racemic compound (compare Abstr., 1905, i, 863).

d-**Bromoisohexoyltriglycyl-l-leucine**, $C_{18}H_{31}O_6N_4Br$, prepared from *d*-**bromoisohexoyldiglycylglycyl chloride** (Abstr., 1907, i, 485) and *l*-leucine, crystallises in small, spherical aggregates of colourless needles, sinters at 179° (corr.), m. p. 182° (corr.), $[\alpha]_D^{20} + 23.5^\circ (\pm 0.3^\circ)$ to $+22.4^\circ (\pm 0.3^\circ)$ in water containing slightly more than the theoretical quantity of sodium hydroxide; the optical rotatory power of the solution when kept becomes gradually smaller. *l*-**Leucyltriglycyl-l-leucine**, $C_{18}H_{33}O_6N_5$, prepared from the substance just described, is obtained as a somewhat hygroscopic, amorphous, white powder, which becomes yellow at 213° (corr.), then sinters, and finally decomposes at 229° (corr.), $[\alpha]_D^{20} + 21.1^\circ (\pm 0.8^\circ)$ to $+21.3^\circ (\pm 0.4^\circ)$ in water.

W. H. G.

Synthesis of Polypeptides. XXX. Derivatives of *l*-Cystine. EMIL FISCHER and OTTO GERNGROSS (*Ber.*, 1909, 42, 1485—1495).—Symmetrical tripeptides containing cystine were prepared from inactive α -halogen fatty acids by Fischer and Suzuki (Abstr., 1905, i, 30), and were probably mixtures of stereoisomerides. A crystalline *di-l-leucyl-l-cystine* is now obtained from *d*-**bromoisohexioic acid**. This, like the synthetic leucyltriglycyltyrosine, is precipitated by ammonium sulphate even from dilute aqueous solution, and may be termed an albumose.

l-Cystine when coupled with halogenacyl chlorides in alkaline solution forms monohalogenacyl as well as dihalogenacyl derivatives. The former are converted by ammonia into the corresponding dipeptides.

Di-d-**bromoisohexoyl-l-cystine** forms pointed, hard prisms in stellar aggregates, m. p. 121 — 123° (corr.), and has $[\alpha]_D^{20} - 133^\circ$. *Di-l-leucyl-l-cystine*, $S_2[CH_2 \cdot CH(CO_2H) \cdot NH \cdot CO \cdot CH(NH_2) \cdot C_4H_9]_2$, is obtained as a granular product, which turns yellow at 200° and decomposes at higher temperatures; it has $[\alpha]_D^{20} - 136.6^\circ$. It is also obtained after some trouble in minute, well-formed prisms or needles, which have a slightly higher rotatory power, $[\alpha]_D^{20} - 141.4^\circ$; it gives a reddish-violet coloration with copper sulphate. Especially characteristic is the precipitation by ammonium sulphate.

Mono-d-**bromoisohexoyl-l-cystine**,

$C_4H_9 \cdot CHBr \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot S \cdot S \cdot CH_2 \cdot CH(CO_2H) \cdot NH_2$, obtained on coupling *d*-**bromoisohexoyl chloride** with excess of cystine, has m. p. 194° (decomp.), $[\alpha]_D^{21} - 130.2^\circ$; it crystallises in colourless plates or needles. When treated with aqueous ammonia it forms *l-leucyl-l-cystine*, which, when heated, darkens at 165° , but could not be obtained quite pure.

Chloroacetyl-l-cystine, prepared by the interaction of chloroacetyl chloride with excess of cystine, crystallises in colourless, rectangular prisms or plates, decomp. 185 — 190° , and has $[\alpha]_D^{17} - 169^\circ$. *Glycyl-l-cystine* was obtained by warming the foregoing with 25% aqueous ammonia at 70° , but could not be completely purified. *Di(chloroacetyl)-l-cystine* crystallises from water + $1H_2O$ in needles, which sinter at 90° . In alcohol the anhydrous substance has $[\alpha]_D^{20} - 120.3^\circ$. E. F. A.

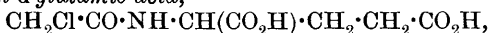
Preparation of Glycocyamines or Guanino-acids. II. HENRIK RAMSAY (*Ber.*, 1909, 42, 1137—1140. Compare this vol., i, 88).—*l*-**Bromopropionic** and *d*- and *l*-**bromoisohexioic acids** have

been converted by a concentrated aqueous solution of guanidine into the corresponding guanino-acids by the method described previously. Despite the fact that a lower temperature, 20° , is maintained, the α -guaninopropionic acid is almost completely racemised; somewhat better results are obtained with the other two active acids, *l*- α -guaninoisohexoic acid and the *d*-isomeride having $[\alpha]_D^{20}$ 4.54° and -4.08° respectively in hydrochloric acid. By warming *l*- α -guaninoisohexoic acid with barium hydroxide, *l*-leucine is obtained. Since *l*- α -bromoisohexoic acid and ammonium hydroxide yield *d*-leucine, Walden's inversion must have occurred at some stage in the preceding reactions. C. S.

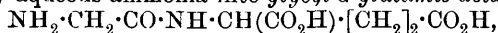
Derivatives of Glutamic Acid. EMIL FISCHER, WALTER KROPP, and ALEX STAHLSCMIDT (*Annalen*, 1909, **365**, 181—200).—The study of the polypeptides of glutamic acid is of the greatest importance, since glutamic acid is present in many vegetable proteins; however, owing to experimental difficulties, only one dipeptide, namely, *l*-leucyl-*d*-glutamic acid, has been described hitherto (Abstr., 1907, i, 901). The present communication treats of the preparation and properties of further polypeptides of glutamic acid. Since the compounds obtained from pure chloroacetyl-*d*-glutamic acid were but slightly optically active, possibly because racemisation had occurred during the processes of preparation, experiments were performed with *dl*-glutamic acid in the hope that better yields would be obtained, but this was not the case.

dl-Glutamic acid, prepared by the method of Schulze and Bosshard (Abstr., 1886, 373), crystallises from water at 37° in needles belonging to the rhombic system; m. p. 199° (corr.), when heated quickly. Measurements of the crystals are given in the original.

Chloroacetyl-d-glutamic acid,

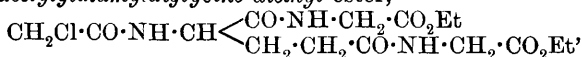


prepared by the action of chloroacetyl chloride on *d*-glutamic acid in the presence of sodium hydroxide at 0° , crystallises in slender prisms or needles, m. p. 143° (corr.), $[\alpha]_D^{20}$ -13.5° ($\pm 0.2^{\circ}$) in water. It is converted by aqueous ammonia into *glycyl-d-glutamic acid*,

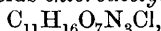


an amorphous, white powder, which sinters at about 165° , m. p. 178° (corr.), $[\alpha]_D^{20}$ -6.3° in water; the *copper* salt, $\text{C}_7\text{H}_{10}\text{O}_5\text{N}_2\text{Cu}\cdot 3\frac{1}{2}\text{H}_2\text{O}$, is a pale blue, granular powder; the *anhydrous* salt decomposes at 213° (corr.).

Chloroacetylglutamylglycine diethyl ester,



is prepared by the action of phosphorus pentachloride on chloroacetylglutamic acid suspended in acetyl chloride, and subsequent treatment of the acid chloride so formed with glycine ethyl ester; it crystallises in spherical aggregates of small, slender needles, sinters at 140° , m. p. 146° (corr.), and when treated with *N*-sodium hydroxide solution and then sulphuric acid, yields *chloroacetylglutamylglycine*,



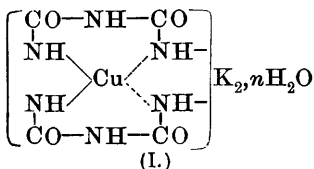
crystallising in spherical aggregates of slender needles, m. p. 173° (decomp., corr.). The latter substance is converted by aqueous ammonia

into *glycylglutamylglycine*, $C_{11}H_{18}O_7N_4$, crystallising in slender needles, which become coloured at about 220° and decompose at 248° (corr.).

The following substances were prepared by the methods employed in the preparation of the active compounds just described.

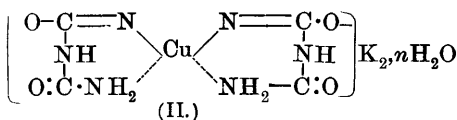
Chloroacetyl-dl-glutamic acid crystallises in microscopic needles and small, long leaflets, sinters at 120° , m. p. 123° . *Glycyl-dl-glutamic acid* is a hygroscopic, amorphous powder; the *copper* salt ($3\frac{1}{2}H_2O$) crystallises in microscopic prisms and plates, and decomposes, when heated rapidly, at 223° (corr.). *Chloroacetylglutamylglycine diethyl ester* and *chloroacetylglutamylglycine*, prepared from *chloroacetyl-dl-glutamic acid*, are almost identical in physical properties with the corresponding compounds derived from *chloroacetyl-d-glutamic acid*; naturally, they are optically quite inactive. W. H. G.

Complex Compounds. II. Compounds Showing the Biuret Reaction. LEO A. TSCHUGAEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 166—184. Compare Abstr., 1907, i, 595).—The author discusses the



structure both of compounds giving the biuret reaction and of the compounds formed by this reaction. He is of opinion that the compounds formed have a cyclic structure; that of the compound obtained when a copper salt, potassium hydroxide, and biuret are used being expressed by (I), or assuming that the

biuret acts in its tautomeric form, by (II). Similar formulæ are given



for the corresponding compounds yielded by dicyanodiamidine and diguanide.

The preparation and properties are described

of the alkali metal salts of succinimide having the composition $[\text{Cu}(C_4H_4O_2N)_4]_m \cdot nH_2O$ (*loc. cit.*).

The work of Ley and Krafft (Abstr., 1907, i, 301), and Ley and Müller (Abstr., 1907, i, 730), is discussed. T. H. P.

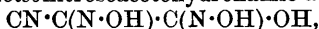
Fulminic Acid. III. Polymerisation of Fulminic Acid. HEINRICH WIELAND and HERMANN HESS (*Ber.*, 1909, 42, 1346—1363).—The work of Ehrenberg (Abstr., 1884, 419; 1885, 1192), Scholvien (*ibid.*, 1885, 39; 1886, 137), and Nef (*ibid.*, 1895, i, 9) on fulminic acid and its derivatives is discussed, and from new experimental data it is shown (a) that fulminic acid can exist in the free state in solution in ether as stated by Scholvien; (b) that metafulminuric acid (*isocyanuric acid*) is the sole product of its spontaneous polymerisation, and

(c) that the formula $\text{N} \begin{smallmatrix} \text{CH}\cdot\text{C}\cdot\text{N}\cdot\text{OH} \\ \diagdown \quad | \\ \text{O}-\text{C}\cdot\text{N}\cdot\text{OH} \end{smallmatrix}$ accounts better for the reactions of metafulminuric acid, and particularly for its conversion by ammonia and alkalis into *cyanoisonitrosoacetohydroxamic acid* (see below), than that proposed by Nef.

Cold dilute sulphuric acid was added to an aqueous solution of sodium fulminate until the latter was just acid to Congo-red paper, and the

liberated fulminic acid was extracted by ether. This solution was then shaken with silver nitrate solution, and slightly acidified with nitric acid, when silver fulminate crystallised out and the aqueous mother liquor was found to contain no sulphuric acid. There is therefore no evidence in favour of Nef's view, that, under the conditions described, free fulminic acid is not formed and dissolved out by the ether, but only an additive compound of this with sulphuric acid. It was also found that on allowing an ethereal solution of fulminic acid to distil under reduced pressure, some fulminic acid was carried over with the ether vapour, and could be absorbed by cooled silver nitrate solution, yielding silver fulminate.

Metafulminuric acid (*isocyanuric acid*), m. p. 85—86° (hydrated), 106° (anhydrous), is best obtained by the action of small quantities of sodium hydroxide on chloroformoxime (Nef, *Abstr.*, 1895, i, 10). It probably contains $1\text{H}_2\text{O}$, not $3\text{H}_2\text{O}$, as stated by Scholvien (*loc. cit.*: compare Palazzo and Tamburello, *Abstr.*, 1907, i, 298). The colour reactions given by the acid with various metallic salts in solution are detailed in the original. The acid is also formed as a first product when ammonia solution reacts in the cold with chloroformoxime, but on warming with ammonia, or by the further action of alkalis on metafulminuric acid, cyanoisonitrosoacetohydroxamic acid,



m. p. 117—118° (Nef, *loc. cit.*), is formed. Scholvien's secondary yellow ammonium salt (*loc. cit.*) is probably ammonium cyano-oximinoacetohydroxamate.

When hydroxylamine reacts with chloroformoxime, or, better, with cyano-oximinoacetohydroxamic acid, the *amino-oxime* of *oximinomalono-hydroxamic acid*, $\text{NH}_2\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{OH}$, is formed, and is best isolated in the form of its well-crystallised *hydrochloride*, m. p. 151—152° (decomp.). The latter gives characteristic reactions with aqueous solutions of a number of metallic salts, liberates iodine from potassium iodide solution, but does not reduce Fehling's solution. The amino-oxime could not be obtained pure; it yields a crystalline *barium* salt and a *tetra-acetyl* derivative, m. p. 177° (decomp.), which is crystalline and difficultly soluble. When heated in aqueous acid or alkaline solution, the amino-oxime is converted

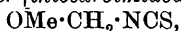
into *amino-oximinooxazalone*, $\text{NH}_2\cdot\text{C}\begin{smallmatrix} \text{C}(\text{N}\cdot\text{OH})\cdot\text{CO} \\ \text{N} \text{-----} \text{O} \end{smallmatrix}$, m. p. 159°

(decomp.), which crystallises from hot water in dull orange-yellow needles. It liberates iodine from potassium iodide solutions, slowly decolorises permanganate, dissolves in sulphuric acid with a yellow coloration, in hydrochloric acid with the formation of hydroxylamine, and in dilute nitric acid with the liberation of hydrocyanic acid. Alkalis convert it into salts of the *amino-oxime* of *oximinomalonic acid*, $\text{NH}_2\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CO}_2\text{H}$, m. p. 166° (decomp.), which is best isolated as the *barium* salt. The acid crystallises from hot water in clusters of colourless needles, is readily soluble in pyridine, and only slightly so in alcohol, ether, or acetic acid. It gives characteristic colorations with aqueous solutions of various metallic salts.

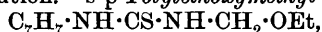
T. A. H.

Thiocyanates and Thiocarbimides. VIII. New Class of Thiocarbimides. Thiocarbimido-ethers. TREAT B. JOHNSON and HERBERT H. GUEST (*Amer. Chem. J.*, 1909, 41, 337—344. Compare Abstr., 1907, i, 910).—Previous work has shown that the interaction of potassium thiocyanate and primary alkyl halides of the type $R\cdot CH_2X$, where R is any saturated or unsaturated organic radicle, leads generally to the formation of thiocyanates; only when R is vinyl or a derivative of vinyl are thiocyanates obtained, which are readily changed to thiocarbimides by heating. Now it is found that chloromethyl ether, chloromethyl ethyl ether, and chloromethyl *iso*-amyl ether react almost quantitatively with potassium thiocyanate to form the corresponding thiocarbimides, the structure of which is proved by desulphurising them by warm alkaline lead acetate, by the formation of carbon disulphide by thiobenzoic acid, and by their combination with ammonia or amines to form a new class of thiocarbimides, $NHR'\cdot CS\cdot NH\cdot CH_2\cdot OR$; the oxygen analogue of the parent substance of this class, monomethylolcarbamide, has been obtained by Einhorn and Hamburger (Abstr., 1908, i, 141). These results are not in harmony with Michael's theory that a strongly negative character of the halide favours the production of thiocarbimides.

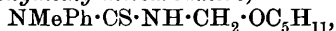
*iso*Thiocyanodimethyl ether [*thiocarbimidodimethyl ether*],



b. p. $138^\circ/770$ mm., and $56-60^\circ/30$ mm., obtained by digesting a solution of chlorodimethyl ether in benzene with potassium thiocyanate for two days at 110° , is a colourless oil with an irritating odour. *Thiocarbimidomethyl ethyl ether*, $OEt\cdot CH_2\cdot NCS$, b. p. $93-97^\circ/97-100$ mm., and *thiocarbimidomethyl isoamyl ether*, $C_5H_{11}\cdot O\cdot CH_2\cdot NCS$, b. p. $208-210^\circ/760$ mm. and $122-125^\circ/34$ mm., possess similar properties. *Ethoxy-methylthiocarbamide*, $OEt\cdot CH_2\cdot NH\cdot CS\cdot NH_2$, obtained from thiocarbimidomethyl ethyl ether and strong aqueous ammonia, has m. p. $92-93^\circ$. *s-Phenylethoxymethylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot CH_2\cdot OEt$, m. p. $125-126^\circ$, is obtained from aniline and thiocarbimidomethyl ethyl ether in ethereal solution. *s-p-Tolylethoxymethyl thiocarbamide*,



m. p. 120° , is decomposed by concentrated ammonium hydroxide at $140-150^\circ$, *p*-toluidine being formed. *s-Phenylisoamylloxymethylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot CH_2\cdot O\cdot C_5H_{11}$, and the corresponding *p-tolyl* compound have m. p. 109° and 119° respectively, whilst *phenylmethylisoamylloxymethylthiocarbamide*,



has m. p. 87° .

C. S.

Organic Mercury Compounds. EINAR BILLMANN and JOHANNES WITT (*Ber.*, 1909, 42, 1067—1070. Compare this vol., i, 17; Schrauth and Schoeller, Abstr., 1908, i, 617).—Polemical. Schrauth and Schoeller have described the formation of hydroxymercuriacetic anhydride by the interaction of sodium hydroxide, malonic acid, and mercuric oxide, whereby carbon dioxide is eliminated. In reality carbon dioxide is not eliminated, and a mercurimalonic acid, previously described by

Biilmann (Abstr., 1902, i, 665), is formed and not a derivative of acetic acid.
E. F. A.

The Study of Hydro-aromatic Substances. EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Report*, 1908, 221—230).—This report contains a reply to Harries and Antoni's criticisms (Abstr., 1903, i, 613) on the work of Crossley and Le Sueur (*Trans.*, 1902, 81, 821), and an account of recent work on hydro-aromatic substances. T. H. P.

[1-Acetyl- Δ^1 -cyclopentene as an Oxidation Product of Δ^1 -cyclo-Hexeneacetic Acid.] LOUIS BOUVEAULT (*Ber.*, 1909, 42, 1055—1057).—Some remarks on a paper by Perkin and Wallach (this vol., i, 154). The formation of cyclopentene from a derivative of cyclohexene is described as unexpected by Perkin and Wallach. It is pointed out that the reverse change is exemplified by the conversion of isolauronic acid into isolauronic acid at 0°, as well as by the conversion of β -campholenic acid into the isophorone of camphor. Confidence is to be placed in the oxidation with permanganate for the determination of constitution in the case of hydrocarbons of the methylcyclohexene type, but not in the case of cyclic, unsaturated hydrocarbons, which contain negative groups in the neighbourhood of the double bond.
E. F. A.

Action of Nitric Acid on Saturated Hydrocarbons. III. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 145—157. Compare this vol., i, 93).—The partial decomposition of the isonitro-compound, formed as an intermediate product in the action of nitric acid on saturated hydrocarbons, into aldehyde or ketone is accompanied by the evolution of nitrous oxide: $2\text{CHR}\cdot\text{NO}\cdot\text{OH} = 2\text{R}\cdot\text{CHO} + \text{N}_2\text{O} + \text{H}_2\text{O}$, and $2\text{CR}_2\cdot\text{NO}\cdot\text{OH} = 2\text{R}_2\text{CO} + \text{N}_2\text{O} + \text{H}_2\text{O}$.

In the action of nitric acid on cyclohexane, the cyclohexanone formed as above is oxidised quantitatively to adipic acid, but the proportion of nitrous oxide formed is about double that indicated by the above equation. The conclusion is drawn that the oxidation of the second methylene group to carboxyl proceeds in the same manner as that of the first group, giving rise in the first stage to $\text{:C:NO}\cdot\text{OH}$, which is converted first into carbonyl, with evolution of nitrous oxide, and ultimately into carboxyl, with breaking of the ring.

The acids formed in the above reaction consist of adipic (80%), glutaric (13%), and succinic (7%) acids.

When cyclohexanone is treated with nitric acid, the proportion of nitrous oxide obtained is in agreement with the above views of the reaction.
T. H. P.

Influence of the Solvent on the Ratio of Isomerides [in Substitution]. LUDWIK BRUNER and J. VORBRÖDT (*Bull. Acad. Sci. Cracow*, 1909, 221—238. Compare Abstr., 1908, i, 146).—The bromination of alkylbenzenes in various solvents in the dark at 25° has been quantitatively studied, and the yields of the various isomerides measured. The ω -bromo-derivatives are estimated, after

washing with ammonium nitrate, by precipitation with silver nitrate and titration of the excess with thiocyanate. When carbon disulphide is the solvent, this must be removed by evaporation before precipitating.

The hydrocarbons employed were toluene, ethylbenzene, the three xylenes, propylbenzene, and *sec*-butylbenzene, and the solvents carbon disulphide, carbon tetrachloride, benzene, chloroform, glacial acetic acid, nitrobenzene, and benzonitrile.

The ratio of chain-substituted to ring-substituted product is influenced by the solvent, ionising solvents favouring substitution in the nucleus. The order of the solvents is as given above, carbon disulphide being the least ionising, and therefore giving the highest yield of *ω*-derivative. Thus with toluene, benzyl bromide forms 85% of the product in carbon disulphide, and only 4% in acetic acid and 2% in nitrobenzene. Since traces of moisture greatly affect the conductivity of nitrobenzene, the latter was tried in presence of phosphoric oxide, without alteration in the yield. With ethylbenzene in carbon tetrachloride or benzene, the reaction at 25° is so rapid that irregular results are obtained. The reaction is more uniform at 10°. With propylbenzene in carbon tetrachloride, the reaction is more rapid in dilute than in concentrated solutions, probably owing to the formation of complex acids from the hydrogen bromide and bromine, so reducing the effective concentration of the latter.

Similar influences prevail in the presence of light. Thus, the bromination of tetra- and penta-methylbenzene has been described as unaffected by light (Korczyński, *Abstr.*, 1902, i, 274), glacial acetic acid being used as the solvent. In carbon disulphide solution, however, the reaction is sensitive to light.

In the side-chain, the methylene group is the most readily substituted, the more so the longer the chain. Meta-substitution very greatly increases the tendency to brominate in the nucleus, the velocity constant for *m*-xylene being about one hundred times as great as those of *o*- and *p*-xylene.

C. H. D.

Certain Reactions of Nitro-derivatives. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 301—305).—From measurements of dispersion and refraction of alkyl nitrates, Brühl (*Abstr.*, 1898, ii, 362) drew the conclusion that these nitrates and nitric acid have a peroxide structure containing the group O·O·N·O. Results tending to confirm this formula have been obtained by several authors (compare Klason and Carlson, *Abstr.*, 1906, i, 787; 1907, i, 1000; Carlson, *Abstr.*, 1907, i, 1001; Gutmann, *Abstr.*, 1908, i, 597). The author's work, however, is in direct disagreement with these results.

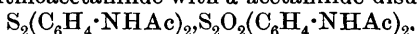
The fact that alkyl nitrates, in presence of alkali, oxidise thiophenol to phenyl disulphide, arsenites to arsenates, and alkali hydrosulphides to polysulphides, with formation of alkali nitrite, is explained by the above-named authors as due to the hydrolysis of the alkyl nitrates by the alkali proceeding in two different ways, yielding (1) alcohol and alkali nitrate, (2) aldehyde and alkali nitrite. The following oxidation processes, effected by aromatic nitro-derivatives, are, however, quite analogous to the above oxidations brought about by the alkyl nitrates:

(1) preparation of azoxy-derivatives by the action of alkoxides on aromatic nitro-derivatives; (2) reduction of nitro-derivatives to azoxy-compounds by means of alkaliarsenites (Loesner, *Abstr.*, 1895, i, 214); (3) interaction of potassium phenyl mercaptan and *m*-nitrobenzoate, yielding *m*-azoxybenzoic acid and phenyl disulphide. In these reactions, it may be assumed that the nitro-derivatives are reduced first to nitroso-derivatives, and the analogy between the reactions of the nitro-derivatives and those of the alkyl nitrates is clearly brought out in the case of, say, thiophenol: $\text{CH}_2\text{R}\cdot\text{O}\cdot\text{NO}_2 + 2\text{Ph}\cdot\text{SK} + \text{H}_2\text{O} = \text{KO}\cdot\text{NO} + \text{Ph}_2\text{S}_2 + \text{KHO} + \text{CH}_2\text{R}\cdot\text{OH}$ and $\text{R}\cdot\text{NO}_2 + 2\text{Ph}\cdot\text{SK} + \text{H}_2\text{O} = \text{R}\cdot\text{NO} + \text{Ph}_2\text{S}_2 + 2\text{KHO}$.

This analogy of behaviour between the NO_2 group in the nitro-derivatives and that in the alkyl nitrates indicates the identity of structure of the two groups, this view being supported by the fact that nitro-derivatives can be obtained by nitration by means of alkyl nitrates in presence of alkoxides: $\text{:CH}_2 + \text{R}\cdot\text{O}\cdot\text{NO}_2 = \text{:CH}\cdot\text{NO}_2 + \text{R}\cdot\text{OH}$.

Other evidence against the peroxide formula for the alkyl nitrates is also adduced (compare Baeyer and Villiger, *Abstr.*, 1901, i, 308, 309; Carlson, *loc. cit.*).
T. H. P.

α - and β -Acetanilide Disulphoxide. OSCAR HINSBERG (*Ber.*, 1909, 42, 1278—1284. Compare this vol., i, 6).—When 4:4'-dithioacetanilide [*p*-acetylaminophenyl disulphide] is left in contact with 3% hydrogen peroxide for some weeks at 25—30°, it is converted into a substance of the formula $\text{C}_{32}\text{H}_{32}\text{O}_6\text{N}_4\text{S}_4$, which appears to be a compound of α -dithioacetanilide with α -acetanilide disulphoxide,



since it decomposes into these two substances on boiling for one to two minutes with glacial acetic acid; when boiled with glacial acetic acid for half an hour, it yields an isomeric β -disulphoxide; the double compound when heated above its melting point is converted into α -, γ -, and probably β -dithioacetanilide.

α -Acetanilide disulphoxide, $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}\cdot\text{SO}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, crystallises from glacial acetic acid with $2\text{C}_2\text{H}_4\text{O}_2$ in yellow plates, m. p. 190° (decomp.); prolonged washing with warm water converts it into a yellow, crystalline powder, which is free from acetic acid, but dissolves in alcohol to a colourless solution.

β -Acetanilide disulphoxide crystallises from its colourless solution in alcohol in the form of yellowish-red rhombohedra, m. p. 233° (decomp.); it crystallises from glacial acetic acid in colourless needles, which contain two molecules of the solvent.

The fact that both these coloured substances give colourless solutions in alcohol is explained by assuming that the alcohol combines with them to form colourless additive compounds of the formula: $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{S}(\text{OH})(\text{OEt})\cdot\text{S}(\text{OH})(\text{OEt})\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$.
P. H.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. FREDERIC S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Brit. Assoc. Report*, 1908, 115—118).—This report deals [with W. W. REED] with

the transformation of the crystalline 2:4-dichloroamino-1-nitroaminobenzene into 2:4-dichloro-6-nitroaniline, with the transformation of the nitroamine in solution, and with preliminary experiments on the molecular rearrangement of the unsubstituted nitroaminobenzene; and [with C. PEARSON] with the wandering of bromine in the transformation of nitroaminobromobenzenes. T. H. P.

Amino-hydroxydiphenylamine. FRITZ ULLMANN and KARL JÜNGEL (*Ber.*, 1909, 42, 1077—1083. Compare Abstr., 1908, i, 298, 975).—Nitro- and amino-hydroxydiphenylamines can be easily obtained by the method described by Ullmann and Dahmen (Abstr., 1908, i, 975), which consists in condensing *p*-chloronitrobenzene-*o*-sulphonic acid with aniline, and the elimination, by heating with dilute mineral acids, of the sulphonyl group from the *p*-nitrodiphenylaminesulphonic acid formed, etc.

4-Nitro-4'-hydroxydiphenylamine-2-sulphonic acid forms a *potassium* salt, $C_{12}H_9O_6N_2SK$, crystallising in red needles, and a *barium* salt, crystallising in orange-yellow needles. The corresponding 4-amino-4'-hydroxydiphenylamine-2-sulphonic acid, formed on reduction of the nitro-compound, crystallises in needles, which give a reddish-brown and, finally, violet coloration with ferric chloride.

4-Nitro-4'-hydroxydiphenylamine forms lustrous, reddish-brown plates, m. p. 183°.

4-Nitro-4'-methoxydiphenylamine, prepared by alkylation with methyl sulphate, crystallises in steel-blue needles, m. p. 151°. The *p*-toluene-sulphonic ester of 4-nitro-4'-hydroxydiphenylamine forms yellow needles, m. p. 143°.

4-Amino-4'-hydroxydiphenylamine is prepared either by reduction of the nitro-compound or by the action of mineral acids on the amino-hydroxydiphenylaminesulphonic acid. It separates in large, almost colourless plates, m. p. 166°. The colourless solution in alkalis becomes a rich blue after a time, owing to formation of indamine; the solution in dilute hydrogen chloride is coloured an intense blue by ferric chloride. The *diacetate* separates in colourless, glistening plates, m. p. 141°.

4-Nitro-4'-methoxydiphenylamine-2-sulphonic acid, from chloronitrobenzenesulphonic acid and *p*-anisidine, forms a *potassium* salt, crystallising in yellow needles. The corresponding *amino*-compound forms almost colourless needles. By the action of mineral acids on the nitro-compound, 4-nitro-4'-methoxydiphenylamine is obtained. 4-Amino-4'-methoxydiphenylamine has m. p. 102°, and is identical with the product obtained by Jacobson and Jaenicke (Abstr., 1897, i, 143) from benzeneazobenzene. Condensation with *o*-anisidine yields 4-nitro-2'-methoxydiphenylamine-2-sulphonic acid, of which the *potassium* salt forms yellow needles. The corresponding 4-amino-derivative, obtained on reduction, crystallises in colourless needles, which become faintly blue on exposure to air.

4-Nitro-2'-methoxydiphenylamine forms yellow needles with a steel-blue reflex, m. p. 111°; 4-amino-2'-methoxydiphenylamine separates in faintly rose-coloured needles, m. p. 80°. E. F. A.

Attempts to Prepare Isomeric Asymmetric Ammonium Compounds. EMIL FRÖHLICH (*Ber.*, 1909, 42, 1561—1565).—An

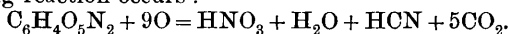
account of unsuccessful attempts to prepare isomeric asymmetric ammonium compounds by the following methods. (1) Addition of methyl or ethyl iodide to a tertiary amine, thus : $\text{NMePhR} + \text{EtI} = \text{NMePhREtI}$; $\text{NEtPhR} + \text{MeI} = \text{NEtPhRMeI}$ ($\text{R} = \text{propyl, isopropyl, butyl, isobutyl, allyl, benzyl}$). (2) Addition of methyl or ethyl sulphate to the tertiary base. This method was useless, however, for the ester interacts with only 1 mol. of the amine, thus : $\text{NEtPhR} + \text{Me}_2\text{SO}_4 = \text{NMeEtPhR} \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OMe}$. Crystalline compounds are obtained, moreover, only when $\text{R} = \text{benzyl}$. When ethyl sulphate is used instead of methyl sulphate, one of the ethyl groups is replaced by benzyl; for example, benzylmethylaniline and ethyl sulphate yield phenyldibenzyl-methylammonium methyl sulphate.

The following are the new compounds described. *Ethylbutylaniline*, $\text{C}_{12}\text{H}_{19}\text{N}$, and *ethylisobutylaniline*, colourless oils, b. p. $237\text{--}242^\circ/760$ mm. and $228\text{--}231^\circ/770$ mm. respectively.

Phenylmethylethylisopropylammonium iodide, $\text{C}_{12}\text{H}_{20}\text{NI}$, small, four-sided plates, m. p. 160° (varies with the rate of heating). *Phenylmethylethylbutylammonium iodide*, $\text{C}_{13}\text{H}_{22}\text{NI}$, colourless prisms, m. p. 142° (variable); the corresponding isobutyl compound is a viscid mass. *Phenyldibenzylmethylammonium methyl sulphate*, $\text{C}_{23}\text{H}_{27}\text{O}_4\text{NS}$, small, crystalline nodules, m. p. 140° . *Phenylbenzylmethylethylammonium methyl sulphate*, $\text{C}_{17}\text{H}_{23}\text{O}_4\text{NS}$, large, colourless prisms, m. p. 120° (variable).
W. H. G.

Electrolysis of Phenyltrialkylammonium Iodides. BRUNO EMMERT (*Ber.*, 1909, 42, 1507—1510).—By the electrolysis of quaternary phenylammonium iodides in aqueous solution with lead cathodes, the hydrogen is fixed by the phenyl residue, yielding benzene, and trialkylamines are formed. In this way trimethylamine is obtained from phenyltrimethylammonium iodide, dimethylethylamine from phenyldimethylethylammonium iodide, methyldiethylamine from phenylmethyldiethylammonium iodide, and methylethylpropylamine from phenylmethylethylpropylammonium iodide, in amounts equivalent to 77% of the theoretical. The same reaction does not take place with platinum cathodes.
E. F. A.

Oxidation of Aromatic Nitro- and Nitroso-derivatives by Ammonium Persulphate. ALPHONSE SEYEWETZ and L. POIZAT (*Compt. rend.*, 1909, 148, 1110—1113. Compare this vol., i, 146).—The nitrogen liberated as hydrogen cyanide when phenols or quinones are heated with nitric acid appears to arise from the decomposition of nitro-derivatives and not from the nitric acid itself. Other oxidising agents are capable of decomposing many nitro-compounds with formation of hydrogen cyanide. Aromatic nitro- or nitroso-derivatives in which the ortho- or para-position is free, or substituted by the OH group, yield hydrogen cyanide readily when boiled with an aqueous solution of ammonium persulphate. In the case of 2:4-dinitrophenol the following reaction occurs :



An explanation of this change is put forward, based on the supposition that the nitro-compound reacts as an oximinoquinone (compare Hantzsch, *Abstr.*, 1899, i, 399).
W. O. W.

Nitration of Certain Derivatives of *p*-Aminophenol.
 FRÉDÉRIC REVERDIN [with A. DE LUC] (*Ber.*, 1909, 42, 1523—1530; *Arch. sci. phys. nat.*, 1909, 27, 383—403. Compare *Abstr.*, 1907, i, 695).—A continuation of the author's work on this subject. It is found as a result of this investigation that derivatives of *p*-anisidine yield mononitro-compounds, whilst under similar conditions, those derivatives of *p*-aminophenol in which the hydroxyl hydrogen is replaced by a benzoyl or toluenesulphonyl group yield dinitro-compounds. Compounds containing methyl attached to the nitrogen are decomposed to a large extent during nitration; the *N*-toluenesulphonyl derivatives are slightly more stable, whilst the *N*-benzoyl compounds yield nitro-derivatives without decomposing appreciably. There is always a tendency during the nitration of benzoyl derivatives for a nitro-group to enter the benzoyl radicle.

4-*p*-Toluenesulphonylaminoanisole, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7$, prepared by the action of *p*-toluenesulphonyl chloride on *p*-anisidine in the presence of sodium acetate, crystallises in slender, pale violet needles, m. p. 114° ; the *acetyl* derivative crystallises in needles, m. p. 148° . The parent substance when treated with nitric acid (D 1.4) in glacial acetic acid at 10 — 22° yields 3-nitro-4-*p*-toluenesulphonylaminoanisole, $\text{C}_7\text{H}_7 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_2(\text{NO}_2) \cdot \text{OMe}$, stout, yellowish-orange prisms, m. p. 105° , and small quantities of the corresponding 3:5-dinitro-derivative. The 2:3-dinitro-derivative is obtained by nitrating with nitric acid (D 1.52) in glacial acetic acid at 20 — 30° , and crystallises in slender, white needles, m. p. 165 — 167° .

4-Methylaminophenyl *o*-toluenesulphonate, $\text{NHMe} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7$, prepared from *p*-methylaminophenol and *p*-toluenesulphonyl chloride, forms colourless, prismatic needles, m. p. 135° . When nitrated with nitric acid (1.4 or 1.52) in glacial acetic acid, it gives a 50% yield of 2:3-dinitro-4-methylaminophenyl *o*-toluenesulphonate,

$\text{C}_7\text{H}_7 \cdot \text{SO}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{NHMe}$, crystallising in yellow needles, m. p. 168 — 169° , and *o*-toluenemethylsulphonamide to the extent of 15—20%.

Benzoyl-*p*-anisidine when treated with nitric acid (D 1.4) at 70 — 80° yields benzoyl-2:3-dinitro-*p*-anisidine,

$\text{OMe} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{NHBz}$, felted, pale yellow needles, m. p. 185° , and with nitric acid (D 1.52) at 40° yields nitrobenzoyl-2:3-dinitro-*p*-anisidine,

$\text{OMe} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, pale yellow needles, m. p. 194 — 195° . Benzoyl-3-nitro-*p*-anisidine, $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{NHBz}$, is obtained by nitrating benzoyl-*p*-anisidine with nitric acid (D 1.4) in glacial acetic acid; it crystallises in orange leaflets, m. p. 140° . When the nitration is performed with nitric acid (1.52) in acetic anhydride, a mixture of the following compounds is obtained: benzoyl-2:3-dinitro-*p*-anisidine, nitrobenzoyl-2:3-dinitro-*p*-anisidine, and benzoyl-2:3:5-(or 2:3:6)trinitro-*p*-anisidine,

$\text{OMe} \cdot \text{C}_6\text{H}(\text{NO}_2)_3 \cdot \text{NHBz}$, m. p. 220 — 230° .

p-Methylaminophenyl benzoate, $\text{NHMe} \cdot \text{C}_6\text{H}_4 \cdot \text{OBz}$, prepared from *p*-methylaminophenol and benzoyl chloride in the presence of sodium acetate, forms white prisms, m. p. 173 — 174° . When treated with

nitric acid (D 1.4—1.52) it yields 2:3-dinitro-4-methylaminophenyl benzoate, $\text{NHMe} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{OBz}$, which crystallises in brownish-yellow needles, m. p. 178°. Nitration by a mixture of concentrated sulphuric acid and nitric acid leads to the formation of nitrobenzoyl-2:3-(or 2:6)-dinitro-4-methylaminophenol, crystallising in lemon-yellow needles, m. p. 203—204°. W. H. G.

So-called Photoanethole. A Contribution to the Chemical Action of Light. PAUL HOERING and KARL PAUL GRÄLERT (*Ber.*, 1909, 42, 1204—1207).—The substance described by de Varda as photoanethole (*Abstr.*, 1891, 1347) is shown to be 4:4'-dimethoxystilbene (compare Wiechell, *Abstr.*, 1894, i, 507). It is probably formed by the action of sunlight on the anisaldehyde present in anethole which has been exposed to the action of the air and light.

4:4'-Dimethoxystilbene dibromide, $\text{C}_{16}\text{H}_{16}\text{O}_2\text{Br}_2$, crystallises in short needles, m. p. 178° (decomp.). W. H. G.

Mechanism of the Resorcinol-Tartaric Colour Reaction. GEORGES DENIGES (*Bull. Soc. chim.*, 1909, [iv], 5, 323—326).—In a previous paper (this vol., ii, 190) it has been shown that the red or reddish-violet colour given by certain substances in presence of sulphuric acid and resorcinol is associated with the presence in these substances of the group $\text{HO} \cdot \overset{|}{\underset{|}{\text{C}}} - \overset{|}{\underset{|}{\text{C}}} \cdot \text{OH}$, or a derivative of this. It is now found that the mechanism of the reaction consists in the formation of aldehydes from these substances, by the action of sulphuric acid and the condensation of these aldehydes with the resorcinol or other phenol used.

The nature of the aldehyde (or aldehydes) formed in a number of cases is discussed. Confirmation of this view is found in the fact that some substances, such as glycerol, which do not give a coloration when the test is applied in the usual manner (*loc. cit.*, and *Abstr.*, 1896, ii, 80), give it after oxidation with permanganate. T. A. H.

Reversible Substitution of Alkoxy Groups in the Benzene Ring. JAN J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 313—320. Compare this vol., i, 150).—When attached to the benzene nucleus and under the influence of *o*- or *p*-nitro-groups, methoxyl can often be replaced by ethoxyl by the action of sodium ethoxide, and ethoxyl by methoxyl by means of sodium methoxide. *m*-Nitro-groups do not influence the substitution, but it is facilitated by increase in the number of nitro-groups in the ortho- and para-positions.

Sodium ethoxide reacts with 2:3:4-trinitroanisole in alcoholic solution to form the diethyl ether of 2:4-dinitroresorcinol, in addition to the corresponding methyl ethyl ether, the first compound resulting from replacement of both OMe and NO_2 by OEt.

With an alcoholic solution of sodium ethoxide, 3-chloro-4:6-dinitroanisole and 3-chloro-2:4:6-trinitroanisole yield respectively the diethyl ether of 4:6-dinitroresorcinol and that of 2:4:6-trinitroresorcinol, both OMe and Cl being replaced by OEt. Sodium methoxide dissolved in methyl alcohol yields with the same two

compounds the corresponding dimethyl ethers, OEt and Cl being replaced by OMe.

A similar solution of sodium methoxide converts the diethyl ether of 2 : 4 : 6-trinitroresorcinol into the corresponding dimethyl ether. A small quantity of sodium dissolved in methyl or ethyl alcohol suffices to start these reactions, but they do not take place in neutral or acid solutions.

The ethyl ethers of 4 : 6-dinitroresorcinol, picric acid, and 2 : 4-dinitrophenol are converted in analogous manner into the corresponding methyl ethers by treatment with sodium methoxide dissolved in methyl alcohol, and these are reconverted into the original ethyl ethers by boiling with a solution of sodium ethoxide in ethyl alcohol.

The greater the number of nitro-groups in the *para*-position to the alkoxy group the more rapid the transformation, so that the ethers of 2 : 4 : 6-trinitroresorcinol and picric acid react more quickly than those of 4 : 6-dinitroresorcinol and 2 : 4-dinitrophenol. The methoxyl group in *p*-nitroanisole is very stable towards sodium ethoxide (compare Luloffs, Abstr., 1902, i, 87). *m*-Nitro-groups exert no influence, so that the methoxyl group in 3 : 5-dinitroanisole is not affected by boiling with an alcoholic solution of sodium ethoxide. The influence of the *o*- and *p*-nitro-groups is well illustrated by the transformation of the dimethyl ether of 3 : 5-dinitrocatechol into 3 : 5-dinitro-2-ethoxyanisole.

Sodium disulphide, Na_2S_2 , and potassium cyanide undergo alcoholic dissociation in alcoholic solution; thus a solution of potassium cyanide in methyl alcohol converts 2 : 4-dinitrophenetole into 2 : 4-dinitroanisole, a similar solution in ethyl alcohol effecting the reverse transformation.

2 : 4 : 6-Trinitro-3-chloro-1-ethoxybenzene is converted by a solution of sodium methoxide in methyl alcohol into 2 : 4 : 6-trinitro-3-ethoxyanisole. This substance is not formed by treating 3-chloro-2 : 4 : 6-trinitroanisole with sodium methoxide, an indication that the replacement of methoxyl by ethoxyl is more readily effected than the converse transformation.

These reactions resemble those described by Lapworth (Proc., 1898, 159; 1903, 23), Meisenheimer (Abstr., 1902, i, 795), Loring Jackson and his students (Abstr., 1898, i, 517; 1900, i, 433; 1903, i, 339), and Merz and Ris (Abstr., 1886, 872). They depend on addition of sodium alkoxide at the nitro-group, with subsequent displacement of one alkyloxy-group by another, the nature of the substituting group being dependent on the particular alcohol employed. A. J. W.

1 : 5- and 1 : 8-Anthradiol [Rufol and Chrysazol]. BR. LAMPE (*Ber.*, 1909, 42, 1413—1418).—Recent work in this field (Abstr., 1904, i, 176, 256) has made it possible to prepare these two compounds in larger quantities than hitherto, and the author has re-investigated their properties.

Antraquinone-1 : 5- and -1 : 8-disulphonic acids were converted into the corresponding potassium anthracenedisulphonates (Abstr., 1882, 855), yield 70—80%, and these substances converted into the two dihydroxyanthracenes, rufol and chrysazol, $\text{C}_{14}\text{H}_8(\text{OH})_2$, respec-

tively, by fusing with potassium hydroxide; yield 80%. Rufol is a yellow, crystalline substance, m. p. 265° (decomp.), and gives a colourless diacetate and other derivatives, as described by Liebermann (Abstr., 1879, 257). Chrysazol is a pale yellow compound, m. p. 225° (decomp.), and gives a colourless, crystalline diacetyl compound, also in agreement with previous observations (Liebermann, Abstr., 1879, 537).

The alkyl ethers of these dihydroxyanthracenes were readily prepared by dissolving them in absolute alcohol, and passing a rapid current of dry hydrogen chloride through the solution warmed to about $50-60^{\circ}$. 1:5-*Anthradiol diethyl ether*, $C_{14}H_8(OEt)_2$, yield 70%, glistening needles, m. p. 179° ; the *dimethyl ether*, $C_{14}H_8(OMe)_2$, yield 75-80%, small, glistening plates, m. p. 224° .

When dissolved in carbon disulphide and treated with a carbon disulphide solution of bromine, the above ethers give respectively the *dibromo-derivative*, $C_{14}H_6Br_2(OEt)_2$, yellow needles, m. p. 250° , and $C_{14}H_6Br_2(OMe)_2$, yellow needles, m. p. 302° . 1:8-*Anthradiol diethyl ether*, $C_{14}H_8(OEt)_2$, yield 70%, brilliant plates, m. p. 139° ; the *dimethyl ether*, $C_{14}H_8(OMe)_2$, yield 70%, glistening plates, m. p. 198° . 1:5- and 1:8-*Anthracenedisulphonyl chlorides*, $C_{14}H_8(SO_2Cl)_2$, are obtained as yellow needles, m. p. 249° and 225° respectively, by treating the dry sodium salt of the anthracenedisulphonic acids with phosphorus pentachloride, and these compounds when treated with alcoholic ammonia solution give the 1:5-*disulphonamide*, m. p. above 330° , and the 1:8-*disulphonamide*, m. p. 333° . Similarly, 1:5- and 1:8-*anthracenedisulphonanilides* have been prepared; they have m. p. 293° and 224° respectively.
J. V. E.

Mechanism of the Action of Sulphur and of Selenium on Organomagnesium Derivatives. HENRI WUYTS (*Bull. Soc. chim.*, 1909, [iv], 5, 405-412).—The author has shown that sulphur reacts with organomagnesium derivatives to form a mixture of the corresponding thiol, monosulphide, and disulphide (Abstr., 1903, i, 686; 1906, i, 257); Taboury found that only the thiol and disulphide were formed, but when selenium replaced the sulphur in the reaction, the monoselenide was one of the products (Abstr., 1903, i, 748; 1904, i, 493; 1905, i, 56, 644; 1906, i, 834; 1907, i, 837).

The author now finds that when the reaction is carried out in an atmosphere of dry hydrogen, and excess of sulphur is avoided, the thiol is the only product, and this is obtained to the extent of 80% of the theoretical quantity; the disulphide is the result of the action of sulphur on the compound formed by the condensation of the thiol with a further quantity of organomagnesium derivative according to the equations: $R \cdot S \cdot H + R \cdot Mg \cdot X = R \cdot S \cdot MgX + R \cdot H$; $2R \cdot S \cdot Mg \cdot X + S = R \cdot S \cdot S \cdot R + S(MgX)_2$, whilst the monosulphide, as already shown (Abstr., 1906, i, 257), is formed from the interaction between the disulphide and the organomagnesium derivative: $R \cdot S \cdot S \cdot R + RMgX = R \cdot S \cdot R + R \cdot S \cdot MgX$. Taking the same precautions, selenophenol can be obtained to the extent of 81.2% of the theoretical quantity by the action of selenium on magnesium phenyl bromide.

The corrected boiling points of synthetic phenol, thiophenol, and

selenophenol prepared as above are phenol, $181.3^{\circ}/760$ mm.; thiophenol, $168.3^{\circ}/760$ mm.; selenophenol, $183.6^{\circ}/760$ mm. M. A. W.

Extraction of Phytosterols and Cholesterols from Fats. A. HEIDUSCHKA and H. W. GLOTH (*Pharm. Zentr.-h.*, 1909, 50, 333—334).—One hundred grams of the fat are saponified with 200 c.c. of alcoholic potassium hydroxide (200 grams in one litre of 70% alcohol), 600 c.c. of water are added, and the solution is placed in a specially constructed cylinder. By means of a special funnel-tube, 400 c.c. of ether are poured down to the bottom of the liquid, and as the ether collects on the surface, the solution is saturated with ether without having recourse to shaking. The cylinder is attached to a flask in which 500 c.c. of ether are being boiled; the ether distillate ascends through the alkaline liquid, meanwhile dissolving the unsaponifiable matters, and collects on the surface, from which at intervals it is syphoned back into the flask. After some four hours, the extraction is complete.

L. DE K.

Catalytic Actions of Colloidal Metals of the Platinum Group. VI. **Reduction Catalysis with Colloidal Palladium.** CARL PAAL and JOSEF GERUM (*Ber.*, 1909, 42, 1553—1560. Compare this vol., i, 358).—An investigation on the reduction of benzonitrile, mandelonitrile, and benzaldoxime with palladium hydrosol and hydrogen at the ordinary temperature.

Benzonitrile yields benzylamine, dibenzylamine, ammonia, and a small quantity of benzaldehyde, thus: (1) $\text{Ph}\cdot\text{CN} + \text{H}_2 = \text{CHPh}\cdot\text{NH}$; (2) $\text{CHPh}\cdot\text{NH} + \text{H}_2\text{O} = \text{Ph}\cdot\text{CHO} + \text{NH}_3$; (3) $3\text{Ph}\cdot\text{CHO} + 2\text{NH}_3 = (\text{CHPh}\cdot\text{N})_2\text{CHPh} + 3\text{H}_2\text{O}$; $(\text{CHPh}\cdot\text{N})_2\text{CHPh} + 3\text{H}_2 = \text{CH}_2\text{Ph}\cdot\text{NH}_2 + (\text{CH}_2\text{Ph})_2\text{NH}$.

The chief products of the catalytic reduction of mandelonitrile are benzylamine, dibenzylamine, ammonia, and benzyl alcohol. The formation of these substances may be explained on the assumption that the hydroxynitrile in aqueous-alcoholic solution is partly dissociated into benzaldehyde and hydrogen cyanide. The latter substance is reduced, yielding ammonia, which combines with benzaldehyde, forming hydrobenzamide; this is then reduced to benzylamine and dibenzylamine. The benzyl alcohol is produced by the reduction of part of the benzaldehyde.

Benzaldoxime yields the same reduction products as benzonitrile. It is probable that the first product of the reduction is benzylideneimine, which undergoes further decomposition, yielding ammonia, benzylamine, dibenzylamine, and benzaldehyde in the manner already described.

W. H. G.

Tri-halogen Substitution Products of Aromatic Compounds. FRANS M. JAEGER (*Zeitsch. Kryst. Min.*, 1909, 46, 266—279).—2:4:6-Tribromobenzophenone, $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{COPh}$, triclinic [$a:b:c = 1.3939:1:1.1065$; $\alpha = 130^{\circ}36'$, $\beta = 122^{\circ}59'$; $\gamma = 58^{\circ}58'$]. 2:4:6-Tribromobenzonitrile, monoclinic [$a:b:c = 1.2113:1:1.1025$; $\beta = 135^{\circ}36\frac{1}{4}'$]. 2:4:6-Tribromobenzamide, monoclinic [$a:b:c = 2.1655:1:1.1092$; $\beta = 96^{\circ}15'$]. 2:4:6-Tribromobenzoyl chloride, triclinic [$a:b:c = 1.9341:1:1.0041$; $\alpha = 89^{\circ}54\frac{3}{4}'$, $\beta = 108^{\circ}43\frac{3}{4}'$; $\gamma = 84^{\circ}21'$]. 2:4:6-Tribromo-

orcinol, $C_6Br_3Me(OH)_2$, triclinic [$a:b:c=1.6985:1.0.7755$; $\alpha=84^\circ42'$; $\beta=74^\circ33'$; $\gamma=91^\circ6'$]. Tri-*p*-iodotriphenylmethane,



rhombic [$a:b:c=0.5765:1.0.8798$]. Tri-*p*-iodotriphenylmethane + 1-benzene, triclinic [$a:b:c=0.5719:1.1.4298$; $\alpha=109^\circ8'$; $\beta=126^\circ21'$; $\gamma=107^\circ32'$]. Tri-*p*-chlorotriphenylcarbinol, rhombic [$a:b:c=0.6009:1.0.9781$]. Tri-*p*-bromotriphenylcarbinol, rhombic [$a:b:c=0.8407:1.0.8081$]. Tri-*p*-iodotriphenylcarbinol, rhombic [$a:b:c=0.8543:1.0.817$]. Tri-*p*-iodotriphenylcarbinol + benzene, triclinic [$a:b:c=1.3991:1.1.6135$; $\alpha=109^\circ16'$; $\beta=117^\circ36'$; $\gamma=62^\circ52'$]. L. J. S.

5-Bromo-2-aminobenzoic Acid: New Method of Preparation.

ALVIN S. WHEELER (*J. Amer. Chem. Soc.*, 1909, 31, 565—569).—The present work was undertaken with the object of converting trichloroethylidene-*o*-aminobenzoic acid (chloral-anthranilic acid) (Niementowski and Orzechowski, Abstr., 1896, i, 187) into a compound containing an asymmetric carbon atom. When, however, this acid is treated with a solution of bromine in glacial acetic acid, the expected asymmetric compound is not obtained, but 5-bromo-2-aminobenzoic acid *hydrobromide*, m. p. 238—240°, is produced. 5-Bromo-2-aminobenzoic acid melts at 218—219° (corr.), and its acetyl derivative at 218—220°.

When trichloroethylidene-di-*o*-aminobenzoic acid (chloral-dianthranilic acid) (Niementowski, Abstr., 1903, i, 91) is similarly treated with bromine, the same product is formed. A large yield of 5-bromo-2-aminobenzoic acid hydrobromide can also be obtained by the direct bromination of anthranilic acid. This reaction affords a much more convenient method of preparing 5-bromo-2-aminobenzoic acid than that described by Alt (Abstr., 1889, 987). E. G.

Action of Aliphatic Aldehydes on Aromatic Glycines. P. GELMO and WILHELM SUIDA (*Ber.*, 1909, 42, 1496—1502).—Formaldehyde and phenylglycine interact in cold aqueous solution, forming a yellow precipitate, $C_{33}H_{32}O_6N_4$, insoluble in most solvents, but dissolving in dilute acids and alkalis. It decomposes at 90—120°, giving carbon dioxide, and, when dissolved in hydrochloric acid, gives a yellow precipitate with platinum chloride. It further forms a thick, yellowish-white precipitate of a *barium* salt, $C_{33}H_{30}O_6N_4Ba$, and a similarly constituted dark green *copper* salt. When acetylated with acetic anhydride, carbon dioxide is eliminated, and two acetyl groups enter the molecule, forming a *compound*, $C_{36}H_{26}O_6N_4$. The original substance, when heated, forms a *base*, $C_{31}H_{32}O_2N_4$, soluble in chloroform, in which solvent the molecular-weight determination agrees with this formula. The base forms a *tetra-acetate*, $C_{39}H_{40}O_6N_4$, and yields with sodium nitrite an orange-red *dinitroso-compound*, $C_{31}H_{30}O_4N_6$.

Other aromatic glycines react with formaldehyde in a similar manner. The product from phenylmethylglycine has the composition $C_{87}H_{40}O_6N_4$. *p*-Tolylglycine, oxanilic acid, phenylacetic acid, phenoxylacetic acid, and hippuric acid do not react with formaldehyde under these conditions. E. F. A.

Isomeric Cinnamic Acids. II. EINAR BILLMANN (*Ber.*, 1909, 42, 1443—1450. Compare this vol., i, 155; also Liebermann, *ibid.*, 155).—Further experiments have confirmed the view that the two

isocinnamic acids and *allo-cinnamic acid* are trimorphous. It is shown that although the three acids have different m. p.'s, they form the same melt, which is the liquid form of all three, and which of the three solids is formed on cooling depends largely on the conditions of the experiment, rapid cooling tending to yield one acid only. Thus the *allo-acid* when fused and then cooled rapidly yields the *iso-acid*, m. p. 42°, when only small amounts are used, but with larger quantities the *allo-acid*, m. p. 68°, is formed. It is not necessary to heat the acids much above their respective m. p.'s in order to obtain the common melt; the process is not one of rearrangement within the molecule; the important factor is the process of fusion. The acid m. p. 42° is comparatively stable, and can be kept for several months in flasks plugged with cotton wool.

The *allo-acid* can be transformed into the *iso-acid*, m. p. 58°, by fusion, then solution of the melt in light petroleum, 60—70° (10 parts), and allowing the solution to cool in a flask provided with a cotton-wool plug. In removing the crystals it is essential that filter-paper and apparatus should be sterile (free from particles of *allo-acid*).

If the solutions are too dilute, the *allo-* and not the *iso-acid* frequently separates. The *iso-acid* m. p. 58° can also be obtained readily from the *allo-acid* by solution in light petroleum and impregnation.

J. J. S.

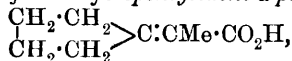
Terpenes and Ethereal Oils. XCIX. Preparation of Unsaturated Cyclic Acids and Hydrocarbons with a Semi-cyclic Linking. OTTO WALLACH (*Annalen*, 1909, 365, 255—277. Compare this vol., i, 399).—It has been shown that in the elimination of water from nopinol-acetic acid, the nature of the dehydrating agent has a marked influence on the course of the reaction (Abstr., 1908, i, 997). It is found as a result of further investigations on this subject that the hydroxy-acids or esters resulting from the condensation of the simple cyclic ketones with ethyl bromoacetate and zinc when treated with potassium hydrogen sulphate or phosphoric oxide yield chiefly unsaturated acids with the ethylene linking in the cyclic nucleus, whereas when the hydroxy-acids are boiled with acetic anhydride the tendency is for the water to be eliminated with the formation of a semi-cyclic linking. For example, ethyl *cyclohexanol-acetate* when treated with potassium hydrogen sulphate or phosphoric oxide is almost completely converted into ethyl Δ^1 -*cyclohexene-acetic acid* (Wallach and Isaac, Abstr., 1906, i, 176), whilst *cyclohexanol acetic acid* when boiled with acetic anhydride yields principally Δ^{α} -*cyclohexeneacetic acid* (Abstr., 1907, i, 616). 4-Methyl*cyclohexane-1-ol-1-acetic acid* behaves in an exactly analogous manner. It is found, as a general rule, that the acid with the semi-cyclic linking has a higher m. p. than the isomeride with the ethylene linking in the nucleus. Further, an acid with a semi-cyclic linking when heated alone yields the same hydrocarbon as the isomeric acid containing the ethylene linking in the nucleus, thus upholding the statement made previously that there is a tendency for unsaturated cyclic acids with an ethylene linking in the nucleus to yield hydrocarbons with a semi-cyclic linking (Abstr., 1908, i, 402).

Although many of the esters of hydroxy-acids formed by the condensation of ketones with halogenated acid esters and zinc when hydrolysed do not yield the hydroxy-acid, but are further dissociated, it is found that the simple cyclic hydroxy-acids, such as *cyclopentanolacetic acid*, *cyclohexanolacetic acid*, *p*-methyl*cyclohexanolacetic acid*, and the corresponding propionic acids, may be obtained by hydrolysing the respective esters. In all cases hitherto studied, it is found that the esters which when hydrolysed break down readily, when heated dissociate into ketone and aliphatic acid, whilst the hydroxy-acids which are found to be stable during their formation from the esters by hydrolysis, when distilled slowly break down into water and an unsaturated acid, which decomposes slightly, yielding carbon dioxide and a hydrocarbon. For example, α -mentholpropionic acid yields menthone and propionic acid, whilst *cyclohexanolacetic acid* decomposes into water, carbon dioxide, and chiefly methylenecyclohexane. The conversion of an unsaturated hydrocarbon with a semi-cyclic linking into a ketone containing an ethylene linking in the nucleus has hitherto been performed only with hexacyclic compounds; the formation of acetyl- Δ^1 -cyclopentene (Δ^1 -cyclopentene methyl ketone) from *cyclopentanone* is described in the present paper.

4-Methylcyclohexane-1-ol-1-acetic acid, m. p. 141° , or $89-90^\circ$ (compare Wallach and Evans, Abstr., 1906, i, 566), when boiled with acetic anhydride yields 1-methylcyclohexylidene-4-acetic acid, m. p. $63-64^\circ$. Perkin and Pope give m. p. about 70° (Trans., 1908, 93, 1084); the *amide* forms glistening leaflets, m. p. $121-122^\circ$. The acid when distilled yields 1-methyl-4-methylenecyclohexane, identical with the hydrocarbon obtained from methyl- Δ^4 -cyclohexeneacetic acid (Wallach and Evans, *loc. cit.*).

[With MAHLON RENTSCHLER.]—1-Methylcyclohexane-1-ol-1- α -propionic acid, $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{C}(\text{OH}) \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$, obtained by hydrolysing the ethyl ester, crystallises in two modifications; the less soluble form has m. p. $110-111^\circ$; the more soluble variety has a lower m. p. The *acid*, m. p. $110-111^\circ$, when heated with acetic anhydride yields 1-methylcyclohexylidene-4- α -propionic acid, obtained as a viscid liquid, which when distilled slowly in hydrogen yields 1-methyl-4-ethylidenecyclohexane, b. p. $152-153^\circ$, $D_{21}^{25} 0.810$, $n_D^{25} 1.4571$ (compare Wallach and Evans, Abstr., 1908, i, 404). The same hydrocarbon is more readily obtained by the dry distillation of 1-methylcyclohexane-1-ol-1- α -propionic acid. The *nitrosochloride* derived from the hydrocarbon has m. p. $108-110^\circ$.

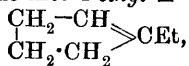
[With KURT VON MARTIUS.]—Ethyl cyclopentane-1-ol-1- α -propionate, $\begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{C}(\text{OH}) \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$, obtained by the action of zinc and ethyl α -bromopropionate on *cyclopentanone*, yields on hydrolysis the crystalline *acid*, m. p. $58-59^\circ$. The latter substance when heated with acetic anhydride yields cyclopentylidene- α -propionic acid,



a crystalline substance, m. p. $107-108^\circ$, which when distilled yields

chiefly *ethylidenecyclopentane*, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C} : \text{CHMe}$, a colourless liquid, b. p. 113—117°, D 0.8020, n_D^{20} 1.4481. The *nitrosochloride* when heated with alcoholic piperidine forms a *nitrolpiperidide*, m. p. 110°, and when boiled with glacial acetic acid and sodium acetate yields the *oxime* of *acetylcyclopentene*, m. p. 90—91°. The latter substance when hydrolysed yields *acetylcyclopentene* (compare Perkin and Wallach, this vol., i, 154).

1-*Ethylcyclopentane-1-ol*, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CEt} \cdot \text{OH}$, prepared from *cyclopentanone* by Grignard's reaction, is a colourless liquid with a camphor-like odour, b. p. 155—157°, D 0.916, $n_D^{21.5}$ 1.4528. It is converted on treatment with zinc chloride into 1-*ethyl-Δ¹-cyclopentene*,



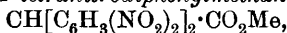
a colourless liquid, b. p. 107—110°, D 0.7975, n_D^{20} 1.4426, which yields a *nitrosochloride*, from which an oily *oxime* was prepared. The latter when hydrolysed gave a substance which is probably 1-*ethyl-Δ¹-cyclopentene-2-one*.
W. H. G.

Ethyl α-Dinitrophenylacetoacetate and Related Compounds.

II. WALTHER BORSCHKE (*Ber.*, 1909, 42, 1310—1318. Compare this vol., i, 232).—The investigation was undertaken with the object of comparing the reactions of the esters of nitroarylacetic acids with those of β-ketonic acids, in view of the analogy which subsists between the nitro-substituted aryl group, (NO₂)_xAr—, and the acid radicle, RCO—, as shown in the acid character of their corresponding hydroxyl derivatives, the nitrophenols, and the carboxylic acids. The present communication contains an account of the reactions of methyl dinitrophenylacetate with benzoyl chloride, nitrous acid, and certain aromatic aldehydes.

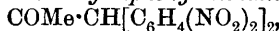
2:4-Dinitrophenylacetic acid, prepared by nitrating phenylacetic acid with a mixture of nitric and sulphuric acids below 60°, has m. p. 179—180°, and not 160°, as stated.

By acting on methyl sodiodinitrophenylacetate with benzoyl chloride and hydrolysing the resulting product with dilute sulphuric acid, a 40% yield of ω-2:4-dinitrophenylacetophenone is obtained. When treated with bromo-2:4-dinitrobenzene, the sodium derivative above-mentioned gives *methyl 2:4:2':4'-tetranitrodiphenylmethane-α-carboxylate*,



which crystallises from a mixture of chloroform and methyl alcohol in rhombic plates, m. p. 159°.

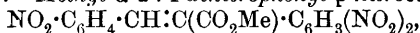
2:4:2':4'-*Tetranitro-α-acetyldiphenylmethane*,



obtained by acting on the sodium derivative of dinitrophenylacetone with bromodinitrobenzene, crystallises from ethyl acetate in yellow, glistening needles, m. p. 183° (decomp.).

Methyl 5-nitrobenzisooxazole-2-carboxylate, $\begin{array}{c} \text{O} - \text{C}_6\text{H}_3 \cdot \text{NO}_2 \\ | \quad | \\ \text{N} = \text{C} \cdot \text{CO}_2\text{Me} \end{array}$, is obtained by shaking a mixture of methyl dinitrophenylacetate and *isoamyl* nitrite

with sodium and methyl alcohol; it crystallises from methyl alcohol in yellowish-white, glistening needles, m. p. 130—131°. On substituting ethyl alcohol for methyl alcohol, the corresponding *ethyl* ester is obtained, which crystallises from ethyl alcohol in yellow leaflets, m. p. 101—102°. *Methyl α-2:4-dinitrophenyl-p-nitrocinnamate*,



is prepared by heating methyl dinitrophenylacetate with nitrobenzaldehyde and a few drops of piperidine at 150° for twenty minutes; it separates from a mixture of ethyl acetate and alcohol in light brown needles, m. p. 169—170°.

3-o-p-Dinitrophenylcoumarin, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}=\text{C} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2 \\ \text{O}-\text{CO} \end{smallmatrix}$, obtained

in a similar manner by the interaction of methyl dinitrophenylacetate and salicylaldehyde in presence of piperidine, crystallises from a large volume of glacial acetic acid in glistening plates, m. p. 249—250°.

3-o-p-Dinitrophenylcarbostyryl, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}=\text{C} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2 \\ \text{NH}-\text{CO} \end{smallmatrix}$, prepared

by condensing the ester with α-aminobenzaldehyde at 180°, crystallises from glacial acetic acid in dark yellow, glistening crystals; it is not visibly altered by heating to 270°. P. H.

Hydrophthalic Acids. VII. Resolution of the Racemic Form of the Fumaroid Δ⁴-Tetrahydrophthalic Acid. GINO ABATI and CESARE DE HORATIIS (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 218—223. Compare this vol., i, 104).—According to von Baeyer, whose extension of Le Bel and van't Hoff's theory to hydrogenated phthalic acids has recently received confirmation (Abstr., 1900, i, 100), *trans*-Δ⁴-tetrahydrophthalic acid should be capable of existing in two optically antipodal forms. Attempts to effect separation of these forms by means of the quinine salts have led to the isolation of two acids: (1) that obtained from the less soluble (in 96% alcohol) quinine salt, which has $[\alpha]_D^{25} + 115.2^\circ$; and (2) the one corresponding with the more soluble quinine salt, and having $[\alpha]_D^{25} - 97.4^\circ$. This difference between the arithmetic magnitudes of the two rotations is explained by the fact that the acid obtained by the reduction of phthalic acid is pseudo-racemic, its rotation being $[\alpha]_D^{25} + 2.9^\circ$, and that of its anhydride, $[\alpha]_D^{25} 4.17^\circ$. The anhydride of the dextrorotatory Δ⁴-tetrahydrophthalic acid has $[\alpha]_D^{25} + 6.6^\circ$.

T. H. P.

Hydrophthalic Acids. VIII. Influence of Presence and Position of the Ethylene Grouping on the Refraction and Dispersion of Hydrophthalic Anhydrides. GINO ABATI and ERNESTO VERGARI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 223—234).—The authors have measured the rotations and dispersions of phthalic anhydride, of the various di-, tetra-, and hexa-hydrophthalic anhydrides, and of citraconic and itaconic anhydrides, in order to ascertain whether the laws of Brühl concerning the rotations and dispersions of compounds containing two neighbouring groups of high refractive power (Trans., 1907, 91, 115) hold for these compounds.

The results obtained directly contradict Brühl's laws. Thus, for the tetrahydrogenated derivatives, the molecular refraction should be greatest for the Δ^1 -anhydride, and should diminish as the distance of the ethylene group from the carbonyls increases; in reality, however, the values for the Δ^1 - and Δ^2 -compounds are slightly below, and the value for the Δ^3 -compound slightly above, the theoretical value.

The most striking feature of the results is the great differences between the refractions of stereoisomerides, in each of the three cases examined the fumaroid derivative having an appreciably higher molecular refraction than the maleinoid form. The difference amounts to 2.68 for the $\Delta^{3:5}$ -dihydro-acid, to 5.08 for the Δ^4 -tetrahydro-anhydride, and to 0.75 for the hexahydroanhydride. In nearly all the cases previously observed, the fumaroid isomeride has slightly the higher refraction.

The specific dispersion does not always correspond with the refraction for the line H_α . Excepting with the four dihydrophthalic anhydrides, where parallelism exists, in none of the cases is there any relation with the constitution of the compounds of the kind formulated by Brühl (*loc. cit.*).
T. H. P.

Gentisic Acid (2:5-Dihydroxybenzoic Acid) and Derivatives. FRANZ VON HEMMELMAYR (*Monatsh.*, 1909, 30, 255—269).—By the action of bromine on gentisic acid, a monobromogentisic acid is formed; excess of bromine eliminates the carboxyl group, forming bromo-anil, and a dibromogentisic acid could not be obtained. The isomeric dihydroxybenzoic acids yield dibromo-derivatives. By the action even of excess of methyl iodide and sodium methoxide, bromogentisic acid monoethyl ether is obtained; in this, probably the hydroxyl in the meta-position to the carboxyl group is methylated. When sodium hydroxide in methyl-alcoholic solution is employed, it is possible also to some extent to methylate the second hydroxyl. When heated at 160° in presence of water, bromoquinol is formed from the bromogentisic acid, which probably has the composition $\text{CO}_2\text{H}\cdot\text{C} \begin{smallmatrix} \text{C}(\text{OH})\text{:CBr} \\ \text{CH}-\text{C}(\text{OH}) \end{smallmatrix} \text{CH}$.

Nitric acid has an oxidising action on gentisic acid; only when very dilute acid is employed was evidence of the formation of a nitro-compound obtained. Nitric acid also acts only as an oxidising agent towards bromo- and diacetyl-gentisic acids.

Bromogentisic acid forms colourless needles, m. p. 238°, which show a blue coloration with ferric chloride. The *barium* salt forms faintly rose-coloured tablets; the *silver* salt separates in colourless needles; the *methyl* ester crystallises in glistening plates, m. p. 135°, and gives a greenish-blue coloration with ferric chloride.

Bromogentisic acid monomethyl ether has m. p. 194°, and gives an intense blue ferric chloride coloration; the *barium* salt forms needles, grouped in feather-like clusters.

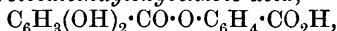
Bromogentisic acid dimethyl ether crystallises in needles, m. p. 122°. *Diacetylgentisic acid* forms colourless crystals, m. p. 118—119°.

E. F. A.

Derivatives of Protocatechuic Acid. TOKUHEI KAMETAKA (*Ber.*, 1909, 42, 1482—1485).—By the interaction of dimethyl-

carbonatoprotocatechuy chloride and ethylglycine in ethereal solution, *ethyl dimethylcarbonatoprotocatechuyglycine* is obtained as a colourless syrup. On hydrolysis with sodium hydroxide, 3 : 4-*dihydroxyhippuric acid*, $C_6H_3(OH)_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, is formed, crystallising in colourless prisms, m. p. 228° (corr. with decomp.).

p-*Dimethylcarbonatoprotocatechuyloxybenzoic acid* forms a crystalline precipitate, which, when heated, softens at 165° , sinters at 180° , m. p. 187.5° (corr.). *p*-*Protocatechuyloxybenzoic acid*,

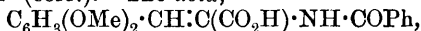


forms microscopic, colourless needles, aggregated in balls, m. p. 270° to a brown liquid. E. F. A.

Derivatives of Benzylphenaceturic Acid. WALTER KROPP and HERMAN DECKER [and, in part, CLEMENS ZOELLNER] (*Ber.*, 1909, 42, 1184—1192).—Various *isoquinoline* derivatives closely related to certain natural alkaloids have been synthesised by Plöchl and Erlenmeyer, jun.'s methods.

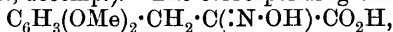
Veratrylidenehippuric anhydride, $C_6H_3(OMe)_2 \cdot CH : C \begin{smallmatrix} N=CPh \\ CO \cdot O \end{smallmatrix}$

obtained by heating methylvanillin and hippuric acid with acetic anhydride and anhydrous sodium acetate, is purified by extracting with cold alcohol and boiling water, and crystallises from benzene in yellow plates, m. p. 152° (corr.). The *acid*,



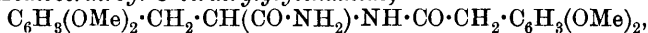
is obtained by boiling the anhydride with 2% sodium carbonate solution and precipitating the clear solution with a mineral acid. It crystallises from hot alcohol in prisms, m. p. 213° (corr.). The *methyl ester*, $C_{19}H_{19}O_5N$, crystallises from methyl alcohol in transparent plates, m. p. 147° (corr.).

3 : 4-*Dimethoxyphenylpyruvic acid*, $C_6H_3(OMe)_2 \cdot CH_2 \cdot CO \cdot CO_2H$, obtained by boiling the anhydride for four hours with 10% sodium hydroxide solution, acidifying, and removing the benzoic acid by steam distillation, crystallises from glacial acetic acid in colourless plates, m. p. 187° (corr., decomp.). The corresponding oxime,

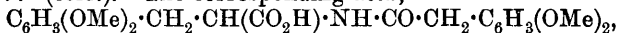


crystallises from hot water in slender needles, m. p. 165° (decomp.).

N-*Homoveratroyl-C-veratrylglycinamide*,



obtained by heating the ketonic acid with aqueous ammonium hydroxide solution at 100° , crystallises from water in needles, m. p. 176 — 177° (corr.). The corresponding *acid*,

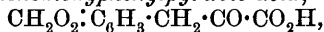


prepared by hydrolysing the amide with sodium hydroxide solution, also crystallises from water in colourless needles, m. p. 156 — 157° (corr.).

Piperonylidenehippuric anhydride, $CH_2 \begin{smallmatrix} O \\ \diagup \diagdown \\ O \end{smallmatrix} C_6H_3 \cdot CH : C \begin{smallmatrix} N=CPh \\ CO \cdot O \end{smallmatrix}$,

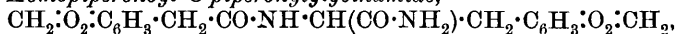
crystallises from benzene in yellow, flat needles, m. p. 197.4° (corr.). The corresponding *acid*, $C_{17}H_{15}O_5N$, turns yellow at 200° , and decomposes and melts at about 235° (corr.). The *methyl ester*, $C_{18}H_{15}O_5N$,

crystallises from methyl alcohol, and has m. p. 151° (corr.). At a slightly higher temperature decomposition begins, and in all probability the anhydride is re-formed. The *ethyl* ester, $C_{19}H_{17}O_5N$, has m. p. 136° (corr.). *Methylenedioxyphenylpyruvic acid*,



crystallises from glacial acetic acid in plates, m. p. 215° (decomp.). The *oxime*, $CH_2O_2:C_6H_3\cdot CH_2\cdot C(:N\cdot OH)\cdot CO_2H$, crystallises from water, and has m. p. $170-171^{\circ}$ (decomp.).

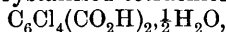
N-Homopiperonoyl-C-piperonylglycinamide,



crystallises from alcohol in needles, m. p. 189.5° (corr.), and the corresponding *acid*, $C_{19}H_{17}O_7N$, crystallises from a mixture of benzene and alcohol in stellar aggregates of needles, m. p. 179° (corr.).

J. J. S.

Tetrachlorophthalic Acid. T. G. DELBRIDGE (*Amer. Chem. J.*, 1909, 41, 393—417).—Crystallised tetrachlorophthalic acid,



has been described by previous authors as anhydrous; when heated to 109° , it is completely converted into tetrachlorophthalic anhydride; hence the observed melting point ($255-257^{\circ}$) is in reality that of the pure anhydride; the m. p.'s of the acid and its anhydride are stated by previous workers to be 250° and 245° respectively. Anhydrous tetrachlorophthalic acid is formed when the acid is crystallised from acetone; a compound containing two molecules of acetone is hereby produced, which, in a current of dry air, loses all its acetone, leaving anhydrous tetrachlorophthalic acid; this anhydrous acid takes up moisture from the air to form the stable acid containing $\frac{1}{2}H_2O$.

P. H.

Tetrachlorophenolphthalein and Some of its Derivatives.

WILLIAM R. ORNDORFF and JOHN A. BLACK (*Amer. Chem. J.*, 1909, 41, 349—393).—Tetrachlorophenolphthalein (compare Graebe, *Abstr.*, 1887, 832) can be prepared by heating a mixture of tetrachlorophthalic anhydride, fuming sulphuric acid containing 15% of sulphur trioxide, and phenol for twelve hours at $145-150^{\circ}$; 65% of the tetrachlorophthalic acid is thereby converted into the tetrachlorophthalein and 10% into tetrachlorofluoran; it crystallises from dilute alcohol in slender needles and from methyl alcohol in monoclinic crystals, and does not melt at 300° ; it dissolves in alkali hydroxides or carbonates; in concentrated solution the colour is red, in thin layers purple, whilst in dilute solution it is violet-red; in very dilute alkaline solution the colour has a bluish tint, which distinguishes it from phenolphthalein.

Tetrachlorofluoran, $O\langle C_6H_4 \rangle C\langle C_6Cl_4 \rangle CO$, obtained as stated above, crystallises from benzene in triclinic prisms; it does not melt at 300° .

Tetrachlorodiacetylphenolphthalein, $C_{20}H_8O_4Cl_4Ac_2$, prepared by heating the tetrachlorophenolphthalein with acetic anhydride and sodium acetate, separates from alcohol in monoclinic crystals, and has m. p. $205-206^{\circ}$.

Tetrachlorophenolphthalein methyl ether, obtained by heating tetrachlorophenolphthalein with sodium in absolute methyl alcohol and methyl iodide for three hours, separates from acetone in monoclinic or triclinic scales; it does not melt at 300°.

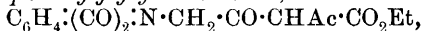
The *dimethyl ether*, obtained by heating the same mixture for 120 hours, is colourless; it forms flattened needles from alcohol, m. p. 152—153°.

Tetrachlorotetrabromophenolphthalein, obtained by adding bromine dissolved in glacial acetic acid to a boiling alcoholic solution of tetrachlorophenolphthalein, separates from benzene in colourless crystals, and does not melt at 300°; it is a stronger acid than tetrachlorophenolphthalein or phenolphthalein, but, like these substances, is sensitive to carbonic acid and cannot therefore be used for titrating carbonates. Its *diacetate*, m. p. 190—191°, crystallises from benzene; the *di-ammonium* salt is an unstable, blue compound; the *disilver* salt was also prepared.

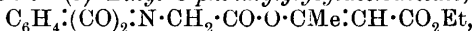
Tetrachlorotetrabromophenolphthalein dimethyl ether is a colourless substance, which separates from benzene in triclinic crystals, m. p. 265—266°; the *diethyl ether*, colourless crystals from benzene, m. p. 201—202°.

Tetrachlorophenolphthalein and tetrachlorotetrabromophenolphthalein can be used as indicators for titrating organic acids or alcoholic solutions; neither of them is esterified by alcohol and hydrochloric or sulphuric acid. P. H.

Action of Phthalylglycyl Chloride on Ethyl Sodiacetoacetate. JOHANNES SCHEIBER (*Ber.*, 1909, 42, 1441—1443).—The products obtained by the action of a benzene or ethereal solution of phthalylglycyl chloride on the sodium derivative of ethyl acetoacetate are: (a) *Ethyl O-phthalylglycylacetoacetate*,



which crystallises from boiling alcohol in brilliant, colourless prisms, m. p. 135—136°. (b) *Ethyl O-phthalylglycylacetoacetate*,



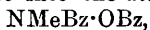
which forms colourless crystals, m. p. 97—98°. (c) *Ethyl diphtalylglycylacetoacetate*, $\text{CAc}(\text{CO}\cdot\text{CH}_2\cdot\text{N}\cdot\text{C}_2\text{O}_2\cdot\text{C}_6\text{H}_4)_2\cdot\text{CO}_2\text{Et}$, long needles from alcohol, m. p. 158—159°. High temperatures favour the formation of a, and working in the cold the formation of b and c, but the yields are poor in all cases. J. J. S.

Oximino-compounds. ERNST BECKMANN (*Annalen*, 1909, 365, 201—214).—Hitherto, aldoximes prepared by the action of free hydroxylamine on various aldehydes have been converted into the corresponding β -modifications by subsequent treatment with hydrogen chloride. It is now found that many aldehydes, for example, benzaldehyde, anisaldehyde, and cuminaldehyde, are converted directly into the hydrochlorides of the β -aldoximes by warming with hydroxylamine hydrochloride in alcohol. It is not possible, however, to obtain isomerides by this new method of preparation if they have not been prepared already by the older method; for example, salicylaldoxime and acetophenoneoxime prepared by this method were found

to be identical with the compounds obtained by other methods; β -modifications were not formed. The hydrochlorides of the β -aldoxime-*N*-ethers may also be prepared directly from the aldehydes by acting on these with *N*-alkylhydroxylamine hydrochlorides. The following substances were prepared by this method: *N*-phenylbenzaloxime, *N*-phenylanisaldoxime, *N*-methylbenzaloxime, *N*-methylanisaldoxime, *N*-methylsalicylaldoxime, *N*-methyl-*p*-hydroxybenzaloxime, and *N*-methylcuminaldoxime. The isomeric *N*-methylbenzaldoximes investigated by Luxmoore (Trans., 1896, 69, 177) are not stereoisomerides (compare Scheiber, following abstract).

[With HANS NETSCHER.]—*N*-Methylanisaldoxime forms colourless crystals, m. p. 76° (compare Scheiber, *loc. cit.*); the hydrochloride forms white crystals, m. p. 183° . Phenylcarbimide acts on the oxime ether, yielding the carbanilido-derivative, $C_{16}H_{16}O_3N_2$, m. p. 85° . *N*-Methylsalicylaldoxime, $C_8H_9O_2N$, forms white crystals, m. p. 134 — 135° ; the hydrochloride has m. p. about 140° . *p*-Hydroxy-*N*-methylbenzaldoxime is obtained as a white, crystalline powder, m. p. 220° (decomp.). *N*-Methylcuminaldoxime, $C_{11}H_{15}ON$, crystallises in glistening, silvery leaflets, m. p. 65° ; the hydrochloride is extremely deliquescent.

N-Methylhydroxylamine reacts with acetophenone and acetobenzophenone, but crystalline products could not be isolated; a crystalline substance, m. p. 114° , was obtained with acetone, and acetylacetone also yields a crystalline substance, m. p. 65° . *N*-Methylhydroxylamine is converted by phenylcarbimide into β -carbanilido-*N*-methylhydroxylamine, m. p. 96 — 98° (compare Kjellin, Abstr., 1894, i, 9), and by benzoyl chloride into the dibenzoyl derivative,



colourless crystals, m. p. 56° .

W. H. G.

Appearance of Stereoisomerism in *N*-Substituted Aldoximes. JOHANNES SCHEIBER (*Annalen*, 1909, 365, 215—239).—Evidence of the existence of stereoisomerides of only two *N*-substituted aldoximes has been published up to the present, although about 140 *N*-substituted aldoximes are known. Of the two cases, that investigated by Luxmoore (Trans., 1896, 69, 177) appeared to be founded on the more weighty evidence. It seemed desirable, therefore, to investigate this subject more thoroughly, and as a result it is found that the supposed stereoisomeric *N*-methylbenzaloxime described by Luxmoore is really a monohydrated form of the *N*-methylbenzaloxime described originally by Goldschmidt and Kjellin (Abstr., 1891, 1477).

Attempts to obtain two modifications of *N*-benzylbenzaloxime and *N*-methylanisaldoxime were unsuccessful. The existence of two forms of the latter compound appeared probable, since a *N*-methylanisaldoxime prepared by Goldschmidt (Abstr., 1892, 974) had m. p. 45° , whilst that described by Beckmann and Netscher (preceding abstract) had m. p. 76° . However, in this case, also, the compound with the lower m. p. was found to be a hydrated form of *N*-methylanisaldoxime, m. p. 76° . Similarly, although two hydrobromides were prepared from *N*-methylanisaldoxime, it was found that the one was a hydrated form of the other.

[With H. FLEISCHMANN and RUDOLF FLEBBE.]—*N*-Methylbenzaloxime hydrobromide is most readily prepared by the action of methylhydroxylamine hydrobromide on benzaldehyde in alcohol. Contrary to Luxmoore's statement, the hydrobromide prepared by the action of methyl bromide on benzalaldoxime is identical with that obtained by the action of hydrogen bromide on *N*-methylbenzaloxime; it is a *monohydrate*, C_8H_9ON, HBr, H_2O , m. p. 67—68°, and passes into the *anhydrous* salt, C_8H_9ON, HBr , m. p. 124°, when kept in a vacuum desiccator. A *hydrobromide*, C_8H_9ON, HBr , m. p. 85°, is obtained by treating a solution of the aldoxime in a perfectly dry mixture of benzene and ether with hydrogen bromide. It yields the monohydrate when crystallised from ether and alcohol.

The hydrobromide, m. p. 67°, when treated with ammonia in alcoholic solution, yields an oil which is, without doubt, the hydrated form of the *N*-ether; a small quantity of the *O*-methyl ester is also formed at the same time. The substance, m. p. 45—49°, described by Luxmoore was never obtained. The oily substance obtained initially becomes semi-solid when kept, owing to the separation of the *N*-methyl ether, m. p. 81—82°.

N-Methylbenzaloxime hydrochloride, C_8H_9ON, HCl , is extremely hygroscopic, and only when perfectly dry has m. p. 140°; the *hydrate*, C_8H_9ON, HCl, H_2O , has m. p. 95—100°.

N-Methylanisaloxime has m. p. 76° (compare Beckmann and Netscher, *loc. cit.*); it rapidly absorbs water from the air, passing into the *hydrate*, $C_9H_{11}O_2N, H_2O$, m. p. about 45°, which is probably identical with the *N*-methylanisaloxime described by Goldschmidt (*loc. cit.*). The *hydrobromide*, $C_9H_{11}O_2N, HBr$, has m. p. 170°; the *hydrate* ($1H_2O$) has m. p. 136°. Attempts to prepare a hydrated form of the hydrochloride were fruitless.

W. H. G.

The Aldehyde Reaction. ANGELO ANGELI and VINCENZO CASTELLANA (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 376—378. Compare this vol., i, 308).—The authors describe experiments made with the view of determining the influences of the solvent and of the experimental conditions on the addition of dihydroxyammonia to aldehydes and to true nitroso-derivatives (compare Jeanrenaud, *Abstr.*, 1889, 870).

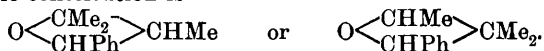
With a sulphydroxamic acid and an aldehyde, four reactions are possible: (1) $R \cdot SO_2 \cdot NH \cdot OH + H_2O = R \cdot SO_2H + NH(OH)_2$; (2) $R \cdot CHO + NH(OH)_2 = OH \cdot CR : N \cdot OH + H_2O$; (3) $2NH(OH)_2 = N_2O + 3H_2O$, and (4) $nR \cdot CHO = (R \cdot CHO)_n$, the yield of hydroxamic acid depending on the velocity of reaction (2). With aliphatic and aromatic aldehydes and their ethers, this reaction is almost instantaneous, and gives good yields in either aqueous or alcoholic solution; with certain unsaturated aldehydes it is slower. Ortho-substitution in aromatic aldehydes, in general, retards the reaction, and in some cases completely stops it. When alcohol is used as solvent, the reaction takes place more readily, so that a good yield of *m*-hydroxybenzhydroxamic acid (*loc. cit.*) may be obtained, provided the calculated proportion of potassium hydroxide is added gradually. Under the

same conditions, salicylhydroxamic acid is obtained in small yield, whilst in aqueous solution the reaction takes place neither with benzenesulphydroxamic acid nor with the sodium salt of nitrohydroxyl-aminic acid; in the latter cases, the abundant evolution of nitrous oxide shows that the change is mainly according to equation (3).

Even in alcoholic solution it is found impossible to obtain hydroxamic acids from aromatic aldehydes containing a hydroxyl in the para-position, although the alkyl ethers of these *p*-hydroxy-aldehydes behave normally.

T. H. P.

Organic Syntheses by means of Sunlight. II. EMANUELE PATERNÒ and G. CHIEFFI (*Gazzetta*, 1909, 39, i, 341—361).—The compound obtained from benzaldehyde and amylene (or β -methyl- Δ^8 -butylene) (this vol., i, 240) has the formula $C_{12}H_{16}O$, is a limpid, colourless, highly refractive liquid, D_0 0.9855, b. p. 230—232° (decomp.), n_D 1.50710, and has the normal molecular weight (157.0—168.7, instead of 176) in freezing benzene. When oxidised with permanganate, it gives benzoic acid, whilst reduction with phosphorus and iodine yields a *hexylbenzene*, $C_{12}H_{18}$, b. p. 175—180°. Its probable constitution is



With anisaldehyde under the influence of sunlight, amylene yields a hydroanisoin, and an *additive* compound, b. p. 260—300° (decomp.); with valeraldehyde, the reaction is complicated by the formation of polymerides of amylene.

The product of the interaction of benzaldehyde and octylene yields two fractions, b. p. 275—300° and 300—340°, which give analytical numbers corresponding closely with an additive compound, $C_{15}H_{22}O$.

The compound of benzophenone and amylene (*loc. cit.*), $O < \begin{array}{c} CPh_2 \\ C_5H_{10} \end{array} >$, m. p. 110—111°, b. p. 305—310° (decomp.), separates from alcohol in large, transparent, monoclinic crystals [ZAMBONINI: $a:b:c = 0.3707:1:0.3692$; $\beta = 103^\circ 23'$]. This compound is very stable towards the action of oxidising agents, bromine converting it into benzopinacolin; on reduction with hydriodic acid, it yields an oily hydrocarbon, $C_{18}H_{22}$, b. p. 281—283°.

The compound obtained from acetophenone and amylene (*loc. cit.*), $C_{13}H_{18}O$, is a transparent liquid, b. p. 232—233°, D_0 0.9792, n_D 1.50710. Amylene also yields *additive* compounds with benzylideneacetone, b. p. 320—340°, with benzoylacetone, b. p. about 300°, and with hexyl acetylmethyl ketone, b. p. above 280°.

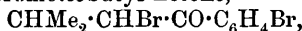
Additive compounds are also formed with hexylene, octylene, hexadecylene, and benzophenone, but here the ketone undergoes reduction to benzopinacone by the higher homologue of amylene, so that the additive compounds are probably formed from hydrocarbons containing two double linkings.

Amylene does not react under the influence of sunlight with hydrocarbons, phenols, alcohols, aceto- and benzo-nitriles, pyridine, piperidine, and organic acids.

T. H. P.

Action of Alkali Hydroxides on α -Bromo-ketones. ELMER P. KOHLER (*Amer. Chem. J.*, 1909, **41**, 417—430).—Potassium hydroxide reacts with α -bromo-ketones to form either unsaturated ketones or α -hydroxy-ketones, as illustrated by the two equations:

(i) $\text{CHPh}_2 \cdot \text{CPhBr} \cdot \text{COPh} + \text{KOH} = \text{CHPh}_2 \cdot \text{CPh} \cdot \text{COPh} + \text{KBr} + \text{H}_2\text{O}$;
 (ii) $\text{CHPh}_2 \cdot \text{CMeBr} \cdot \text{COPh} + \text{KOH} = \text{CHPh}_2 \cdot \text{CMe(OH)} \cdot \text{COPh} + \text{KBr}$;
 but the formation of an unsaturated ketone is only observed when the bromo-ketone contains two aryl groups in the β -position. Klages, however, states (*Chem. Zeit.*, 1908, **33**, 318) that phenyl vinyl ketone and its homologues are easily obtained by the action of potassium hydroxide on α -bromo-ketones. The present author, however, finds that the substance described by Klages as phenyl vinyl ketone, b. p. 217—219°, is in reality a mixture of phenyl methyl diketone, b. p. 217—219°, phenyl ethyl ketone, b. p. 220—221°, and benzoyl-methylcarbinol, and that no unsaturated ketone can be detected among the products of this reaction, or of the action of potassium hydroxide on *p*-bromophenyl α -bromoisobutyl ketone,

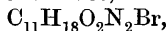


which substance, having a tertiary hydrogen atom in the β -position, might be expected to lose hydrogen bromide readily.

The formation of the diketone mentioned above is explained by the equation: $2\text{R} \cdot \text{CO} \cdot \text{CHBrR}' + 2\text{KOH} = \text{R} \cdot \text{CO} \cdot \text{CO} \cdot \text{R}' + \text{R} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{R}' + 2\text{KBr} + \text{H}_2\text{O}$.

p-Bromophenyl methyl diketone, $\text{C}_6\text{H}_4\text{Br} \cdot \text{CO} \cdot \text{COMe}$, obtained by the action of potassium hydroxide on *p*-bromophenyl α -bromocethyl ketone, is a yellow solid, m. p. 48°; the *phenylhydrazone*, $\text{C}_{15}\text{H}_{13}\text{ON}_2\text{Br}$, m. p. 199°, separates from alcohol in thin, yellow plates, and the *dioxime*, $\text{C}_9\text{H}_9\text{O}_2\text{N}_2\text{Br}$, m. p. 237°, forms small, lustrous prisms from alcohol; it readily forms an additive compound with sodium hydrogen sulphite. *p*-Bromophenyl ethyl ketone and *p*-bromophenyl α -hydroxyethyl ketone, $\text{OH} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Br}$, are formed also in the above reaction; the latter is a pale yellow oil, b. p. 169°/15 mm., the *acetyl* derivative, $\text{C}_{11}\text{H}_{11}\text{O}_3\text{Br}$, of which forms a viscous, colourless liquid, b. p. 183—185°/16 mm.

p-Bromophenyl α -bromoisobutyl ketone, when treated with potassium hydroxide, gave a yellow liquid, b. p. 168—169°/15 mm., which could not be proved to be a pure substance, and gave a *dioxime*,



m. p. 229°, fine needles from alcohol; the only other product of the reaction which was identified was *p*-bromophenyl isobutyl ketone, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Br}$, m. p. 48°, which crystallises from methyl alcohol in large plates, and gives an *oxime*, $\text{C}_{11}\text{H}_{14}\text{ONBr}$, needles, m. p. 91—92°.

P. H.

Nitroanthrone. ARTHUR HANTZSCH and A. KORCZYŃSKI (*Ber.*, 1909, **42**, 1216—1219).—The authors have succeeded in isolating a third modification of nitroanthrone, which is designated *nitroanthranol*, $\text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{C}(\text{NO}_2)_2 \cdot \text{C}_6\text{H}_4$. It is obtained as canary-yellow needles by rapidly cooling an ethereal solution of the red modification (*aci*-nitroanthrone) in the entire absence of moisture. Nitroanthranol

is extremely unstable, and changes rapidly into *aci*-nitroanthrone, which in turn passes into the colourless nitroanthrone.

aci-Nitroanthrone is most readily prepared by passing ammonia into an ethereal solution of nitroanthrone, subsequently treating the ammonium salt at -70° with hydrogen chloride and evaporating the solution over solid potassium hydroxide (compare Meisenheimer and Connerade, Abstr., 1904, i, 391).

The absorption spectrum of nitroanthrone in chloroform is quite different from that of the sodium salt (sodium *aci*-nitroanthrone) in ethyl alcohol; the latter has two marked bands in the ultra-violet and one in the visible part of the spectrum; the former shows more or less general absorption.

The salts of *aci*-nitroanthrone, like those of the *aci*-nitrophenols, exist in red, yellow, and orange forms. The *ammonium* salt is red; the *potassium*, *rubidium*, *methylammonium*, and *dimethylammonium* salts are orange; the *benzylammonium* salt is yellow.

Attempts to prepare red *aci*-nitroanthrone ethers were unsuccessful.
W. H. G.

Attempts to Prepare Methylcyclopentanetetrone. OTTO DIELS and ALEX BÖCKING (*Ber.*, 1909, 42, 1576—1583. Compare Abstr., 1906, i, 438).—Alcoholic 1-methylcyclopentane-2:4:5-trione, ethyl nitrite, and a few drops of acetyl chloride react at 0° to form 3-oximino-

1-methylcyclopentane-2:4:5-trione, $\begin{array}{c} \text{CHMe}\cdot\text{CO} \\ \text{CO} \text{---} \text{CO} \end{array} > \text{C:NOH}$, which separates from hot water in pale yellow prisms, darkens at 130° and decomposes at 172° (corr.), readily absorbs $1\frac{1}{2}$ —2 mols. H_2O from the air, forms an *oxime*, $\text{C}_6\text{H}_6\text{O}_4\text{N}_2$, which decomposes at 164° (corr.), and a *salt* with dimethylaniline, $\text{C}_{14}\text{H}_{17}\text{O}_4\text{N}_2$, m. p. 124° (decomp.), but does not react with phenylcarbimide, methyl sulphate, or diazomethane; the nitrogen cannot be eliminated without profound decomposition.

1-Methylcyclopentane-2:4:5-trione condenses readily with benzaldehyde, furfuraldehyde, and *p*-hydroxybenzaldehyde, the *furfurylidene* derivative, $\text{C}_{11}\text{H}_8\text{O}_4$, m. p. 199° (decomp.; corr.), crystallising in reddish-yellow prisms, but attempts to form ozonides from the condensation products, by the decomposition of which the tetrone might be produced, resulted only in complete decomposition.

Dichloro-1-methylcyclopentane-2:4:5-trione, $\text{C}_6\text{H}_4\text{O}_3\text{Cl}_2$, m. p. 149° (corr.), is formed by treating 1-methylcyclopentane-2:4:5-trione with a solution of chlorine in chloroform at 0° .
C. S.

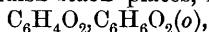
Additive Compounds of Phenols and Quinones. KURT H. MEYER (*Ber.*, 1909, 42, 1149—1153).—It is usually stated that a quinone (1 mol.) forms additive compounds with monohydric phenols (2 mols.) or dihydric phenols (1 mol.) (Jackson and Oenslager, Abstr., 1896, i, 293; Posner, *ibid.*, 1904, i, 1029). Siegmund (this vol., i, 109) describes an exception in the case of catechol, two molecules of which combine with one of benzoquinone. A number of additive compounds formed by the union of one molecule of a quinone with one of a monohydric phenol are described in the paper.

The author does not agree that these compounds are formed by the

aid of partial valencies of the atoms, but regards them as true additive compounds, formed by the addition of the phenol molecules to the oxygen atoms of the quinones (compare Abstr., 1908, i, 731).

Benzophenone forms the following compounds: $C_6H_4O_2, C_6H_4Cl \cdot OH$, orange-yellow needles, m. p. 85° ; $C_6H_4O_2, 2C_6H_4Cl \cdot OH$, dark brown needles, m. p. 72° ; $C_6H_4O_2, C_6H_4Br \cdot OH$, orange-red needles, m. p. 77° ; $C_6H_4O_2, 2C_6H_4Br \cdot OH$, dark reddish-brown needles, m. p. 62° . The compounds with two molecules of phenol are relatively unstable, and when warmed with light petroleum readily yield the compounds containing one molecule of the phenol.

$C_6H_4O_2, C_{10}H_7 \cdot OH(a)$, dark red plates, m. p. 100° (decomp.); $C_6H_4O_2, 2C_{10}H_7 \cdot OH$, dark red needles, m. p. 120° (decomp.); $C_6H_4O_2, C_{10}H_7 \cdot OH(\beta)$, reddish-black plates, m. p. 85° ;



long, dark green or, in reflected light, red needles, m. p. $100-150^\circ$.

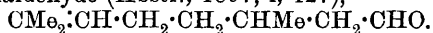
Compound with α -naphthaquinone, $C_{10}H_6O_2, C_{10}H_7 \cdot OH(a)$, red needles, m. p. 97° .

Compound with phenanthraquinone, $C_{10}H_6O_2, C_{10}H_7 \cdot OH(a)$, red plates, m. p. 139° .

Most of the compounds were prepared by crystallising mixtures of the components from light petroleum, and in most cases an excess of one of the components was necessary. The compounds are unstable, and are decomposed to a large extent in solution. J. J. S.

Chemical Action of Light. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ann. Chim. Phys.*, 1909, [viii], 16, 474—520. Compare Abstr., 1901, i, 329, 390, 547; 1902, i, 433; 1903, i, 39, 171, 562; 1904, i, 161; 1905, i, 335, 414; 1906, i, 10; 1907, i, 19, 119, 484).—A detailed account of work already published (compare Abstr., 1907, i, 587; 1908, i, 277, 555). M. A. W.

Chemical Action of Light. XIV. GIACOMO L. CIAMICIAN and PAUL SILBER (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 317—322; *Ber.*, 1909, 42, 1510—1515).—The authors have shown previously that, in aqueous-alcoholic solution, menthone is decomposed in two ways by the action of light, yielding decoic acid and an aldehyde (Abstr., 1907, i, 587), the latter being regarded as probably identical with Wallach's menthocitronellaldehyde (Abstr., 1897, i, 427),



They now find, however, that the acid $C_{10}H_{18}O_2$, corresponding with this aldehyde, has b. p. $252-253^\circ$, whilst Wallach's menthononic acid (*loc. cit.*), corresponding with menthocitronellaldehyde, has b. p. $257-261^\circ$. On oxidation, firstly with alkaline permanganate and then with chromic acid, the acid b. p. $252-253^\circ$ yields isobutyric and β -methylglutaric acids, so that the corresponding aldehyde is probably not identical with Wallach's citronellaldehyde, but has the constitution $CHMe_2 \cdot CH \cdot CH \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CHO$. There is a possibility, however, of the double bond being displaced by the action of alkaline permanganate (compare Harries and Schauwecker, Abstr., 1901, i, 730; Perkin and Wallach, this vol., i, 154).

When exposed to the air, menthone undergoes oxidation to the

ketonic acid, $\text{CHMe}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared by Arth (Abstr., 1886, 892) and by Beckmann and Mehrländer (Abstr., 1896, i, 312) by oxidising menthol with chromic acid, and obtained in the form of the oxime by Baeyer and Manasse (Abstr., 1894, i, 522) by treating menthone with amyl nitrite and hydrochloric acid and hydrolysing the nitrosomenthone thus formed (compare also Baeyer and Oehler, Abstr., 1896, i, 247). It is probable that the conversion of menthone to the ketonic acid proceeds by way of an intermediate hydroxy-acid, $\text{CHMe}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$; this view is supported by the observation that the crude ketonic acid, after distillation, was not completely soluble in sodium carbonate, but left a residue having the characteristic odour of lactones.

It will be seen that the action of light on organic compounds may lead to different results, according as oxygen is present or absent. A similar fact was observed in the case of stilbene (Abstr., 1903, i, 171; 1904, i, 161), and also with the yellow and white $\alpha\beta$ -diphenyl- $\Delta^{\alpha\gamma\epsilon\eta}$ -octatetrenes (this vol., i, 219).

T. H. P.

Dynamic Isomerism. HENRY E. ARMSTRONG, THOMAS M. LOWRY, SYDNEY YOUNG, CECIL H. DESCH, JAMES J. DOBBIE, MARTIN O. FORSTER, and ARTHUR LAPWORTH (*Brit. Assoc. Report*, 1908, 112—115).—This report deals with the use of carbonyl chloride as an agent for arresting isomeric change (compare Lowry and Magson, *Trans.*, 1908, 93, 119—132), and with the relationship between absorption spectra and isomeric change with halogen, nitro- and sulpho-derivatives of camphor.

T. H. P.

Compounds of Ketones and Aldehydes with Acids. ALEXIS A. SHUKOFF and F. S. KASATKIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 157—166).—The authors have investigated the compounds formed by camphor with nitric, phosphoric, hydrochloric, hydriodic, and nitrous acids, by benzophenone and benzaldehyde with nitric acid, and by heptaldehyde and methyl nonyl ketone with phosphoric acid (compare Baeyer and Villiger, Abstr., 1901, i, 658; Archibald and McIntosh, *Trans.*, 1904, 85, 919; McIntosh, *Trans.*, 1905, 87, 784).

The interaction of recrystallised camphor (1 mol.) and nearly anhydrous nitric acid (1 mol.) yields an almost colourless, viscid liquid, which dissolves readily in the organic solvents and gradually solidifies to long, acicular crystals, $\text{C}_{10}\text{H}_{16}\text{O} \cdot \text{HNO}_3$, m. p. 24° . The freezing-point curve for mixtures of camphor and nitric acid exhibits two maxima, indicating the existence of the two compounds: (1) $\text{C}_{10}\text{H}_{16}\text{O} \cdot \text{HNO}_3$, solidifying at 24.2° , and (2) $(\text{C}_{10}\text{H}_{16}\text{O})_2 \cdot \text{HNO}_3$, solidifying at 2.2° . The latter compound separates when a mixture of the two substances containing 32.6—44.6 mols. per cent. of acid is crystallised from light petroleum.

Camphor and phosphoric acid yield the compound, $\text{C}_{10}\text{H}_{16}\text{O} \cdot \text{H}_3\text{PO}_4$, which solidifies in short, colourless crystals, m. p. about 29° . This compound corresponds with the only maximum of the freezing-point curve, which exhibits two minima answering to the eutectics of this compound in camphor and phosphoric acid.

Camphor and hydriodic acid give the compound $C_{10}H_{16}O, HI$, m. p. 29—30° (compare Fleischer and Kékulé, Abstr., 1873, 1228).

On passing dry hydrogen chloride into a vessel containing powdered camphor, a liquid is obtained, which absorbs moisture from the air, decomposes into its constituents, and solidifies at -4.2° to a colourless, crystalline mass.

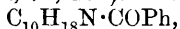
Similarly, dry nitrous anhydride and camphor yield an almost colourless, transparent liquid, which does not solidify at -35° .

Benzophenone and nitric acid in molecular proportions yield the compound, CPh_2O, HNO_3 , m. p. 39°, which can be recrystallised from ether. The existence of this compound is interesting, since, according to Claisen (Abstr., 1896, i, 464; 1898, i, 421) and Baeyer (Abstr., 1901, i, 658), benzophenone should not give double compounds with acids.

Benzaldehyde and nitric acid give the compound, C_7H_6O, HNO_3 , m. p. $+5.4^{\circ}$.

In the case of heptaldehyde and methyl nonyl ketone with phosphoric acid, compounds solidifying at $+12^{\circ}$ and $+3^{\circ}$ respectively were obtained, but their compositions were not determined. T. H. P.

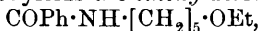
Decomposition of Camphidine by means of Phosphorus Pentachloride, and New Derivatives of ϵ -Chlorobenzoylamylamine. JULIUS VON BRAUN (Ber., 1909, 42, 1429—1436. Compare Abstr., 1905, i, 596; 1907, i, 79, 105).—*Benzoylcamphidine*,



distils, at 217—220°/11 mm., and sets to a crystalline mass, m. p. 61°. When its chloroform solution is warmed gently with phosphorus pentachloride or pentabromide, the corresponding halogenated amides, $-NCX_2Ph$, are formed, and are precipitated as hygroscopic masses on the addition of light petroleum. The halogen is immediately replaced by oxygen in the presence of water.

The chlorinated amide, $C_{10}H_{18}Cl \cdot NH \cdot CPh$, can be obtained by treating benzoylcamphidine with the pentachloride under certain well-defined conditions. It crystallises from alcohol in long, slender needles, m. p. 113°, and has $[\alpha]_D^{18.5} + 32.4^{\circ}$ in benzene solution. This compound is extremely stable; it can be heated to a temperature considerably above its m. p., or can be boiled with alkalis without losing benzoic acid or hydrogen chloride, and does not react with nascent hydrogen or potassium cyanide; but when heated at 110—120° for several hours with fuming hydrochloric acid, a small amount of benzoic acid is formed. Boiling with sodium methoxide or sodium ethoxide solutions regenerates the original benzoylcamphidine.

ϵ -Chlorobenzoylamylamine (Abstr., 1905, i, 596) is also stable towards reducing agents, but when boiled with a solution of sodium ethoxide in ethyl alcohol yields the *ethoxy*-derivative.



b. p. 225—228°/14 mm. The *methoxy*-compound, $C_{12}H_{19}O_2N$, has b. p. 219—222°/12 mm. Both compounds are stable towards alkaline hydrolysing agents, but are decomposed by hydrochloric acid at high

temperatures. Distillation with phosphorus pentachloride gives rise to benzonitrile and methoxy- or ethoxy-chloroamylenes.

Benzoylphthalylcadaverine, $\text{COPh}\cdot\text{NH}\cdot[\text{CH}_2]_5\cdot\text{N}\cdot\text{C}_2\text{O}_2\cdot\text{C}_6\text{H}_4$, obtained by the action of potassium phthalimide on ϵ -chlorobenzoylamylamine, crystallises from hot alcohol in felted needles, m. p. 126° . When heated at 125° with hydrochloric acid, it yields both benzoic and phthalic acids, but the former in smaller quantity, so that the phthalyl group appears to be removed more easily than the benzoyl. The dibenzoyl and diphtalyl compounds are both more resistant than the mixed diacyl derivative towards hydrochloric acid. J. J. S.

The Terpene and Camphor Series. V. Structure of Guaiol. A. L. GANDURIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 288—298. Compare Tschugaeff, Abstr., 1908, i, 93).—The author has investigated guaial and its derivatives (compare Wallach and Tuttle, Abstr., 1894, i, 538), his results indicating that this substance is a dicyclic, monohydric, tertiary alcohol, $\text{C}_{15}\text{H}_{25}\cdot\text{OH}$, the molecule of which contains one ethylene linking.

The esterification constant of guaial with acetic anhydride gradually falls in magnitude, the mean value being 0.00068, which, together with the irregular course of the esterification, indicates that the alcohol is a tertiary one. This conclusion is confirmed by the behaviour of guaial when heated with zinc dust (compare Semmler, Abstr., 1894, i, 611), under which conditions it yields *dihydroguaiene*, $\text{C}_{15}\text{H}_{26}$, a colourless liquid, b. p. $122^\circ/11$ mm., $[\alpha]_D^{18.5} - 26.65^\circ$, D_4^0 0.9089, D_4^{25} 0.8914, $n_D^{20.2}$ 1.49317.

Guaial methyl ether, $\text{C}_{15}\text{H}_{25}\cdot\text{OMe}$, is a faintly yellow liquid, b. p. $141\text{—}143^\circ/9$ mm., $[\alpha]_D^{20} - 31.81^\circ$, D_4^0 0.9513, D_4^{25} 0.9332, $n_D^{18.5}$ 1.48963. The value of the molecular refraction indicates that this compound, and hence also guaial itself, is a dicyclic compound with one ethylene linking.

Guaiene (compare Wallach and Tuttle, Abstr., 1894, i, 438), $\text{C}_{15}\text{H}_{24}$, is a colourless liquid, b. p. $124^\circ/11$ mm., $[\alpha]_D^{25} - 66.11^\circ$, D_4^0 0.9133, D_4^{25} 0.8954, n_D^{25} 1.49468; the molecular refraction, 66.46, is in agreement with the theoretical number (66.28) for a dicyclic hydrocarbon containing two ethylene linkings. T. H. P.

Crystals of Juniperol. H. RAMSAY (*Zeitsch. Kryst. Min.*, 1909, 46, 281—282).—Juniperol, $\text{C}_{15}\text{H}_{24}\text{O}$, the sesquiterpene alcohol from oil of juniper bark, is triclinal [$a:b:c = 0.7243:1:0.7574$; $a = 90^\circ 14'$, $\beta = 103^\circ 30'$, $\gamma = 90^\circ 5'$]. L. J. S.

Terpenes and Ethereal Oils. XCVIII. Transformation of Pulegone into *iso*Pulegone during Oximation in Alkaline Solution. OTTO WALLACH [with ADOLF ROSENBAACH and RUDOLF MÜLLER] (*Annalen*, 1909, 365, 240—254. Compare Abstr., 1908, i, 997).—It would appear from the results of recent work on the reduction of 1:2-unsaturated compounds that pulegoneoxime should yield menthylamine when reduced. The oxime derived from pulegone yields, however, a crystalline base, $\text{C}_{10}\text{H}_{17}\cdot\text{NH}_2$ (compare Wallach, Abstr., 1894, i, 46; 1896, i, 309), from which it seems probable that

f f 2

the oxime is really *isopulegoneoxime*. The m. p.'s for the latter substance recorded by various investigators are, however, extremely divergent (compare Tiemann and Schmidt, *Abstr.*, 1897, i, 198; Barbier and Léser, *Abstr.*, 1897, i, 537; Harries and Roeder, *Abstr.*, 1900, i, 182; Semmler, *Abstr.*, 1905, i, 222). The author has therefore repeated his experiments on the direct formation of an oxime from pulegone. It is found that pulegone in the presence of alkali and hydroxylamine rapidly changes into *isopulegone*, and that the oxime formed is *isopulegoneoxime*. In the preparation of the oxime a certain proportion of the pulegone is hydrolysed by the alkali, as a result of which acetoxime and *cyclomethylhexanoneoxime* are also formed.

isoPulegoneoxime has m. p. 120—121°, $[\alpha]_D^{25} - 25.833^\circ$ in methyl alcohol. In agreement with the observation made previously (*loc. cit.*), it yields pulegone when decomposed by sulphuric acid; when decomposed by oxalic acid, however, it yields *isopulegone*. The base produced by reducing the oxime forms a *hydrochloride*, $C_{10}H_{19}N.HCl$, obtained as a white powder, and is converted by nitrous acid into *isopulegol*.

It is shown definitely that the oxime derived directly from pulegone is identical with the oxime of *isopulegone* prepared from pulegone hydrobromide by treatment with lead nitrate. In agreement with the statement of Tiemann and Schmidt (*loc. cit.*), two oximes are obtained from *isopulegone* prepared from citronellaldehyde; *isopulegone* prepared in this way is shown to be a mixture of active and inactive ketones, yielding in consequence active *isopulegoneoxime*, m. p. 120—121°, and inactive *isopulegoneoxime*, m. p. 138—139°. The fact that Harries (*loc. cit.*) obtained an oxime, m. p. 143°, shows that by his method of preparation an oxime free from active components is formed.

W. H. G.

New Method of Isomerisation in the Terpene Series. GÉZA AUSTERWEIL (*Compt. rend.*, 1909, 148, 1197—1199).—An 18% yield of a bornyl ester is obtained when pinene is heated to a moderate temperature in an autoclave with an organic acid. When the pressure is increased by connecting the autoclave to a bottle of liquid carbon dioxide, and the heating is continued for several hours at 200°, the yield is considerably increased. The limonene formed simultaneously is separated by steam distillation. The borneol obtained by hydrolysis of the ester is optically active.

W. O. W.

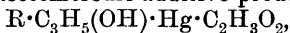
Caryophyllene. CARL W. HAARMANN (*Ber.*, 1909, 42, 1062—1067. Compare Deussen, this vol., i, 171).—Caryophyllene, when oxidised with permanganate equivalent to 8 atoms of oxygen, forms a *glycol*, $C_{14}H_{22}O_4$, m. p. 120°, b. p. 210°/10 mm., identical with that described by Deussen (*loc. cit.*). It forms an *oxime*, m. p. 188.5°, and when heated with 1% sulphuric acid is converted into a *compound*, $C_{14}H_{20}O_3$, b. p. 193°/20 mm., which does not form an oxime. When further oxidised with chromic acid, the glycol is converted into an *aldehyde*, $C_{14}H_{20}O_4$, m. p. 156—157°, which forms a *monophenylhydrazone*, m. p. 167°. On further oxidation of the glycol with permanganate at room temperature, an *acid*, $C_{14}H_{20}O_5$, m. p. 171° (decomp.), is obtained. This forms

a sparingly soluble *sodium* salt, but is not a lactonic acid. When oxidised at 50°, an *acid*, m. p. 201—202°, and an *acid*, m. p. 162°, are obtained.

Further products obtained on oxidation of caryophyllene are an *acid*, $C_{10}H_{16}O_3$ (compare Deussen, *loc. cit.*), b. p. 195—197°/23 mm., and a *compound*, $C_{11}H_{18}O_3$, m. p. 122°, which is stable towards permanganate. On oxidation of caryophyllene at 100°, *aa*-dimethylsuccinic acid is formed. When oxidised with ozone, an ozonide, $C_{15}H_{22}O_7$, is formed.

E. F. A.

Separation of Allyl and Propenyl Compounds in Ethereal Oils. LUIGI BALBINO (*Ber.*, 1909, 42, 1502—1506. *Atti R. Accad. Lincei*, 1909, [v], 18, i, 372—376. Compare *Abstr.*, 1906, i, 186).—When treated with cold saturated aqueous mercuric acetate, allyl compounds form the acetomercuri-additive product,



whereas propenyl compounds give rise to the corresponding glycols, the mercuric acetate being reduced to mercurous compounds or to mercury. It is now found that when a definite quantity of mercuric acetate is added to a mixture of propenyl and allyl compounds, only the acetomercuri-derivative of the allyl compound is formed, and the propenyl derivative remains unaltered. It can be isolated by extraction with ether or steam distillation. Subsequently, the acetomercuri-compound may be reduced by means of zinc and sodium hydroxide, and the allyl compound recovered by steam distillation. The method has been applied to the separation of anethole and chavicol methyl ether, of safrole and *isosafrole* of myristicin and *isomyristicin*, and lastly of *apiole* and *isoapiole*.

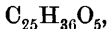
E. F. A.

Composition of the Oil of an African Balsam. HUGO VON SODEN (*Chem. Zeit.*, 1909, 33, 428).—An African balsam yielded on distillation in steam about 45% of a volatile oil, which on being subjected to the usual tests, such as treatment with hydrogen chloride in ethereal solution, etc., proved to be composed mainly of *d*-cadinine. The investigation is, however, being continued.

L. DE K.

American Colophony. I. Resin of the Norway Pine. GEORGE B. FRANKFORTER (*J. Amer. Chem. Soc.*, 1909, 31, 561—565).—Previous work on the investigation of resins is reviewed, and the conclusion is drawn that every resin contains at least one distinct and characteristic acid in addition to abietic acid or one of its isomerides.

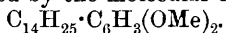
A sample of oleo-resin obtained from the Norway pine (*Pinus resinosa*) was a colourless, mobile liquid, which had D_4^{20} 0.8137, $[\alpha]_D^{20} + 4^\circ$, n_D^{20} 1.4788. After removing the terpenes, which constituted about 20% of the whole, a nearly white, brittle resin, m. p. 81—85°, remained. This resin, on fractional precipitation from its solution in ether or alcohol, yielded a mixture of resinic and abietic acids, which were separated by means of their ammonium salts. *Resinic acid*,



m. p. 97—98°, forms a white, crystalline powder; its *ammonium* and *barium* salts are described. The abietic acid melted at 129—130°.

E. G

Main Constituent of Japanese Lac. Urushiol and Urushiol Dimethyl Ether. RIKŌ MAJIMA (*Ber.*, 1909, 42, 1418—1423. Compare Abstr., 1907, i, 1032).—By distilling in a high vacuum, the so-called "urushic acid" is separated from accompanying substances of high molecular complexity, and is found to contain two hydroxyl groups, but no carboxyl group, and, for this reason, the name *urushiol* is proposed as better representing its nature. Urushiol is a viscid, brown oil having D_4^{25} 0.9687; it reduces ammoniacal silver nitrate solution, and otherwise behaves like the raw material; it is vigorously attacked by nitric acid, D 1.2, and also by bromine. It does not contain nitrogen, and, from combustions and molecular-weight determinations, it is considered to have the molecular formula $C_{20}H_{30}O_2$. Besides yielding a dimethyl ether and a diacetyl compound, it behaves in general as a dihydroxyphenol. When purified urushiol is boiled with sodium ethoxide and methyl iodide in an atmosphere of hydrogen, a somewhat crude methylated product is obtained as an oil. Purified by fractional distillation, it was obtained as a colourless oil, having b. p. 190—195° and D_4^{25} 0.9419, and, according to results of analysis, molecular-weight determinations, and molecular dispersions, is probably to be represented by the molecular formula



It is considered probable that the non-volatile portion obtained from fractionating the purified urushiol consists chiefly of highly polymerised urushiol.

J. V. E.

Crystalline Chlorophylls. ARMAND GAUTIER (*Bull. Soc. chim.*, 1909, [iv], 5, 319—320).—In connexion with the publication of the paper by Willstätter and Benz (Abstr., 1908, i, 199), the author points out that he first prepared chlorophyll in a crystalline condition, and established certain facts regarding its composition, etc., which have since been confirmed (Abstr., 1880, 266).

T. A. H.

Bilirubin. MAURICE PIETTRE (*Compt. rend.*, 1909, 148, 1213—1215).—A new colouring matter, to which the name *biliflavin* is given, has been isolated from biliary calculi of oxen. This resembles bilirubin, and occurs in small, yellow crystals containing 9.7% nitrogen. Hydrolysis of bilirubin and biliflavin leads to the production of a colourless substance, having the characters of a higher fatty acid, and containing 71.85—72.19% carbon and 12.5—12.62% hydrogen.

Attention is drawn to the intimate connexion existing between hæmatin and the pigments of the bile (compare Abstr., 1906, i, 55).

W. O. W.

Constitution of Tannin. V. MAXIMILIAN NIERENSTEIN (*Ber.*, 1909, 42, 1122—1126. Compare Abstr., 1908, i, 897).—Penta-acetyl-leucotannin, obtained by the reduction of penta-acetyltannin or prepared from the leucotannin present in tannin, is hydrolysed by boiling dilute sulphuric acid, yielding gallic acid and gallaldehyde, and, when dissolved in 40% acetic acid, is oxidised by boiling dilute sulphuric acid and potassium persulphate, forming, together with a small quantity of ellagic acid, a red powder, to which the name *purpurotannin* is given.

Purpurotannin yields naphthalene when distilled with zinc dust. Penta-acetyl-leucotannin forms trihydroxyglutaric acid when oxidised with potassium permanganate and dilute sulphuric acid. C. S.

Tannin from the Bark of Eucalyptus Occidentalis. J. DEKKER (*Arch. Néerland*, 1909, ii, 14, 50—80).—The tannin precipitated by ether from the alcoholic extract of the bark of *Eucalyptus occidentalis* (maletto-bark) has the empirical formula $(C_{19}H_{20}O_9)_n$ [Strauss and Gschwendner, *Abstr.*, 1906, i, 596, give $(C_{43}H_{50}O_{20})_2$]; on heating with acetic anhydride and sodium acetate it loses water and yields the acetyl derivative, $C_{38}H_{28}O_{17}Ac_{10}$, and on benzylation in alkaline solution it undergoes oxidation and forms the benzoyl derivative, $C_{19}H_{25}O_{12}Bz_5$; when heated with zinc dust and a 15% solution of sodium hydroxide, the tannin yields small quantities of gallic acid and phloroglucinol, whilst on dry distillation it yields pyrogallol and traces of other phenols.

When the maletto tannin is boiled with dilute sulphuric acid, no sugar is formed, but the substance loses water and yields the sparingly soluble red compound (maletto-red), $C_{57}H_{50}O_{22}$, which forms an acetyl derivative, $C_{57}H_{35}O_{20}Ac_{15}$. M. A. W.

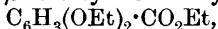
[Completely Methylated Flavone Derivatives.] JOSEF HERZIG and BR. HOFMANN (*Ber.*, 1909, 42, 1424. Compare this vol., i, 165).—A reply to Waliaschko (this vol., i, 248) on the preparation of trimethyl- and pentamethyl-quercetin. J. V. E.

Synthesis of Xanthophanic Acid: 7-Hydroxychromone-6-carboxylic Acid. V. CARL LIEBERMANN and SIMON LINDENBAUM (*Ber.*, 1909, 42, 1392—1405. Compare *Abstr.*, 1908, i, 548).—The authors' experiments in the direction of synthesising xanthophanic acid have led to the synthesis of 7-hydroxychromone-6-carboxylic acid, from which they hope to obtain xanthophanic acid.

Condensation of ethyl resacetophenonecarboxylate with ethyl ethoxymethyleneacetoacetate in presence of a small proportion of sodium ethoxide in alcoholic solution (*loc. cit.*) leads to the formation of an ester, $CO_2Et \cdot C_6H_2(OH) < \begin{smallmatrix} O-C \cdot CAc \cdot CH \cdot OH \\ || \\ CO \cdot CH \end{smallmatrix} (?)$, which crystal-

lises from a mixture of benzene and light petroleum in almost colourless, silky needles, m. p. 163—165°. When hydrolysed with potassium hydroxide, this ester yields an acid, $C_{14}H_{10}O_7$ (?), crystallising from acetic acid in almost colourless needles, m. p. 201—203° (decomp.); the barium, $(C_{14}H_9O_7)_2Ba$, and copper salts were analysed. As these compounds are not closely related to xanthophanic acid, they were not investigated further.

Starting from β -resorecylic acid, the action of silver oxide and ethyl iodide yields ethyl β -resorcyate diethyl ether,

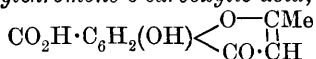


as a faintly brown oil, and this is converted into β -resorecylic acid diethyl ether by alcoholic potassium hydroxide solution. The mixture of resacetophenonecarboxylic acid mono- and di-ethyl ethers obtained by treating β -resorecylic acid diethyl ether with acetyl chloride and

aluminium chlorides (Abstr., 1908, i, 548) is then treated with silver oxide and ethyl iodide, by which means it is converted into *ethyl resacetophenonecarboxylate diethyl ether*, $C_6H_2Ac(OEt)_2 \cdot CO_2Et$, which crystallises from light petroleum in slender, white needles, m. p. 95—97°, and on heating with concentrated hydriodic acid loses all its ethyl groups, yielding resacetophenonecarboxylic acid.

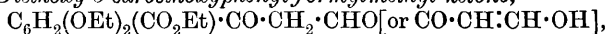
Condensation of ethyl resacetophenonecarboxylate diethyl ether with ethyl acetate in presence of sodium yields *ethyl 2:4-diethoxybenzoylacetone-5-carboxylate*, $CO_2Et \cdot C_6H_2(OEt)_2 \cdot CO \cdot CH_2Ac$, which crystallises from alcohol in greenish-yellow leaflets, m. p. 138—140°, and gives with sulphuric acid an orange-yellow solution showing green fluorescence.

7-Hydroxy-2-methylchromone-6-carboxylic acid,

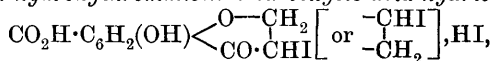


(compare Bloch and von Kostanecki, Abstr., 1900, i, 308), obtained by treating ethyl 2:4-diethoxybenzoylacetone-5-carboxylate with fuming hydriodic acid, separates in colourless, silky needles, m. p. 301° (decomp.), and in alcoholic solution gives a reddish-brown coloration with ferric chloride; its solutions in alkali hydroxide or carbonate show bluish-green, and those in concentrated sulphuric acid, bright green, fluorescence.

2:4-Diethoxy-5-carbethoxyphenyl formylmethyl ketone,



obtained by the condensation of ethyl resacetophenonecarboxylate diethyl ether with ethyl formate in presence of sodium, crystallises from light petroleum in shining, colourless needles, m. p. 116—117°, and, when treated with alkali, is either saponified or resolved into the β -diketone. When this compound is melted with half its weight of ethyl acetate in a water-bath, and a few bubbles of hydrogen chloride are passed into the cooled paste, a beautiful red coloration, changing to brown, is obtained, the crystalline compound formed being under investigation. When this compound is heated with a glacial acetic acid solution of hydrogen iodide, it is converted into 2[or 3]-iodo-7-hydroxychromanone-6-carboxylic acid hydriodide,



which separates in faintly yellow, shining needles, m. p. 217° (decomp.), and loses its hydrogen iodide when treated with sulphuric acid, giving the carboxylic acid, which crystallises from acetic acid as the *acetate*, $C_{10}H_7O_5I, C_2H_4O_2$, decomposing at 270—280°.

7-Hydroxychromone-6-carboxylic acid, $CO_2H \cdot C_6H_2(OH) < \begin{array}{c} O-CH \\ | \\ CO \cdot CH \end{array}$,

obtained by the action of 2% potassium hydroxide solution on 2(or 3)-iodo-7-hydroxychromanone-6-carboxylic acid hydriodide, separates as an almost white, crystalline powder, m. p. 297° (decomp.), gives a red coloration with ferric chloride in alcoholic solution, and forms yellow solutions with faint green fluorescence with alkali hydroxide or carbonate, and a yellow, non-fluorescent solution with concentrated sulphuric acid.

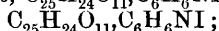
When heated with an acetic acid solution of hydrogen iodide in a sealed tube, 2:4-diethoxy-5-carbethoxyphenyl formylmethyl ketone yields an acid colouring matter, $C_{20}H_{14}O_8$ (?), which separates in orange-red, crystalline flocks, and seems to retain the chromone group, since it gives a fluorescent solution in concentrated sulphuric acid.

T. H. P.

Glaucophanic and Xanthophanic Acids. VI. CARL LIEBERMANN and H. TRUCHSÄSS (*Ber.*, 1909, 42, 1405—1412).—From the too high yields of "transformation products" yielded by the glaucophanic acids, the authors concluded that the formula $C_{27}H_{26}O_{12}$, ascribed by Claisen (*Abstr.*, 1897, i, 594) to ethylglaucophanic acid, is not quite accurate (*Abstr.*, 1907, i, 890).

The authors have attempted to settle the composition of this acid by analysis, but the results of their work render it only more probable that the formula is $C_{25}H_{24}O_{11}$, rather than $C_{27}H_{26}O_{12}$.

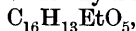
Ethylglaucophanic acid forms a number of sparingly soluble salts, which do not lend themselves to the ordinary methods of molecular-weight determination. The following salts have been prepared and analysed: *p*-Bromoaniline, $C_{25}H_{24}O_{11}, C_6H_6NBr$; *p*-iodoaniline,



pyridine, $C_{25}H_{24}O_{11}, C_5H_5N$; *p*-bromoquinoline, $C_{25}H_{24}O_{11}, C_9H_6NBr$; *p*-iodoquinoline, $C_{25}H_{24}O_{11}, C_9H_6NI$; rubidium, $C_{25}H_{23}O_{11}Rb$, and caesium.

Taking the formula $C_{25}H_{24}O_{11}$ as correct, the molecule contains two methyl groups, and the formula of methylglaucophanic acid must be $C_{23}H_{20}O_{11}$.

The by-products from ethyl- ($C_{20}H_{22}O_5$) and methyl-glaucophanic acids ($C_{18}H_{18}O_5$) contain in each case two alkyl groups, and the de-alkylated residue after estimation of the alkyloxy-groups (compare *Abstr.*, 1906, i, 556) has the composition $C_{16}H_{14}O_5$, crystallises from acetic acid in stable, colourless needles, m. p. 274°, and exhibits the behaviour of an acid ester; it functions as a dibasic acid, and, on hydrolysis with alcoholic potassium hydroxide, yields the ester,



m. p. 212—214°. Both the "by-products" yield hydrazones; that from the ethyl "by-product," $C_{20}H_{24}O_4N_2$, crystallising from a mixture of benzene and light petroleum in white flocks, m. p. 127°, and that from the methyl "by-product" having m. p. 141—142°. As these "by-products" contain two carbethoxy- (or carbmethoxy-) groups and one keto-group, the chemical functions of all the oxygen atoms are accounted for.

T. H. P.

Thiosalicylic [*o*-Thiolbenzoic] Acid and Thioxanthone. FRITZ MAYER (*Ber.*, 1909, 42, 1132—1137).—The paper gives merely an account of some derivatives of thiosalicylic acid. The acid and acetic anhydride when heated at 140° for six hours yield phenyl disulphide and thioxanthone, $C_6H_4 \begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} C_6H_4$, m. p. 209°, which forms yellow crystals and gives a fluorescent, green solution in concentrated sulphuric acid. The same two products are obtained by the distillation of *phenyl-*

thiosalicylate (thiosalol), $\text{SH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Ph}$, m. p. 91° , which is obtained from phenol, thiosalicylic acid, and phosphoryl chloride at 135° . By heating bromobenzene, methyl thiosalicylate, copper powder, and alcoholic sodium methoxide with a little xylene for four hours at 160° , distilling the product with steam, boiling the residue with sodium hydroxide, and acidifying the alkaline solution, *o*-phenylthiolbenzoic acid is obtained, which is readily converted into thioxanthone by concentrated sulphuric acid. Thioxanthone, suspended in an alcoholic solution of potassium ethoxide, is boiled with zinc dust, whereby thioxanthinol is formed, which is changed to thioxanthone by heating at 160 — 170° with glycerol (1 part) and 15 parts of sulphuric acid (62° Bé). Xanthhydrol under similar conditions yields xanthone.

When thioxanthone, dissolved in hot glacial acetic acid, is treated with zinc dust and subsequently with hydrochloric acid, *dithioxanthylene*, $\text{S} \langle \text{C}_6\text{H}_4 \rangle \text{C} : \text{C} \langle \text{C}_6\text{H}_4 \rangle \text{S}$, m. p. 346° , is obtained, which crystallises from nitrobenzene in pale yellow needles. C. S.

Thianthren [Diphenylene Disulphide]. KARL FRIES and W. VOLK (*Ber.*, 1909, 42, 1170—1176).—Thiophenols react with concentrated sulphuric acid, yielding disulphides (Stenhouse, *Annalen*, 1869, 149, 250), but these in their turn dissolve in the concentrated acid, yielding characteristic blue- or violet-coloured solutions, from which water precipitates colourless compounds. The second reaction is one of oxidation, as sulphur dioxide is evolved copiously during the process of solution. Thianthren derivatives have been isolated from the precipitates, and the blue or violet colour of the sulphuric acid solutions are due to these compounds.

Thianthren, 3 : 7-dimethylthianthren, naphthathianthren, and 2 : 4 : 6 : 8-tetrachloro-3 : 7-dihydroxythianthren have been obtained in this way from thiophenol, thio-*p*-cresol, thio- β -naphthol, and dichlorothioquinol respectively. Other colourless products are formed at the same time, but so far these have not been investigated. The yield of thianthren derivatives usually varies from 10—20%, but in the case of thio-*p*-cresol reaches 50%. The disulphides are undoubtedly first oxidised to disulphoxides, since the latter yield the thianthren derivatives more readily than the disulphides.

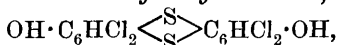
The thianthrens give coloured compounds with sulphuric, nitric, and trichloroacetic acids, and also with aluminium chloride, antimony pentachloride, ferric chloride, and stannic chloride.

3 : 7-Dimethylthianthren crystallises from glacial acetic acid in long, colourless, compact needles, m. p. 123° . Jacobson and Ney (*Abstr.*, 1889, 772) give 116° , and Krafft and Lyons (*ibid.*, 1896, i, 297) give 117 — 118° . With ferric chloride it yields compact crystals of the compound, $\text{C}_{14}\text{H}_{12}\text{S}_2 \cdot \text{FeCl}_3$, which has a bluish-black lustre. 3 : 7-Dimethylthianthrene monoxide, $\text{C}_6\text{H}_3\text{Me} \langle \text{SO} \rangle \text{C}_6\text{H}_3\text{Me}$, obtained by the action of dilute nitric acid (D 1.2) on dimethylthianthren, crystallises from methyl alcohol in quadratic prisms, m. p. 94° . It dissolves in concentrated sulphuric acid, yielding a violet-coloured solution,

which gradually changes to blue, and the subsequent addition of water liberates dimethylthianthren.

3:7-Dimethylthianthren dioxide, $C_6H_3Me \begin{smallmatrix} \text{SO} \\ \text{SO} \end{smallmatrix} C_6H_3Me$, obtained by the prolonged action of nitric acid on the thianthren, also crystallises from methyl alcohol in needles, and has m. p. 194° . The corresponding disulphone (Cohen and Skirrow, *Trans.*, 1899, **75**, 890) crystallises in cubes, m. p. 286° , and dissolves in concentrated sulphuric acid to a colourless solution.

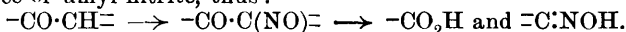
2:4:6:8-Tetrachloro-3:7-dihydroxythianthren,



crystallises from glacial acetic acid in colourless needles, m. p. above 300° .

Naphthathianthren [*Dinaphthylene disulphide*], $C_{10}H_6 \begin{smallmatrix} \text{S} \\ \text{S} \end{smallmatrix} C_{10}H_6$, crystallises from light petroleum in long, colourless needles, m. p. 184° .
J. J. S.

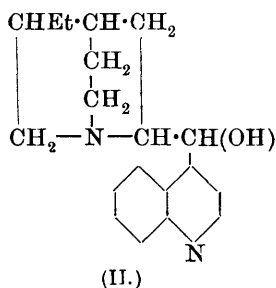
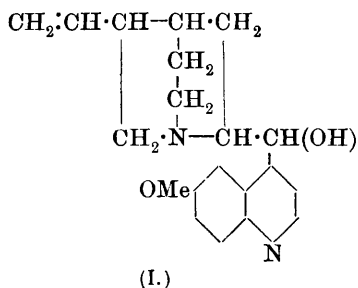
Cinchona Alkaloids. X. Fission of the Ketones from Cinchona Bases. PAUL RABE [with ERICH KULIGA and WILHELM NAUMANN] (*Annalen*, 1909, **365**, 353—365. Compare this vol., i, 252). —Quininone is decomposed by nitrous acid (amyl nitrite), yielding quinic acid and an oxime, $C_9H_{14}ON_2$; from this it follows that quinone contains the grouping $-CO \cdot CH=$, which breaks under the influence of amyl nitrite, thus:



The oxime when hydrolysed yields hydroxylamine and meroquinine, and is consequently α -oximino- β' -vinylquinuclidine. Quinine must therefore have the constitution represented by (I), likewise also quinidine, since it yields quinone when oxidised.

Cinchonidine gives rise to the same ketone as cinchonine, and must therefore have the same formula (compare *Abstr.*, 1908, i, 100).

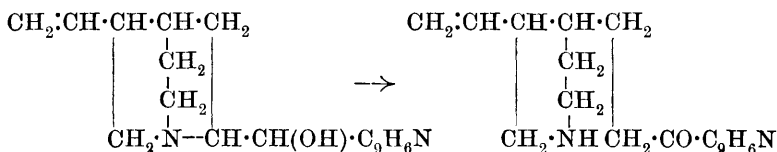
Hydrocinchoninone, when treated with nitrous acid, yields cinchonic acid and α -oximino- β' -ethylquinuclidine, consequently hydrocinchonine has the formula (II).



α -Oximino- β' -ethylquinuclidine, $C_9H_{16}ON_2$, obtained by the action of amyl nitrite and sodium ethoxide on hydrocinchoninone, crystallises in

small, white needles, m. p. 133—134°. When boiled with hydrochloric acid, it yields cincholeponic acid hydrochloride. W. H. G.

Cinchona Alkaloids. XI. Identity of Methylcinchonine and Methylcinchonidine. PAUL RABE (*Annalen*, 1909, 365, 366—376).—It follows from the author's work on the fission of the cinchona toxins (Abstr., 1907, i, 78, 790), and on the constitution of the cinchona alkaloids (preceding abstract), that the transformation of cinchonine into cinchotoxine takes place thus :



In other words, the cinchona alkaloids are 1 : 2-hydramines, and are characterised by a great tendency to pass into imino-ketones. This property is of great importance in explaining the isomerism of cinchonine and cinchonidine. The hydrogen sulphates of these alkaloids yield the same substance, namely, cinchotoxine, when heated (compare von Miller and Rohde, Abstr., 1895, i, 434 ; 1901, i, 95). On the other hand, the recorded m. p.'s of methyl-, ethyl-, and benzyl-cinchonine are different from those of the corresponding alkylcinchonidines. In order to ascertain definitely whether the corresponding alkyl derivatives were different, the properties of several derivatives of methylcinchonine and methylcinchonidine were compared, and found to be identical. In future, therefore, these two bases are to be regarded as methylcinchotoxine.

[With FRITZ BRAASCH.]—*Methylcinchotoxine*, prepared either from cinchonine methiodide or cinchonidine methiodide, forms cubical crystals, m. p. 74—75°, $[\alpha]_D^{20} + 35\cdot28^\circ$ to $+37\cdot97^\circ$ (in chloroform). The methiodide has m. p. 197° : Claus and Müller give m. p. 201° (Abstr., 1881, 289). The *semicarbazone*, $\text{C}_{21}\text{H}_{27}\text{ON}_5$, forms white flakes, sinters at 204°, m. p. 210° (decomp.) ; the *picrate*, $\text{C}_{26}\text{H}_{27}\text{O}_8\text{N}_5$, forms yellow crystals, sinters at 95°, m. p. 120° ; the *picrolonate*, $\text{C}_{30}\text{H}_{32}\text{O}_6\text{N}_6$, crystallises in nodules of small needles, m. p. 152—153°.

W. H. G.

Methiodides of Cinchonic Esters and their Colour. HERMAN DECKER and PERCY REMFRY (*J. pr. Chem.*, 1909, [ii], 79, 339—351).—*Ethyl cinchonate methiodide*, $\text{C}_9\text{NH}_8\cdot\text{CO}_2\text{Et}\cdot\text{MeI}$, is obtained by heating the ester and methyl sulphate for half an hour at 100°, dissolving the product in water, neutralising by sodium hydrogen carbonate, and adding solid potassium iodide. It separates from water in yellow crystals, m. p. 57°, containing $2\text{H}_2\text{O}$, which is readily lost, yielding red, anhydrous crystals, m. p. 63°. The red form gives a yellow solution in water, a red solution in alcohol, and a fine red solution in chloroform, thus showing the diminution of colour intensity with hydrate formation (compare Decker and Hock, Abstr., 1904, i, 450). The *picrate* forms yellow crystals, m. p. 140°. *Methyl cinchonate methiodide*, $\text{C}_{12}\text{H}_{12}\text{O}_2\text{NI}$, m. p. 178°, obtained from the sodium salt

and methyl sulphate at 100° and precipitation by potassium iodide, forms red crystals. The red chloroform solution becomes pale yellow by the addition of a little water, and turns red again by the addition of solid potassium iodide. The *picrate*, m. p. 146°, and the *dichromate* are mentioned.

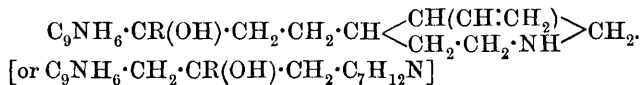
These ester-methiodides, unlike 1-methylquinolinium salts, which by treatment with alkali yield methylquinoline and methyltetrahydroquinoline (Decker, Abstr., 1903, i, 718), are hydrolysed with extraordinary ease by dilute ammonium or sodium hydroxide, yielding, after acidification and addition of potassium iodide, cinchonic acid methiodide, m. p. 224°. The esters, by warming with concentrated ammonium hydroxide, acidification, and addition of potassium iodide, yield *cinchonamide methiodide*, $C_9NH_6 \cdot CO \cdot NH_2 \cdot MeI$, m. p. 233°; the *picrate* has m. p. 198°.

The betaine of 1-methylcinchonic acid has m. p. 218° (Claus, 235°).

The paper also contains a reply to Hantzsch (this vol., ii, 198).

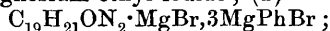
C. S.

Constitution of Cinchonicine (Cinchotoxine). I. Action of Organo-magnesium Haloids on Cinchonicine: *R*-Cinchotoxols. EZIO COMANUCCI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], 15, 32—43).—The groups present in the molecule of cinchonicine capable of reacting with organo-magnesium haloids are: $\cdot N$, $\cdot NH$, $\cdot CO$, and $\cdot CH \cdot CH_2$. The formula of α -cinchonicine being probably $C_9NH_6 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH < \begin{smallmatrix} CH(CH \cdot CH_2) \\ CH_2 \cdot CH_2 \cdot NH \end{smallmatrix} > CH_2$, the final product, after treating the complex organo-magnesium derivative with water, dilute acid, and finally ammonia, will have the constitution:



To the secondary alcohol, corresponding with cinchonicine and not yet prepared, the author gives the name of cinchotoxol, its derivatives, represented by the above formula, being termed *R*-cinchotoxols.

[With NICOLA MELONE.]—The following complex compounds have been obtained: (1) $C_{19}H_{21}ON_2 \cdot MgI, 3MgEtI$, pale yellow powder, from cinchonicine and magnesium ethyl iodide; (2)



(3) $C_{19}H_{21}ON_2 \cdot MgBr, 3Mg(C_{10}H_7)Br$, from magnesium α -naphthyl bromide.

Ethylcinchotoxol, $C_{19}H_{22}N_2Et \cdot OH$, is obtained as an amorphous, yellow powder, m. p. 84° (decomp.), having a bitter taste (compare Abstr., 1907, i, 1068).

Phenylcinchotoxol, $C_{19}H_{22}N_2Ph \cdot OH$, is a very bitter, amorphous substance, m. p. 104—106° (decomp.).

α -*Naphthylcinchotoxol*, $C_{19}H_{22}N_2(C_{10}H_7) \cdot OH$, is a yellowish-red, bitter, amorphous powder, m. p. 132—134°.

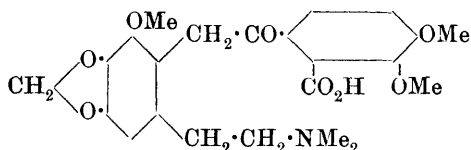
T. H. P.

Decomposition of Laudanosine. HERMAN DECKER and LUCAS GALATTY (*Ber.*, 1909, 42, 1179—1183).—An 85% yield of *laudanoso-methine*, $NMe_2 \cdot CH_2 \cdot CH_2 \cdot C_6H_2(OMe)_2 \cdot CH \cdot CH \cdot C_6H_3(OMe)_2$, is formed

when the quaternary salt obtained by the addition of methyl sulphate to laudanosine (Pictet and Athanescu, Abstr., 1900, i, 685) is boiled twice with ten times its weight of 15% potassium hydroxide solution for two hours, and the mixture extracted with ether after each boiling. It crystallises from light petroleum in long, felted needles, m. p. 96—97°. A small amount of a compound, m. p. about 320°, is formed at the same time, and yields soluble alkali salts. The methine is readily soluble in dilute acetic or sulphuric acids. The *hydrochloride*, $C_{22}H_{30}O_4NCl \cdot H_2O$, crystallises from hot water in long, felted needles, m. p. 220°. It is very sparingly soluble in cold water, and in the anhydrous form is very hygroscopic. The *platinichloride* decomposes readily, and melts at about 180°. The *hydrobromide* turns brown at 203°, and has m. p. 214°. When heated, the hydrochloride and hydrobromide yield dimethylamine. The *mercuribromide*, $C_{22}H_{30}O_4NBr_3Hg$, crystallises in lemon-yellow-coloured needles, m. p. 169—170°. The *picrate*, $C_{28}H_{32}O_{11}N_4$, is obtained as a precipitate on adding a benzene solution of picric acid to an ethereal solution of the base, and crystallises from boiling alcohol in dark red cubes, m. p. 181°.

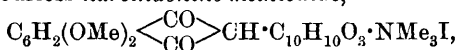
When the methine is warmed with methyl sulphate and then with potassium hydroxide solution, trimethylamine is evolved and ether extracts from the liquid, *laudanosen* (*tetramethoxy-o-vinylstilbene*), $CH_2:CH \cdot C_6H_2(OMe)_2 \cdot CH:CH \cdot C_6H_3(OMe)_2$, which crystallises from warm alcohol in large needles, m. p. 94—95°. J. J. S.

Narceine. MARTIN FREUND and PAUL OPPENHEIM (*Ber.*, 1909, 42, 1084—1101).—Of the two formulæ of narceine proposed by Freund and Frankforter (Abstr. 1894, i, 58), the annexed one is to be accepted, the

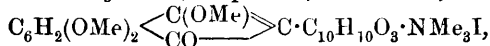


ambiguous position of the methoxyl group having been determined by Freund and Becker's degradation of cotarnine to norcotarnone (Abstr., 1903, i, 572).

The presence of the group $\cdot CH_2 \cdot CO \cdot$ is proved by the fact that the two methods by which deoxybenzoiccarboxylic acid is changed into 2-phenyldiketohydrindene are equally applicable for the conversion of narceine (which is a substituted deoxybenzoiccarboxylic acid according to the preceding formula) to narcindonine (Abstr., 1907, i, 235). The parallelism between 2-phenyldiketohydrindene and narcindonine is extended in the present communication. Since narcindonine and its sodium salt, $C_{23}H_{24}O_7NNa$, are intensely red, they receive an enolic formula, whilst the salts of narcindonine with acids (*hydrochloride*, m. p. 255°; *hydriodide*, m. p. 246°) being colourless, have the ketonic formula. Colourless *narcindonine methiodide*,

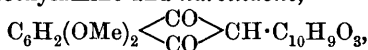


m. p. 217°, forms a red sodium salt, from which yellowish-red *narcindonine methiodide methyl ether*, m. p. 207°, is obtained,

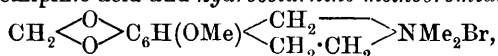


in which the presence of four methoxy-groups is shown by Zeisel's method.

Narcindonine methiodide is decomposed by boiling alcoholic sodium ethoxide into trimethylamine and *narcindone*,



m. p. 136—137°, which, like 2-phenyldiketohydrindene, is colourless, but forms coloured alkali salts. By the action of bromine on the sodium derivative of narcindonine in glacial acetic acid, *bromonarcindonine hydrobromide*, $\text{C}_{23}\text{H}_{25}\text{O}_7\text{NBr}_2$, is obtained, which separates from glacial acetic acid in colourless plates containing $1\frac{1}{2}$ mols. $\text{C}_2\text{H}_4\text{O}_2$, darkening at 140° and decomposing at 150°. The corresponding base cannot be prepared. When the hydrobromide is evaporated with dilute sodium hydroxide, hemipinic acid and *hydrocotarnine methobromide*,

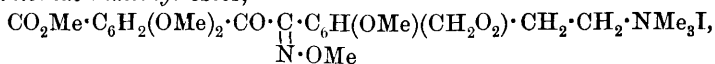


which decomposes at 221°, are produced. The identity of the latter is proved by converting it into the corresponding *methiodide*, m. p. 206°, which is identical with that obtained from hydrocotarnine. When the decomposition of bromonarcindonine hydrobromide is attempted by evaporating it with ammonium hydroxide, hemipinimide is formed together with the hydrobromide of a base, which is not decomposed by ammonium hydroxide, but is changed by concentrated sodium hydroxide into a base which immediately isomerises to hydrocotarnine methobromide.

When hydrocotarnine methobromide is heated with concentrated sodium hydroxide, it yields an oily base, which forms a *methiodide*, $\text{C}_{14}\text{H}_{20}\text{O}_3\text{NI}$, m. p. 193°. The base is proved to be Freund and Bamberg's *N*-methyldehydrocotarnine (Abstr., 1902, i, 556) by converting hydrocotarnine methiodide, obtained from cotarnine, into the methochloride, which, by decomposition with concentrated alkali, yields the same oily base, forming a methiodide, m. p. 193°, as is obtained above. The preceding transformations are all in harmony with the proposed formula of narceine, and afford evidence for the presence of the group $\cdot\text{CH}_2\cdot\text{CO}\cdot$. The latter point is also proved by the fact that narceine, like deoxybenzoin, forms an oximino-compound. Narceine, when treated with alcoholic sodium ethoxide and ethyl nitrite at 0° for two days in a closed vessel, yields *oximinonarceine*, $\text{C}_{23}\text{H}_{26}\text{O}_9\text{N}_2$, which has been obtained in three forms. The product obtained in the preceding preparation separates from alcohol in white plates, m. p. 178°, containing 1 mol. $\text{C}_2\text{H}_6\text{O}$. The yellow alkaline solution of this compound yields, by acidification with acetic acid, white plates, m. p. 173°, containing 1 mol. H_2O . The alcohol and the water in these two compounds are retained very firmly, but in boiling water both, without dissolving, yield free oximinonarceine, m. p. 196°. By prolonged heating at 115—120°, the forms containing water or alcohol yield a brown, viscous mass, from which have been isolated hemipinic acid and 2-cyano-3-methoxy-4:5-methylenedioxy-1-dimethyl-aminoethylbenzene, $\text{C}_{13}\text{H}_{16}\text{O}_3\text{N}_2$, m. p. 50° (*hydrochloride*, $\text{C}_{13}\text{H}_{16}\text{O}_3\text{N}_2\cdot\text{HCl}$, m. p. 204°), which forms a *methiodide*, $\text{C}_{14}\text{H}_{19}\text{O}_3\text{N}_2\text{I}$, decomposing at

225—226°, which is decomposed by dilute alkalis, yielding trimethylamine and Roser's 2-cyano-3-methoxy-4:5-methylenedioxy-1-vinylbenzene (Abstr., 1890, 528), obtained by the degradation of cotarnine.

Oximinonarceine, when digested on the water-bath with alcoholic sodium ethoxide and excess of methyl iodide, yields *oximinonarceine methiodide dimethyl ester*,

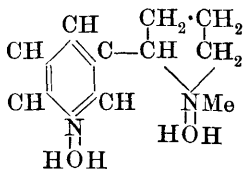


m. p. 247°, which is decomposed by boiling sodium hydroxide or ethoxide, yielding trimethylamine, hemipinic acid, and cyanomethoxymethylenedioxyvinylbenzene. Oximinonarceine, when rapidly heated to 150°, decomposes into hemipinic acid, dimethylamine, and Roser's compound.

The most important results in the paper are the proof of the presence of the group $\cdot\text{CH}_2\cdot\text{CO}$ in narceine, and the discovery that the degradation products of narceine are substances which have long been known as the products of the decomposition of narcotine.

C. S.

The Binary System. Nicotine and Water. DEMETRIUS TSAKALOTOS (*Bull. Soc. chim.*, 1909, [iv], 5, 397—404).—Hudson has shown (Abstr., 1904, ii, 446) that the complete mutual solubility curve of nicotine and water is a closed one, and this result has been confirmed by the author, although the temperatures of saturation were from 1° to 5° lower than those obtained by Hudson. The author has also measured the viscosity coefficients of mixtures of water and nicotine, and the resulting curve shows a maximum at the concentration of 78% of nicotine, and indicates the formation of a molecular combination between the water and nicotine (Abstr., 1908, ii, 260; i, 498, 598), probably of the annexed constitution.



The curve obtained by plotting the index of refraction against the concentration of the several mixtures is a straight line, as is also the curve similarly obtained for mixtures of aniline and *m*-cresol (Abstr., 1908, ii, 260); it follows, therefore, that the refraction is not affected by association in the liquid state.

M. A. W.

2:5-Dimethylpyrroline-5-carboxylic Acid. N. SCHLESINGER (*Ber.*, 1909, 42, 1159—1160. Compare Zelinsky and Schlesinger, Abstr., 1907, i, 720).—When the acid is mixed with twice its weight of lime and the mixture distilled in small quantities, 2:5-dimethylpyrroline and 2:5-dimethylpyrroline can be detected in the distillate.

J. J. S.

Formation of Double Salts in Non-aqueous Solvents. LIVIO CAMBI (*Gazzetta*, 1909, 39, i, 361—370).—In addition to the salts already described (Abstr., 1907, i, 460), the author gives an account of the formation and properties of the following: $\text{CuCl}_2\cdot\text{LiCl}\cdot\text{C}_5\text{H}_5\text{N}$, separating from pyridine; $\text{NiI}_2\cdot 2\text{NaI}\cdot 9\text{COMe}_2$; $\text{CoI}_2\cdot\text{CdI}_2\cdot 6\text{C}_5\text{H}_5\text{O}$; $\text{CoI}_2\cdot 2\text{NaI}\cdot 6\text{Ac}_2\text{O}$.

T. H. P.

1:2-Hydramines. I. β -Piperidyl- α -phenylethyl Alcohol. PAUL RABE and WILHELM SCHNEIDER (*Annalen*, 1909, 365, 377—382).—The stability of β -piperidyl- α -phenylethyl alcohol has been studied with the object of determining whether 1:2-hydramines in general behave like the alkaloids (compare this vol., i, 408); in other words, to see if compounds with the grouping $\text{N} \cdot \text{C} \cdot \text{CH} \cdot \text{OH}$ disintegrate readily, owing to the separation of the nitrogen from the carbon atom. It is found that the sulphate of β -piperidyl- α -phenylethyl alcohol, when heated, does not decompose, neither does the hydramine undergo fission when boiled with acetic acid, nor when its methiodide is heated with sodium acetate in acetic acid; that is, this hydramine is far more stable than the alkaloids. Only in one respect does it resemble the alkaloids, and that is in the behaviour of the methiodide towards alkalis, whereby it is converted into acetophenone and 1-methylpiperidine.

[With FRITZ BRAASCH.]— β -Piperidyl- α -phenylethyl alcohol,
 $\text{C}_5\text{H}_{10}\text{N} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{OH}$,

prepared by reducing piperidylacetophenone with sodium and alcohol, has m. p. 67—68°, b. p. 188°/20 mm.; the following derivatives were prepared: *sulphate*, white needles, m. p. 140°; *picrate*, yellow, prismatic needles, m. p. 135°; *picrolonate*, orange needles, m. p. 163°; *platinichloride*, brownish-yellow scales, m. p. 194—195°; *methiodide*,

$\text{C}_{13}\text{H}_{19}\text{ON} \cdot \text{MeI}$,
 colourless needles, m. 136—137°.

W. H. G.

Condensation of 4-Picoline, 2:6-Lutidine, and 2:4:6-Tri-methylpyridine with Cinnamaldehyde and Anisaldehyde. HEINRICH PROSKE (*Ber.*, 1909, 42, 1450—1457).—A small yield of α -phenyl- δ -4-pyridylbutadiene, $\text{C}_5\text{NH}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CHPh}$, is obtained by heating 4-picoline with cinnamaldehyde and a little freshly-melted zinc chloride for eight hours at 170—180°. The unaltered aldehyde and base can be removed by steam distillation, the latter after the solution has been made alkaline, and the condensation product finally extracted with ether. It crystallises from alcohol in colourless plates, m. p. 137—138°. The *aurichloride*, $\text{C}_{15}\text{H}_{13}\text{N} \cdot \text{HAuCl}_4$, forms a reddish-brown precipitate, m. p. 168—169°. The *mercurichloride* forms a lemon-yellow precipitate, which decomposes when recrystallised.

α -Phenyl- δ -(6-methyl-4-pyridyl)butadiene, $\text{C}_{16}\text{H}_{15}\text{N}$, obtained by heating 2:6-lutidine and cinnamaldehyde at 160—170° for eight hours, crystallises from alcohol, and has m. p. 103—104°. The *picrate* has m. p. 214—215°; the *platinichloride* crystallises from dilute alcohol in lemon-yellow needles, m. p. 173—174°, and the *aurichloride* forms a brownish-red, flocculent precipitate, m. p. 170—171°.

2:4:6-Trimethylpyridine, cinnamaldehyde, and zinc chloride yield α -phenyl- δ -(4:6-dimethyl-2-pyridyl)butadiene, $\text{C}_{17}\text{H}_{17}\text{N}$, which is a pale red oil, b. p. 238—245°/21 mm. The *aurichloride* has m. p. 135—136°.

4-Methoxy-4-stilbazole, $\text{C}_{14}\text{H}_{13}\text{ON}$, is formed when 4-methylpyridine hydrochloride, anisaldehyde, and zinc chloride are heated for three days at 160—170°. It crystallises from dilute alcohol in glistening needles, m. p. 99—100°, after sintering at 91°.

The *mercurichloride*, $C_{14}H_{13}ON, HCl, HgCl_2$, forms a pale yellow, flocculent precipitate, m. p. 186—187°. The *hydrochloride* crystallises from water in small, yellow needles, m. p. 178—179°; the *nitrate* has m. p. 148—149°; the *platinichloride*, m. p. 201—203°, and the *aurichloride* forms an orange-coloured precipitate, which is decomposed on recrystallisation.

4'-Methoxy-6-methyl-2-stilbazole, $C_{15}H_{15}ON$, crystallises from benzene or amyl alcohol in brilliant, glistening plates, m. p. 181—182°. The *hydrochloride* forms lemon-yellow needles, m. p. 214—215° (decomp.); the *nitrate* forms pale yellow needles, m. p. 130—131°; the *picrate* has m. p. 175—176°; the *hydriodide* crystallises from alcohol in long, yellow, glistening needles, m. p. 216—217°; the *sulphate* forms orange-yellow needles, m. p. 209—210°; the *mercurichloride* melts at 209—210°, after sintering at 197°; the *aurichloride* separates from its alcoholic solution as yellowish-red needles, m. p. 170—171°, after sintering at 165°, and the *platinichloride* has m. p. 234°. When reduced with phosphorus and hydriodic acid, the base forms the *dihydro-derivative*, $C_{15}H_{17}ON$, which crystallises from alcohol and melts at 90—91°. The corresponding *hydrochloride* sinters at 270° and melts at 278—279°.

4'-Methoxy-6-methyl-2-stilbazole condenses with anisaldehyde in the presence of zinc chloride at 160—170°, yielding 2:6-di-p-methoxystyrylpyridine, $C_{23}H_{21}O_2N$. The *hydrochloride*, $C_{23}H_{21}O_2N, HCl$, crystallises from alcohol in golden-yellow plates, m. p. 148—149°. The *platinichloride* has m. p. 242—243°; the *mercurichloride*, m. p. 236—237°, and the *nitrate*, m. p. 148—149°.

p-Methoxy-4:6-dimethyl-2-stilbazole, $C_{16}H_{17}ON$, is a yellow oil, b. p. 230—235°/20 mm. The *mercurichloride* has m. p. 190°; the *platinichloride*, m. p. 176—177°, and the *aurichloride*, m. p. 175—176°.

2:6-Di-p-methoxystyryl-4-methylpyridine, $C_{24}H_{23}O_2N$, obtained from 2:4:6-trimethylpyridine and anisaldehyde, has m. p. 132—133°. The *mercurichloride* has m. p. 192°, after sintering at 177°; the *platinichloride*, m. p. 178—179°, and the *aurichloride*, m. p. 150—151°. Most of the salts cannot be recrystallised. J. J. S.

Condensation of γ -Picoline, 2:6-Lutidine, and γ -Collidine [2:4:6-Trimethylpyridine] with Piperonaldehyde and Salicylaldehyde. WALTHER BRAMSCH (*Ber.*, 1909, 42, 1193—1197).— γ -Picoline (4-methylpyridine) and piperonaldehyde condense when heated with zinc chloride under pressure at 180°, yielding γ -piperonylidene-picoline, $C_{14}H_{11}O_2N$, obtained as a white, flocculent substance, m. p. 98°. The following salts were prepared: *hydrochloride*,

$C_{14}H_{11}O_2N, HCl$,
long, yellow needles, m. p. 238°; *mercurichloride*,

$C_{14}H_{11}O_2N, HCl, HgCl_2$,
pale yellow needles, m. p. 187°; *platinichloride*,

$(C_{14}H_{11}O_2N)_2, H_2PtCl_6$,
dark yellow needles, m. p. 204°; *aurichloride*, $C_{14}H_{11}O_2N, HAuCl_4$,
reddish-brown powder, m. p. 170°.

Piperonylidene-2:6-lutidine, $C_{15}H_{13}O_2N$, prepared from piperonaldehyde and 2:6-lutidine (2:6-dimethylpyridine), is a white substance, m. p. 109°; the crystalline *hydrochloride* has m. p. 275°; the

mercurichloride forms small, dark yellow needles, m. p. 225° ; the *platinichloride* has m. p. 215° ; the *aurichloride* crystallises in reddish-brown needles, m. p. 185° .

Piperonylidene-2:4:6-trimethylpyridine, $C_{16}H_{15}O_2N$, prepared from 2:4:6-trimethylpyridine and piperonaldehyde, is a pale yellow, viscid oil, b. p. $55-60^{\circ}/50-60$ mm.; the *hydrochloride* crystallises in slender, white, silky needles, m. p. 262° ; the *mercurichloride* forms pale yellow needles, m. p. $223-224^{\circ}$; the crystalline *platinichloride* has m. p. 224° ; the *aurichloride* is a brownish-red, flocculent substance, m. p. 156° . When 2:4:6-trimethylpyridine is heated with a large excess of piperonaldehyde it yields *dipiperonylidene-2:4:6-trimethylpyridine* $C_{24}H_{19}O_4N$, crystallising in white needles, m. p. 154° ; the *mercurichloride*, $C_{24}H_{19}O_4N, HCl, HgCl_2$, forms reddish-brown needles, m. p. $236-237^{\circ}$.

2'-Hydroxy-4-stilbazole, $C_{13}H_{11}ON$, prepared from salicylaldehyde and γ -picoline, forms white flakes, m. p. $120-122^{\circ}$, b. p. $200-210^{\circ}/50-60$ mm.

2'-Hydroxy-6-methyl-2-stilbazole, $C_{14}H_{13}ON$, prepared from salicylaldehyde and 2:6-lutidine, crystallises in long, white needles, m. p. 199° ; the *hydrochloride*, $C_{14}H_{13}ON, HCl$, forms long, pale yellow needles, which do not melt at 300° ; the *mercurichloride* is a pale yellow, flocculent substance, m. p. 155° ; the *platinichloride* is a yellow powder, which does not melt at 300° ; the *aurichloride* is a brown powder, m. p. $177-178^{\circ}$.

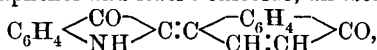
2'-Hydroxy-4:6-dimethyl-2-stilbazole, $C_{15}H_{15}ON$, obtained by the condensation of 2:4:6-trimethylpyridine with salicylaldehyde, is a pale yellow oil, b. p. $170-175^{\circ}/20-25$ mm.; the *hydrochloride* forms long, yellow needles, m. p. 260° ; the *mercurichloride* is a yellow, flocculent substance, m. p. 160° ; the *platinichloride* has m. p. $204-205^{\circ}$.

The bases described in this paper are decomposed when reduced with sodium and ethyl or amyl alcohol.

W. H. G.

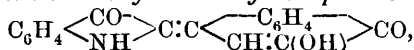
Indigoid Dyes. IV. Indigoid and Indolignoid Dyes of the Naphthalene Series and their Decomposition Products (Hydroxynaphthaldehydes). A. BEZDIK and PAUL FRIEDLÄNDER (*Monatsh.*, 1909, 30, 271-286. Compare *Abstr.*, 1908, i, 673, 674).

—In addition to the indigoid dye, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{C:C} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH:CH} \end{smallmatrix} \text{C}_6H_4$, obtained from α -naphthol and isatin chloride, an isomeride,



is also formed. These two compounds have very similar properties; the latter is characterised by the chain $-\text{CO}\cdot\text{C}:\text{C}\cdot\text{C}:\text{C}\cdot\text{CO}-$. A series of substances containing this chain have been prepared, and the group name *lignone* is proposed, the above compound being termed by the authors 2-indole-1-naphthaleneindolignone.

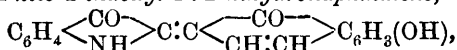
3-Hydroxy-4-keto-1-indoxyl-1:4-dihydronaphthalene,



prepared by the interaction of 1:2-dihydroxynaphthalene and isatin

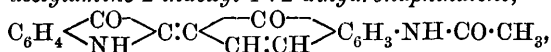
chloride, forms glistening, brown needles, and dyes mordanted fabrics a greenish-blue.

5-Hydroxy-1-keto-2-indoxyl-1 : 2-dihydronaphthalene,



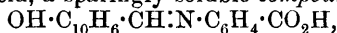
is obtained in copper-red-coloured, glistening needles by the interaction of 1:5-dihydroxynaphthalene with α -isatin anilide and acetic anhydride. When heated, it forms a carmine-red vapour; sodium hydroxide converts it into 1:5-dihydroxy-2-naphthaldehyde. It dissolves in concentrated sulphuric acid with a blue coloration, and is sulphonated on heating.

1-Keto-5-acetylamino-2-indoxyl-1 : 2-dihydronaphthalene,



prepared from 5-amino-1-naphthol and α -isatinanilide, forms dark violet needles. The isomeric *1-keto-4-acetylamino-2-indoxyl-1 : 2-dihydronaphthalene*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C}:\text{C} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}:\text{C}(\text{NHAc}) \end{array} \text{C}_6\text{H}_4$, is obtained from 4-acetylamino-1-naphthol and isatinanilide.

1-Hydroxy-2-naphthaldehyde, prepared by heating 1-oxy-2-indoxyl-naphthalene with 10% sodium hydroxide, crystallises in greenish-yellow needles, m. p. 59° , has a characteristic cinnamon-like odour, dissolves in alkalis with a yellow colour, and gives a green coloration with ferric chloride. The *oxime* crystallises in faintly yellow-coloured needles, m. p. 145° ; the *phenylhydrazone* forms plates, m. p. $115-116^\circ$. With anthranilic acid, a sparingly soluble compound,



is obtained, crystallising in bright red, quadratic plates (decomp. above 200°). *1-Methoxy-2-naphthaldehyde*, prepared by means of methyl sulphate, forms colourless crystals, m. p. 47° . *1:2- α -Naphthapyrone*, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}:\text{CH} \end{array} \text{CO}$, prepared by boiling the hydroxyaldehyde with

sodium acetate and acetic anhydride, forms faintly coloured needles, m. p. 138° , is insoluble in sodium carbonate, slightly volatile in steam, and has a slight, though definite, coumarin odour.

1:2-Dimethoxynaphthalene, prepared by methylation with methyl sulphate, has b. p. $278-280^\circ$, m. p. 31° , and forms a picrate, crystallising in red needles, m. p. 97° . A mixture of β -methoxy- α -naphthol and α -methoxy- β -naphthol is obtained at the same time, the former of which is very easily oxidised in alkaline solution, and could not be isolated. α -Methoxy- β -naphthol forms colourless, stout, monoclinic plates, m. p. 90.5° .

1-Hydroxy-4-methoxy-2-naphthaldehyde has, like methylgentisic aldehyde, an intense citron-yellow colour, and dyes the skin a fast yellow. It gives a dark green coloration with ferric chloride, and dissolves in alkalis, giving orange-yellow solutions.

3-Chloro-4-hydroxy-1-naphthaldehyde is obtained from the indolignone of 2-chloro- α -naphthol; it forms colourless needles, m. p. 245° (decomp.).

2:5-Dihydroxy-2-naphthaldehyde forms minute, voluminous needles, m. p. 215° , and gives a dark olive-green ferric chloride coloration.

1-Hydroxy-5-methoxy-2-naphthaldehyde crystallises in citron-yellow needles, m. p. 128°. E. F. A.

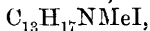
Binuclear Quinones. PAUL FRIEDLÄNDER (*Ber.*, 1909, 42, 1058—1062. Compare preceding abstract).—3-Hydroxy-4-keto-1-indoxyl-1:4-dihydronaphthalene, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} : C : C \begin{smallmatrix} \text{CH} : \text{C}(\text{OH}) \\ \diagdown \quad \diagup \\ C_6H_4 \end{smallmatrix} : CO$, prepared from 1:2-dihydroxynaphthalene and isatin chloride, forms dark green needles of metallic lustre or lustrous, bronze needles; it dissolves in alkalis with a dark green or olive-yellow coloration, and dyes mordanted fabrics a greenish-blue.

10-Keto-9-indoxylantracene, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} : C : C \begin{smallmatrix} C_6H_4 \\ \diagdown \quad \diagup \\ C_6H_4 \end{smallmatrix} : CO$, prepared from isatin chloride and anthranol, forms dark brownish-red or transparent, ruby-red crystals.

10-Keto-9-thionaphthylantracene, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} : C : C \begin{smallmatrix} C_6H_4 \\ \diagdown \quad \diagup \\ C_6H_4 \end{smallmatrix} : CO$, forms lustrous, brown needles, m. p. 219°. The above dyes are somewhat redder than the corresponding indigoids, and, like them, are decomposed by alkalis into anthranilic acid and an hydroxyaldehyde, which in this case belongs to the para-series E. F. A.

Action of Grignard Reagents on Quaternary Ammonium Halides. MARTIN FREUND and LUDWIG RICHARD (*Ber.*, 1909, 42, 1101—1121).—Quaternary ammonium halides, which react with alkalis to form ψ -bases, interact easily with organo-magnesium halides, yielding substances which differ from the ψ -bases by containing a hydrocarbon residue in place of the hydroxyl group. Quinoline, cotarnine, hydrastinine, berberine, phenylacridine, and crystal-violet have been examined already (*Abstr.*, 1905, i, 151, 156, 159). The present paper is a continuation of the subject, and deals mainly with two questions, whether the entrant radicle is always attached to the 2-carbon atom in quinoline derivatives, and secondly, what is the action when the 2-carbon atom is already substituted. The interaction of quinoline methiodide and ethereal magnesium ethyl bromide leads to the formation of 1-methyl-2-ethyl-2-dihydroquinoline, $C_6H_4 \begin{smallmatrix} \text{CH}=\text{CH} \\ \diagup \quad \diagdown \\ \text{NMe} \cdot \text{CHEt} \end{smallmatrix}$, b. p. 265°, or 141—142°/21 mm. (*platinichloride*, $2C_{12}H_{15}N, H_2PtCl_6$, m. p. 176°), which is reduced by tin and 20% hydrochloric acid to the corresponding *tetrahydroquinoline*, $C_{12}H_{17}N$, b. p. 265—267°, of which the *hydrochloride*, *hydrobromide*, and *hydriodide* have m. p. 207°, 196°, and 193° respectively. In a similar way, quinoline methiodide and magnesium methyl iodide yield 1:2-dimethyldihydroquinoline (*platinichloride*, m. p. 178°), which is reduced to 1:2-dimethyltetrahydroquinoline. Since it has been already shown (*loc. cit.*) that 2-phenyl-1-methyldihydroquinoline is produced in the same way, it may be stated that the action of organo-magnesium halides on quaternary quinolinium halides is a general method for the production of 2-substituted dihydroquinolines, which are reduced to the corresponding tetrahydroquinolines.

The presence of a substituent in the 2-position does not appear to influence the reaction, since 2-methylquinoline methiodide reacts in an analogous manner with magnesium methyl, ethyl, or phenyl halides. 1:2:2-Trimethyldihydroquinoline, $C_{12}H_{15}N$, b. p. 273—275°, forms a *picrate*, m. p. 138°, and is reduced to the *tetrahydro*-compound, $C_{12}H_{17}N$, b. p. 269—270° (*picrate*, m. p. 178°). 1:2-Dimethyl-2-ethyldihydroquinoline, b. p. 279—284°, forms a *methiodide*,

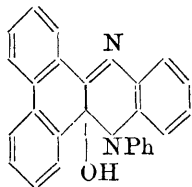


m. p. 260—261°, and is reduced to the *tetrahydro*-compound, b. p. 278—284°, of which the *hydrochloride* and the *picrate* have m. p. 208° and 138° respectively. 2-Phenyl-1:2-dimethyldihydroquinoline, b. p. 310—330° (decomp.), forms a *picrate*, m. p. 170—172°.

The preceding rule appears to be applicable to azonium bases, for Kehrman's 1:2:3-triphenylquinoxaline bromide, which forms a ψ -base (Hantzsch and Kalb, Abstr., 1900, i, 113), reacts with magnesium ethyl iodide (2 mols.) to yield 1:2:3-triphenyl-2-ethyl-

dihydroquinoxaline, $CPhEt \begin{matrix} \text{CPh:N} \\ | \\ NPh \cdot C_6H_4 \end{matrix}$, m. p. 198—199°.

Phenazonium compounds have also been examined. Flavinduline bromide, which forms a ψ -base (Hantzsch and Osswald, Abstr., 1900, i, 256), reacts with organo-magnesium halides in a way that does not confirm Hantzsch and Osswald's formula of the ψ -base, but points rather to the annexed constitution, for yellow basic compounds, having a hydrocarbon residue in the place of the hydroxyl group in the figure, are produced together with colourless, non-basic isomerides, in which the hydrocarbon residue has wandered to the unsubstituted nitrogen atom. For example, the interaction of flavinduline bromide and magnesium benzyl chloride leads to the formation of a mixture of N-phenyl- α -benzyl-



dihydrophenanthraphenazine, $C_{33}H_{24}N_2$, m. p. 175—179°, which forms yellow crystals and a red hydrochloride, and N-phenyl-N'-benzyl-dihydrophenanthraphenazine, $C_{33}H_{24}N_2$, m. p. 185°, which is colourless and does not form salts. The former of these two compounds is changed to the latter at 120—130°. Flavinduline bromide reacts, (a) with magnesium ethyl bromide (5 mols.) to form N-phenyl- α -ethyl-dihydrophenanthraphenazine, $C_{28}H_{22}N_2$, m. p. 172°, which exists only in the yellow modification and forms a *hydrochloride*, m. p. 196°, and a *hydrobromide*, m. p. 190°; (b) with magnesium methyl iodide to form the corresponding yellow *methyl* compound, $C_{27}H_{20}N_2$, m. p. 176°, which also forms red salts, and (c) with magnesium phenyl bromide to form colourless crystals of N:N'-diphenyldihydrophenanthraphenazine, $C_{32}H_{22}N_2$, m. p. 243°, which does not form salts.

Brilliant-green (the hydrochloride of tetraethyldiaminotriphenylcarbinol) behaves like crystal-violet (Freund and Beck, *loc. cit.*), yielding with magnesium benzyl chloride, tetraethyldiaminotriphenylbenzylmethane, $CH_2Ph \cdot CPh(C_6H_4 \cdot NEt_2)_3$, m. p. 151°, which forms colourless crystals and pale green solutions; the *hydriodide* has m. p. 260°, and the *methiodide*, m. p. 148°. Brilliant-green reacts

in a similar way with magnesium ethyl bromide, forming tetraethyl-diaminotriphenylethylmethane, which is isolated as the *hydrogen sulphate*, $C_{29}H_{38}N_2 \cdot 2H_2SO_4$, m. p. 205° (the *hydriodide* has m. p. $220-223^\circ$), and with magnesium propyl iodide, forming the corresponding propyl compound, which is also isolated as the *hydrogen sulphate*, $C_{30}H_{40}N_2 \cdot 2H_2SO_4$, m. p. 230° . C. S.

Formation of Acid Chlorides. HANS MEYER and RICHARD TURNAU (*Ber.*, 1909, 42, 1163—1169. Compare Abstr., 1906, i, 138).—Both malonic and *isosuccinic* acids give good yields of chlorides by the action of thionyl chloride. 2-Hydroxy-3-methylcinchonic acid yields the normal chloride when heated with thionyl chloride in open vessels; when heated under pressure, however, it yields the chloride of 2-chloro-3-methylcinchonic acid. The formation of this chloro-derivative is undoubtedly due to the action of the hydrogen chloride on the hydroxy-chloride.

The differences noticed by Meyer and Turnau (Abstr., 1905, i, 155, 666; 1907, i, 344), and Besthorn and Ibele (*ibid.*, 1905, i, 612; 1906, i, 605), in the action of thionyl chloride on quinoline-2-carboxylic acid are accounted for by the fact that the chloride used by Meyer and Turnau contained small amounts of sulphur dioxide, which readily transforms Besthorn and Ibele's unimolecular quinaldinic chloride (m. p. $97-98^\circ$) into Meyer's polymeride, m. p. 170° .

When the thionyl chloride is distilled over dimethylaniline, the sulphur dioxide is removed, and the purified product yields no trace of the polymeride. The polymeric chloride is formed from quinoline-2-carboxylic acid, also, when the acid has not been recrystallised, owing to the fact that the impure acid contains traces of nitric acid.

J. J. S.

Synthesis of Ethyl Quinaldineoxalate and Lepidineoxalate by means of Potassium Ethoxide. WILHELM WISLICENUS and EMIL KLEISINGER (*Ber.*, 1909, 42, 1140—1143. Compare Abstr., 1897, i, 488).—Potassium ethoxide is a more efficient condensing agent than sodium ethoxide. When a cold alcoholic ethereal solution of potassium ethoxide is treated with equal molecular quantities of ethyl oxalate and quinaldine, the *potassium* derivative of ethyl quinaldineoxalate, $C_9NH_8 \cdot CH:C(OK) \cdot CO_2Et$, is obtained as a hygroscopic, yellow substance, which is decomposed by water, the liberated potassium hydroxide hydrolysing one-half of the resulting ethyl quinaldineoxalate into its constituents. The potassium derivative, by treatment with the calculated quantity of dilute sulphuric acid, yields a colourless *sulphate*, from which ammonium hydroxide liberates *ethyl quinaldineoxalate*, $C_{14}H_{13}O_3N$, m. p. $130-132^\circ$. The ester crystallises in yellow needles or prisms, and has pronounced amphoterie properties; it is hydrolysed by 6% sulphuric acid, yielding the acid (*loc. cit.*), which decomposes at $167-168^\circ$.

The corresponding 4-methylquinoline derivatives are obtained in a similar way. 4-Methylquinolineoxalic acid has m. p. $224-225^\circ$ (decomp.); the *ethyl* ester has m. p. $194-196^\circ$. C. S.

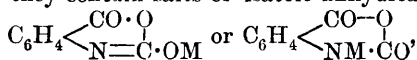
Preparation and Reactivity of 3-Methylquinoline. WILHELM WISLICENUS and HEINRICH ELVERT (*Ber.*, 1909, 42, 1144—1145).—By mixing *o*-aminobenzaldehyde and propaldehyde, a yellowish-white, crystalline substance, $\text{CHEt}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO})_2$, m. p. 103—105°, is obtained. 3-Methylquinoline is obtained in 80—85% yield by heating molecular quantities of propaldehyde and *o*-aminobenzaldehyde at 220° for one hour; it does not condense with ethyl oxalate (preceding abstract). C. S.

Occurrence of Hydroacridine in Coal Tars. HERMAN DECKER and GEORGES DUNANT (*Ber.*, 1909, 42, 1178—1179).—Coal tars appear to contain dihydroacridine, since the crude acridine when treated with excess of methyl sulphate and then with sodium carbonate yields a precipitate of 10-methyldihydroacridine (Pictet and Patry, *Abstr.*, 1902, i, 644). J. J. S.

Hofmann's Reaction. IV. Behaviour of Isatoic Anhydride with Alkalis and with Barium Hydroxide. ERNST MOHR (*J. pr. Chem.*, 1909, [ii], 79, 281—329. Compare *Abstr.*, 1905, i, 890; 1906, i, 252, 357; this vol., i, 190).—The paper deals mainly with the remarkable changes which isatoic anhydride undergoes in alkaline solutions of different concentrations. The chief result is that the anhydride yields two series of salts.

Solutions of the salts of the one series are obtained by dissolving isatoic anhydride (1 mol.) in 5 or more molecules of dilute alkali, for example, sodium hydroxide, at the ordinary temperature. Such solutions yield carbon dioxide and anthranilic acid by acidification. That the solution before acidification cannot contain sodium carbonate and anthranilate is proved by the following experiment. Two solutions, one of isatoic anhydride and the other of anthranilic acid, dissolved in equal amounts of barium hydroxide, are treated with calcium hypochlorite; the former remains clear for a few minutes, and then slowly develops a rose-red colour, whilst the solution of barium anthranilate gives a deep bluish-violet coloration. The solution obtained from isatoic anhydride and an excess of alkali hydroxide probably contains the normal isatoate; it is proved experimentally that such a solution decomposes slowly in the presence of excess of alkali, rapidly with only a slight excess, yielding carbonate and anthranilate.

Salts of the second series are obtained by dissolving 1 mol. of isatoic anhydride in a small excess of an alkali hydroxide at the lowest convenient temperature. Such solutions have a blue fluorescence and regenerate the anhydride by immediate acidification, or by treatment with a saturated solution of ammonium chloride or of sodium hydrogen carbonate at 0°; they contain salts of isatoic anhydride,

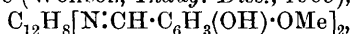


and not normal isatoates, as Erdmann supposes. The *potassium* and the *barium* salts have been isolated. The solutions of such salts are very unstable; at the ordinary temperature isatoic anhydride is spontaneously deposited, and the solution contains carbonate and anthranoylanthranilate, whilst, by boiling, carbon dioxide is evolved,

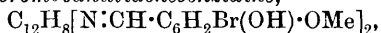
and the filtered solution yields pure anthranoylanthranilic acid by acidification. C. S.

Vanillidene- and Piperonylidene-benzidines. HENRY A. TORREY and E. D. CLARKE (*J. Amer. Chem. Soc.*, 1909, 31, 583—585).—When a solution of vanillin is treated with benzidine, a precipitate of vanillidenebenzidine is produced. This observation led to a study of the reaction in the hope that it might be of value for the estimation of vanillin. It was found, however, that the method was unsatisfactory, since both mono- and di-vanillidene derivatives of benzidine are produced according to the amount of benzidine added.

Vanillidenebenzidine, $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, m. p. about 181° , forms bright yellow crystals and dissolves in glacial acetic acid, giving a red solution, from which it separates on cooling as a moss-like mass of crimson crystals; when the latter are washed with dilute alcohol, the substance regains its original yellow colour. Di-vanillidenebenzidine (Wolfson, *Inaug. Diss.*, 1905),

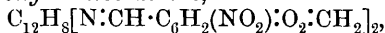


m. p. $220-221.5^\circ$, is a yellow substance. On treating this compound with a hot alcoholic solution of salicylaldehyde, the vanillidene complex is replaced by the salicylidene group. By the action of benzidine on bromovanillin, *bisbromovanillidenebenzidine*,



is obtained as a yellow, crystalline substance, which is turned red by acids and decomposes slowly at 232° .

Bis-6-nitropiperonylidenebenzidine,



obtained by mixing hot alcoholic solutions of 6-nitropiperonal and benzidine, is a dark yellow, crystalline substance, which decomposes at 273° . *Bisbromopiperonylidenebenzidine*, $\text{C}_{12}\text{H}_8[\text{N} : \text{CH} \cdot \text{C}_6\text{H}_2\text{Br} : \text{O}_2 : \text{CH}_2]_2$, m. p. 257° (decomp.), forms yellow crystals. E. G.

Hydrazones of Sugars. A. RECLAIRE (*Ber.*, 1909, 42, 1424. Compare Abstr., 1908, i, 1013).—*Xylose-o-nitrophenylhydrazone*, $\text{C}_{11}\text{H}_{15}\text{O}_6\text{N}_3$, crystallises from methyl alcohol in long, red needles, m. p. 123° . *Sorbose-o-nitrophenylosazone*, $\text{C}_{18}\text{H}_{22}\text{O}_8\text{N}_6$, is a dark red powder, m. p. $211-212^\circ$. J. V. E.

Method of Formation of Benzoylphenylhydrazine. ANGELO ANGELI and VINCENZO CASTELLANA (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 322—324).—The great similarity in behaviour between hydroxylamine derivatives and hydrazine derivatives renders it almost certain that the action of alkalis on phenylsulphonehydrazobenzene, studied by Hantzsch and Glogauer (Abstr., 1898, i, 78), which proceeds according to the equation $\text{R} \cdot \text{SO}_2 \cdot \text{NPh} \cdot \text{NHPh} = \text{R} \cdot \text{SO}_2\text{H} + \text{NPh} : \text{NPh}$, is analogous to the action of an alkali on the sulphydroxamic acids, an intermediate compound, $\text{NHPh} \cdot \text{NPh} \cdot \text{OH}$, being formed, which loses water, yielding azobenzene.

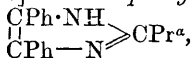
The authors have studied the action of potassium hydroxide on benzenesulphonephenylhydrazine, $\text{SO}_2\text{Ph} \cdot \text{NH} \cdot \text{NHPh}$, which yields an unstable salt, rapidly decomposing according to the equation $\text{NHPh} \cdot \text{NH} \cdot \text{OH} = \text{C}_6\text{H}_6 + \text{N}_2 + \text{H}_2\text{O}$. It is found, indeed, that with

benzaldehyde, this unstable intermediate compound yields benzoyl-phenylhydrazine, $\text{NHPh}\cdot\text{NH}\cdot\text{OH} + \text{Ph}\cdot\text{CHO} = \text{NHPh}\cdot\text{NHBz} + \text{H}_2\text{O}$.

T. H. P.

Glyoxalines. BR. RADZISZEWSKI (*Bull. Acad. Sci. Cracow*, 1909, 213—219).—Glyoxalines may be prepared by saturating an alcoholic solution of benzil and an aldehyde with ammonia gas and precipitating with water. The methyl derivatives are prepared by warming the alcoholic solution with an excess of methyl iodide.

[With BR. WYSOCHAŃSKI.]—4:5-Diphenyl-2-propylglyoxaline,



prepared from benzil and butaldehyde, forms pale yellow needles, m. p. 205.5°. This and the following glyoxalines oxidise slowly in alkaline alcoholic solutions with phosphorescence. The *hydrochloride* forms colourless crystals, m. p. 233.5°; the *oxalate*, needles, m. p. 210°. The *methyl ether*, $\text{C}_{18}\text{H}_{17}\text{N}_2\text{Me}$, melts below 110°.

[With M. BEISER.]—4:5-Diphenyl-2-isopropylglyoxaline, $\text{C}_{18}\text{H}_{18}\text{N}_2$, forms pale yellow needles, m. p. 246°. The *hydrochloride*, needles, m. p. 227°; the *platinichloride*, $(\text{C}_{18}\text{H}_{18}\text{N}_2)_2\cdot\text{H}_2\text{PtCl}_6\cdot 3\text{H}_2\text{O}$, orange crystals, m. p. above 290° (decomp.), and the *methyl ether*, m. p. 97°.

[With H. BUKOWSKA.]—4:5-Diphenyl-2-amylglyoxaline, $\text{C}_{20}\text{H}_{22}\text{N}_2$, from hexaldehyde, forms colourless needles, m. p. 252°. The *hydrochloride*, m. p. 161°; *platinichloride*, $(\text{C}_{20}\text{H}_{22}\text{N}_2)_2\cdot\text{H}_2\text{PtCl}_6$, yellow crystals, m. p. 272° (decomp.), and *methyl ether*, m. p. 127°.

[With A. JAKALO.]—4:5-Diphenyl-2-hexylglyoxaline, $\text{C}_{21}\text{H}_{24}\text{N}_2$, forms colourless needles, m. p. 167°; *hydrochloride*, scales, m. p. 133°; *picrate*, needles, m. p. 170°; *oxalate*, $(\text{C}_{21}\text{H}_{24}\text{N}_2)_2\cdot\text{C}_2\text{H}_2\text{O}_4\cdot\text{H}_2\text{O}$, m. p. 190°; *methyl ether*, m. p. 164°.

[With S. STENZEL.]—4:5-Diphenyl-2-o-tolylglyoxaline, $\text{C}_{22}\text{H}_{18}\text{N}_2$, from o-tolualdehyde, m. p. 252°; *hydrochloride*, m. p. 120°; *platinichloride*, decomp., 225°; *methyl ether*, m. p. 259°.

4:5-Diphenyl-2-m-tolylglyoxaline, m. p. about 300°; *hydrochloride*, m. p. 125°; *platinichloride*, m. p. 230° (decomp.); *ethyl ether*, $\text{C}_{22}\text{H}_{17}\text{N}_2\text{Et}$, m. p. above 310°.

[With J. ROHM.]—The following compounds are better prepared by heating the aldehyde with benzil, ammonium carbonate, and a little alcohol at 180° for six to eight hours. 4:5-Diphenyl-2-p-tolylglyoxaline forms colourless crystals, m. p. 233°; *hydrochloride*, m. p. 120°; *platinichloride*, decomp. about 250°; *methyl ether*, m. p. 217°. 4:5-Diphenyl-2-hydroxymethoxyphenylglyoxaline, $\text{C}_{22}\text{H}_{18}\text{O}_2\text{N}_2$, from vanillin, m. p. 243°; *hydrochloride*, m. p. 154°; *platinichloride*, decomp. about 230°; *methyl ether*, m. p. 230°.

4:5-Diphenyl-2-a-naphthylglyoxaline, $\text{C}_{25}\text{H}_{18}\text{N}_2$, m. p. 283°; *hydrochloride*, decomp., 180°; *platinichloride*, decomp. about 230°; *methyl ether*, m. p. 291°.

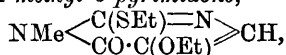
C. H. D.

Electrolytic Reduction of a Nitro-derivative of Pyrazolone. GOTTFRIED KÜMMEL and E. REMY (*Zeitsch. Elektrochem.*, 1909, 15, 254. Compare Abstr., 1907, i, 145).—Nitro-1-phenyl-3-pyrazolone dissolved in alcoholic sulphuric acid is electrolysed with a large

cathode and small anode of lead at 80°. The reduction takes place in exactly the same way as is the case with aromatic nitro-compounds, the final product being the amino-derivative, of which more than 86% of the theoretical yield is obtained. *Amino-1-phenyl-3-pyrazolone* forms colourless needles, m. p. 257°. T. E.

Pyrimidines. XLII. Synthesis of 5-Hydroxy-1-methyl-uracil. TREAT B. JOHNSON and D. BREESE JONES (*J. Amer. Chem. Soc.*, 1909, 31, 590—596).—Johnson and McCollum (Abstr., 1906, i, 704) have obtained 5-hydroxyuracil (*isobarbituric acid*) in quantitative yield by the hydrolysis of 5-ethoxy-2-ethylthiol-6-pyrimidone. Johnson and Jones (this vol., i, 60) have shown that *N*-alkyl derivatives of this thiolpyrimidine can be readily prepared, and that, on hydrolysis, they yield *N*-alkyl derivatives of 5-hydroxyuracil; 5-hydroxy-1-benzyluracil and 5-hydroxy-3-benzyluracil were prepared in this way. The present investigation was carried out with the object of obtaining the *N*-methyl derivatives of 5-ethoxy-2-ethylthiol-6-pyrimidone and submitting them to hydrolysis.

When 5-ethoxy-2-ethylthiol-6-pyrimidone is treated with methyl iodide, a mixture of the 1- and 3-methyl derivatives is produced containing about 70% of the theoretical yield of the 1-methyl compound. *5-Ethoxy-2-ethylthiol-1-methyl-6-pyrimidone*,



m. p. 50°, crystallises in plates; it combines with potassium iodide to form the compound, $3\text{C}_9\text{H}_{14}\text{O}_2\text{N}_2\text{S}_2\cdot 2\text{KI}$. When this pyrimidine is hydrolysed with hydrobromic acid, it is converted into a mixture of

2-thio-5-hydroxy-1-methyluracil, $\text{NMe} \begin{array}{c} \text{CS—NH} \\ \text{CO}\cdot\text{C(OH)} \end{array} \text{CH}$, which forms slender prisms and has no definite m. p., and *2:6-diketo-5-ethoxy-1-methylpyrimidine*, $\text{NMe} \begin{array}{c} \text{CO—NH} \\ \text{CO}\cdot\text{C(OEt)} \end{array} \text{CH}$, m. p. about 240° (decomp.),

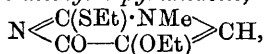
which crystallises in short prisms. If *2:6-diketo-5-ethoxy-1-methylpyrimidine* or *5-ethoxy-2-ethylthiol-1-methyl-6-pyrimidone* is heated with concentrated hydrochloric acid at 120—130°, *5-hydroxy-1-methyl-*

uracil, $\text{NMe} \begin{array}{c} \text{CO—NH} \\ \text{CO}\cdot\text{C(OH)} \end{array} \text{CH}$, m. p. 247° (decomp.), is produced,

which forms radiating prisms. By the action of chloroacetic acid on *2-thio-5-hydroxy-1-methyluracil*, *5-hydroxy-1-methyl-6-pyrimidone-2-*

thiolacetic acid, $\text{NMe} \begin{array}{c} \text{C(S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H)}:\text{N} \\ \text{CO—C(OH)} \end{array} \text{CH}$, is obtained, which forms stout prisms and decomposes at 217°.

5-Ethoxy-2-ethylthiol-3-methyl-6-pyrimidone,



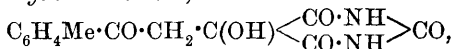
m. p. 149—151°, crystallises in small prisms, and combines with potassium iodide to form the compound, $3\text{C}_9\text{H}_{14}\text{O}_2\text{N}_2\text{S}_2\cdot 2\text{KI}$, which, on treatment with hydrochloric acid, yields *2-thio-5-ethoxy-3-methyl-6-*

pyrimidone, $\text{NH} \begin{array}{c} \text{CS—NMe} \\ \text{CO}\cdot\text{C(OEt)} \end{array} \text{CH}$, m. p. 210—211°, which forms long needles,

E. G.

Condensation Products of Alloxan. OTTO KÜHLING and B. SCHNEIDER (*Ber.*, 1909, 42, 1285—1296. Compare Kühling, *Abstr.*, 1908, i, 571).—In continuation of the study of the condensation of alloxan with aromatic ketones (*Abstr.*, 1905, i, 944), an account is given of the condensation of alloxan with *p*-methyl- and *p*-methoxyacetophenone, together with the preparation and properties of some new derivatives of ethoxyphenacyldialuric and phenacyldialuric acids.

p-Methylphenacyldialuric acid,

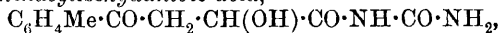


obtained in 78% yield by saturating an alcoholic solution of *p*-methylacetophenone and alloxan with hydrogen chloride at -7° , crystallises from a mixture of acetone and water in white leaflets containing one molecule of solvent: m. p. $241\text{--}242^\circ$ (decomp.); its sodium salt is a white, amorphous solid; its acetyl derivative forms leaflets, m. p. 220° (decomp.); the benzoyl derivative, $\text{C}_{20}\text{H}_{16}\text{O}_6\text{N}_2$, forms white prisms, m. p. 215° (decomp.).

p-Methylphenacyltartronic acid, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\begin{matrix} \text{CO}\cdot\text{NH} \\ \text{CO}_2\text{H} \end{matrix}$ is

obtained by warming *p*-methylphenacyldialuric acid with dilute aqueous sodium carbonate solution; it forms white aggregates of needles, which soften at 139° , m. p. 158° (decomp.); the lead salt, $(\text{C}_{13}\text{H}_{13}\text{O}_6\text{N}_2)_2\text{Pb}$, forms needle-shaped prisms.

p-Methylphenacylisohydantoic acid,



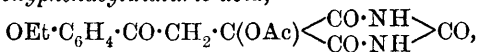
prepared by boiling *p*-methylphenacyltartronic acid in acetone, crystallises in white, prismatic leaflets, m. p. $163\text{--}164^\circ$ (decomp.).

p-Methoxyphenacyldialuric acid, $\text{C}_{13}\text{H}_{12}\text{O}_6\text{N}_2$, from *p*-methoxyacetophenone and alloxan, forms white, prismatic leaflets, m. p. 227° (decomp.); its acetyl derivative forms white, rectangular leaflets, m. p. 197° (decomp.); benzoyl derivative, white, prismatic leaflets, m. p. 240° (decomp.).

p-Methoxyphenacyltartronic acid, $\text{C}_{13}\text{H}_{14}\text{O}_7\text{N}_2$, by action of sodium carbonate on *p*-methoxyphenacyldialuric acid, crystallises from a mixture of acetone and water or ether in aggregates of slender needles: m. p. 144° (slight decomp.), then becomes semi-solid, and decomposes completely at 157° ; the lead salt, $(\text{C}_{13}\text{H}_{13}\text{O}_7\text{N}_2)_2\text{Pb}$, forms white needles.

p-Methoxyphenacylisohydantoic acid, $\text{C}_{12}\text{H}_{14}\text{O}_5\text{N}_2$, by heating the previous acid with acetone or by boiling an aqueous solution of *p*-methoxyphenacyldialuric acid, crystallises from acetone.

Acetyl-*p*-ethoxyphenacyldialuric acid,

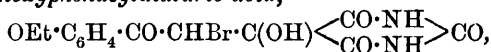


white, rectangular leaflets from aqueous acetone, m. p. 207° (decomp.); the corresponding benzoyl derivative forms white, prismatic leaflets from alcohol, m. p. 224° (decomp.).

p-Ethoxyphenacyltartronic acid, $\text{C}_{14}\text{H}_{16}\text{O}_7\text{N}_2$, separates from acetone in aggregates of white needles, m. p. 134° , and decomposes completely at 157° , like the corresponding methoxy-acid; its lead salt, $(\text{C}_{14}\text{H}_{15}\text{O}_7\text{N}_2)_2\text{Pb}$, is amorphous.

p-Ethoxyphenacylisohydantoic acid, $C_{13}H_{16}O_5N_2$, prepared from the preceding acid and acetone, forms columnar prisms from acetone, m. p. 162—163° (decomp.).

Bromo-p-ethoxyphenacyldialuric acid,



by action of bromine on a glacial acetic acid solution of *p*-ethoxyphenacyldialuric acid, separates from aqueous acetone in white, concentrically grouped needles, sinters at 171°, and decomposes at 201°; the *acetyl* derivative, $C_{16}H_{15}O_7N_2Br$, leaflets from aqueous alcohol, sinters at 165°, m. p. 178—179° (decomp.).

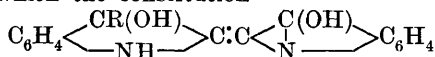
Bromophenacyldialuric acid, $COPh \cdot CHBr \cdot C(OH) \begin{array}{c} \diagup CO \cdot NH \\ \diagdown CO \cdot NH \end{array} CO$,

prepared in similar manner, forms concentrically grouped needles, m. p. 217° (decomp.); the *silver* salt, $C_{12}H_6O_5N_2BrAg_3$, was analysed; the *acetyl* derivative, $C_{14}H_{11}O_6N_2Br$, forms rectangular prisms; it sinters at 181°, m. p. 194° (decomp.).

Benzoylphenacyldialuric acid, $C_{19}H_{14}O_6N_2$, prepared by benzoylating phenacyldialuric acid, forms prismatic needles from alcohol, m. p. 252° (decomp.).
P. H.

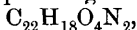
Action of Grignard Reagents on Vat Dyes. I. Indigo.

FRANZ SACHS and HANS KANTOROWICZ (*Ber.*, 1909, 42, 1565—1576).—Synthetic indigotin dissolves readily in a large excess of ethereal organo-magnesium halide, yielding, after the usual treatment, substances to which the constitution

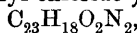


is ascribed, although the evidence is not conclusive; in some cases a small quantity of an acid is also produced. Magnesium methyl bromide yields a *substance*, $C_{17}H_{14}O_2N_2$, m. p. 209° (decomp.). Magnesium ethyl bromide yields a *substance*, $C_{18}H_{16}O_2N_2$, m. p. 245° (decomp.), which separates from alcohol in orange-coloured crystals, forms a *diethyl* derivative, $C_{22}H_{24}O_2N_2$, m. p. 95·5°, and is oxidised by potassium permanganate to the *substance*, $C_{18}H_{16}O_2N_2(OH)_2$, m. p. 111°. Magnesium propyl bromide yields the *substance*, $C_{19}H_{18}O_2N_2$, m. p. 222°. Magnesium isobutyl bromide yields the *substance*, $C_{20}H_{20}O_2N_2$, m. p. 220°. From magnesium *isoamyl* bromide are produced a red *substance*, $C_{21}H_{22}O_2N_2$, m. p. 211°, and a colourless *acid*, m. p. 148°, the *silver* salt of which, $C_{21}H_{21}O_3N_2Ag$, has m. p. 207° (decomp.). Magnesium phenyl bromide yields a colourless *acid*, $C_{22}H_{16}O_3N_2$, m. p. 228°, and a red *substance*, $C_{22}H_{16}O_2N_2$, m. p. 231°, which forms a *diethyl* derivative, $C_{26}H_{24}O_2N_2$, m. p. 104°, a *sulphate*,
($C_{22}H_{14}ON_2$)₂·H₂SO₄,

and is oxidised by potassium permanganate to the *substance*,



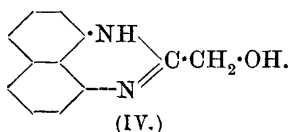
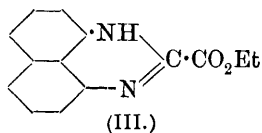
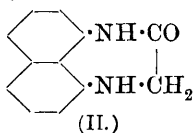
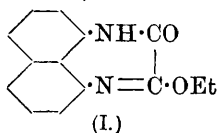
m. p. 198°. Magnesium benzyl chloride yields a *substance*,



m. p. 182°. Magnesium *p*-tolyl bromide yield an *acid*, m. p. 223—230° (decomp.), and an orange-yellow *substance*, $C_{23}H_{18}O_2N_2$, m. p. 239° (decomp.).
C. S.

Ring Formations in the Peri-Position of the Naphthalene Series. I. FRANZ SACHS [with BRUNO MYLO, GEORG MEYERHEIM, W. BRUNETTI, J. DAMM, H. MÖHRKE, M. SCHWABACHER, M. STEINER, and ARTHUR VOSS] (*Annalen*, 1909, 365, 53—166. Compare Kehrman and Engelke, this vol., i, 150).—A large number of important dyes have been prepared recently, in the formation of which a homo- or hetero-cyclic ring becomes attached to an anthracene molecule through the agency of one of the peri-positions (compare Bally, *Abstr.*, 1905, i, 237; *Farbenfabriken vorm. Friedr. Bayer & Co.*, *Abstr.*, 1908, i, 456). In order to gain some knowledge, therefore, of the part played by this type of ring formation in the production of dyes, the preparation and properties of compounds derived from naphthalene by condensation in the peri-position have been exhaustively studied. All the compounds described in this paper were prepared from 1:8-naphthylenediamine by condensation with monocarboxylic acids, oxalic acid, malonic acid, phthalic acid and other acids forming anhydrides, carbonic acid derivatives, substances containing sulphur, ketones, diketones, and ketocarboxylic acids.

It has been found impossible to build up seven-membered ring systems from 1:8-naphthylenediamine. In agreement with the view put forward by Hinsberg (*Abstr.*, 1889, 717), it is shown that the compounds investigated by Meyer and Müller (*Abstr.*, 1897, i, 356), to which formulæ were assigned containing seven-membered ring systems (I and II), have in reality the constitutional formulæ III and IV.



The parent compound of the substances described later is prepared by the action of formic acid on 1:8-naphthylenediamine, and has the annexed formula. This substance is designated perimidine; by this name attention is directed to the *peri*-position of the naphthalene nucleus and the *imidine*-like arrangement of the nitrogen atoms. The 2-methyl derivative is already known (Sachs, *Abstr.*, 1906, i, 829).

An interesting reaction occurs when a substituted acetoacetic ester is heated in aqueous solution with 1:8-naphthylenediamine hydrochloride; the Me·CO- group being eliminated from the ester to form 2-methylperimidine and replaced by hydrogen. It is thus possible by this method to prepare esters of the higher aliphatic acids; for example, ethyl propionate and ethyl β -phenylpropionate are obtained from ethyl ethylacetoacetate and ethyl benzylacetoacetate respectively.

As the result of this investigation, it is found, in agreement with

the statement made originally by Bamberger (Abstr., 1887, 495), that ring formation takes place more readily in the peri-position than in the ortho-position. Further, unlike the simple derivatives of *o*-phenylenediamine, such as phenyleneazoimide and benziminazole, which are colourless, the peri-derivatives are highly coloured provided an ethylene linking is present in the new ring. The simple members of the series are yellow, yellowish-green, orange, and red, but compounds having more intense and deeper colours are produced by nitration, reduction, etc. The dyes obtained in this manner are extremely fast, so that the presence of the peri-ring confers valuable dyeing properties on a compound.

I. 1 : 8-Naphthylenediamine and Monocarboxylic Acid.—Perimidine, $C_{11}H_8N_2$, obtained by the interaction of the diamine and formic acid, either alone or in alcoholic solution, or by heating the base with chloroform and calcium oxide at 140° , forms green crystals, m. p. 222° . The following salts were prepared and analysed: *hydrochloride*, $C_{11}H_8N_2 \cdot HCl$, yellowish-green needles, decomposing at 300° ; *nitrate*, $C_{11}H_8N_2 \cdot HNO_3$, long, green needles; *picrate*, $C_{11}H_8N_2 \cdot C_6H_3O_7N_3$, short, brownish-green needles, m. p. 226° ; *hydrogen sulphate*,

$C_{11}H_8N_2 \cdot H_2SO_4$, crystals, decomposing slowly at 300° ; *sulphate*, $(C_{11}H_8N_2)_2 \cdot H_2SO_4$, decomposing at 250° ; *platinichloride*, $C_{22}H_{16}N_4 \cdot H_2PtCl_6$, pale yellow powder; *formate*, $C_{11}H_8N_2 \cdot H \cdot CO_2H$, m. p. 143° ; *acetate*,

$C_{11}H_8N_2 \cdot Me \cdot CO_2H$, pale yellow, crystalline aggregates, m. p. 130° ; *oxalate*,

$C_{11}H_8N_2 \cdot C_2H_2O_4$, yellow, crystalline powder, decomposing at 270° ; *malonate*,

$C_{11}H_8N_2 \cdot C_3H_4O_4$, m. p. 158° ; *pyruvate*, $C_{11}H_8N_2 \cdot C_3H_3O_3$. Perimidine is converted by nitric acid (D 1.40) in glacial acetic acid into a vermilion *nitro*-derivative and a *dinitroperimidine*, crystallising in small, yellowish-brown needles. Perimidine couples with *p*-nitrodiazobenzene acetate, yielding *p*-nitrobenzeneazoperimidine, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \begin{smallmatrix} \text{N} \\ \diagup \text{NH} \end{smallmatrix} > CH$, obtained as blue crystals.

The following derivatives of 2-methylperimidine have been prepared: *hydrochloride*, yellow needles, which darken at 300° but do not melt; *nitrate*, $C_{12}H_{10}N_2 \cdot HNO_3$; *acetate*, m. p. 130 – 140° ; *oxalate*, m. p. 232° ; *picrate*, short, dark yellow needles, m. p. 258° ; *p*-nitrobenzeneazo-2-methylperimidine, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \begin{smallmatrix} \text{N} \\ \diagup \text{NH} \end{smallmatrix} > CMe$, violet crystals, decomposing at 165 – 190° ; *m*-nitrobenzeneazo-2-methylperimidine, $C_{18}H_{18}O_2N_5$, brownish-red crystals.

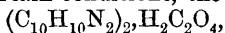
2-Ethylperimidine, $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \diagup \text{NH} \end{smallmatrix} > CEt$, obtained by the action of propionic anhydride on the diamine, crystallises in faintly yellow, felted needles, m. p. 161° ; the *hydrochloride*, long, silky needles, decomposing at 220° ; *sulphate*, yellow needles, m. p. 199° ; *oxalate*, fine yellow, crystalline powder, m. p. 207° ; *picrate*, orange-red, glistening precipitate, m. p. 230° (decomp.), and *acetate*, decomposing above 260° , were prepared.

2-Propylperimidine, $C_{14}H_{14}N_2$, crystallises in yellow, felted needles, m. p. 157° ; the *hydrochloride*, yellow needles, decomposing at 240° ; *sulphate*, m. p. 232° ; *picrate*, yellowish-brown, crystalline powder, m. p. 220° (decomp.); *oxalate*, yellow needles, m. p. 222° , and *nitrate*, golden-yellow, crystalline precipitate, decomposing at 257° , were prepared.

2-Phenylperimidine hydrochloride is obtained as yellow needles, decomposing at 240° , by the action of benzyl chloride on the diamine in benzene. The free base has m. p. 187° (compare Noelting, Abstr., 1902, i, 315). The *nitrate*, yellow powder, decomposing at 180° , and *picrate*, yellow needles, were prepared and analysed.

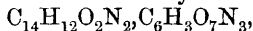
2-Benzylperimidine, $C_{18}H_{14}N_2$, prepared by the action of phenylacetyl chloride on the diamine, crystallises in slender, pale yellowish-green needles, m. p. 194° ; the *nitrate* forms yellow needles, m. p. 238° ; the *sulphate* forms golden-yellow needles, m. p. 231° ; the *hydrochloride* crystallises in yellow needles, and decomposes above 180° ; the *picrate* forms yellow needles, m. p. about 210° .

II. 1:8-Naphthylenediamine and Oxalic or Malonic Acid.—Oxalic acid interacts with the diamine in a variety of ways, depending on the conditions. In cold alcoholic solution they combine to form the *oxalate*, $C_{10}H_{10}N_2 \cdot C_2H_2O_4 \cdot 2H_2O$, obtained as a white precipitate decomposing at 270° ; under certain conditions, the *oxalate*,



m. p. 205° , is obtained. Condensation between the diamine and oxalic acid takes place when an aqueous solution of the oxalate is boiled, resulting in the formation of perimidine-2-carboxylic acid. The latter substance is also formed when oxalic acid and the diamine are heated together at 100 — 140° .

Ethyl perimidine-2-carboxylate, $C_{10}H_6 \begin{smallmatrix} \text{NH} \\ \text{---N---} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{Et}$, is prepared by heating the diamine with ethyl oxalate (compare de Aguiar, this Journ., 1874, 699; Meyer and Müller, loc. cit.). *Perimidine ethyl oxalate*, $C_{11}H_8N_2 \cdot \text{CO}_2\text{H} \cdot \text{CO}_2\text{Et}$, is formed at the same time; it may also be prepared by treating perimidine in alcoholic solution with ethyl hydrogen oxalate, and crystallises in rosettes of straw-yellow crystals, m. p. 204° . Ethyl perimidine-2-carboxylate forms a *picrate*,



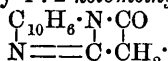
obtained as dark violet crystals, m. p. above 200° (decomp.), and an *oxalate*, reddish-brown, fibrous crystals, m. p. 248° . It is converted by concentrated hydrochloric acid under pressure at 140 — 160° into

perimidine-2-carboxylic acid, $C_{10}H_6 \begin{smallmatrix} \text{NH} \\ \text{---N---} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$, obtained as golden, glistening scales decomposing above 250° . The *alkali* salts of the latter substance are unstable; the *hydrochloride*, $C_{12}H_8O_2N_2 \cdot \text{HCl}$, prepared by the action of dry hydrogen chloride on the acid suspended in glacial acetic acid, has an intense red colour. All attempts to prepare the chloride and amide of perimidine-2-carboxylic acid were unsuccessful; the *anilide*, $C_{11}H_7N_2 \cdot \text{CO} \cdot \text{NHPh}$, obtained by heating the ethyl ester and aniline together at 160° , forms bright red, nodular crystals, m. p. 278° . Ethyl perimidine-2-carboxylate, when heated with 1:8-naphthylenediamine at 140 — 150° , yields 2:2-diperimidyl,

$C_{10}H_6 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} > C \cdot C \begin{smallmatrix} \text{NH} \\ \diagdown \quad \diagup \\ \text{N} \end{smallmatrix} < C_{10}H_6$, obtained as dark red crystals, which do not melt at 300° . The ethyl ester is reduced by zinc dust and acetic acid, yielding *2-hydroxymethylperimidine*, $C_{11}H_7N_2 \cdot CH_2 \cdot OH$, which crystallises in slender, greenish-yellow needles, m. p. 221° ; the latter substance may be synthesised by heating 1:8-naphthylenediamine with glycollic acid or chloroacetic acid. The following derivatives of the ethyl ester were also prepared and analysed: *acetate*, lemon-yellow powder, m. p. $130-140^\circ$ (decomp.); *picrate*, long, glistening, yellow lamellæ, decomposing at $230-240^\circ$; *oxalate*, yellow crystals, m. p. 223° ; *malonate*, and *nitrate*.

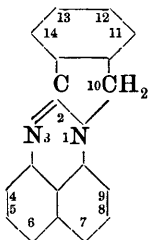
Methyl perimidine-2-carboxylate, $C_{11}H_7N_2 \cdot CO_2Me$, prepared from the diamine and methyl oxalate, crystallises in aggregates of long, red needles, m. p. 197° .

1:8-Naphthylenediamine, when heated with malonic acid at $100-150^\circ$, yields 2-methylperimidine malonate and a substance crystallising in small scales with a silvery-grey lustre, m. p. 210° (decomp.), which is probably 1:2-*ketomethylenepirimidine*,

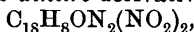


Ethyl perimidylacetate, $C_{11}H_7N_2 \cdot CH_2 \cdot CO_2Et$, is obtained when the diamine is boiled with ethyl malonate; it forms sulphur-yellow crystals, m. p. 152° ; a substance (C=73.75, H=5.25, N=12.75) is obtained at the same time as a pale yellow powder. *Methyl perimidylacetate*, $C_{14}H_{12}O_2N_2$, prepared in a similar manner, has m. p. 184° .

III. 1:8-Naphthylenediamine with *Phthalic Acid and other Dicarboxylic Acids which form Anhydrides*.—The parent substance of the compounds described in this division is designated *phthaloperine*, and has the annexed formula. A 100%



yield of 10-*phthaloperinone*, $\begin{array}{c} C_6H_4 \cdot C \cdot N \\ CO - N \cdot C_{10}H_6 \end{array}$, is obtained when the diamine is heated with phthalic anhydride at $150-230^\circ$; it sublimes, forming stellate groups of long, soft, scarlet needles, m. p. $229-230^\circ$ (corr.). It is converted by concentrated nitric acid at the ordinary temperature into a *dinitro*-derivative,



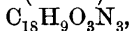
which crystallises in red needles, m. p. 247° , and is reduced by ammonium sulphide to the corresponding *diamino*-derivative, $C_{18}H_8ON_2(NH_2)_2$, red crystals, m. p. $255-260^\circ$. *Dibromophthaloperinone*, $C_{18}H_8ON_2Br_2$, obtained by the action of bromine in acetic acid on phthaloperinone, crystallises in small, slender, red needles, and decomposes at 240° . Phthaloperinone, when reduced with zinc dust and acetic acid, yields *diphthaloperinyl ether*, $C_{10}H_6 \begin{smallmatrix} N \cdot C \cdot C_6H_4 \\ \diagup \quad \diagdown \\ N \cdot CH \cdot O \cdot CH \cdot N \end{smallmatrix} < C_{10}H_6$, a yellow substance, which commences to decompose at a red heat. Phthaloperinone reacts with magnesium methyl iodide, yielding 10-*hydroxy-10-methylphthaloperine*, $C_{19}H_{14}ON_2$, which crystallises in olive-brown rhombohedra, m. p. 241° ;

the *hydriodide*, $C_{19}H_{14}ON_2 \cdot HI$, is red; the *picrate* is a brownish-red powder.

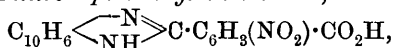
The following compounds are obtained by similar methods: 10-*hydroxy-10-ethylphthaloperine*, $C_{20}H_{16}ON_2$, olive-brown crystals, m. p. 243° ; 10-*hydroxy-10-phenylphthaloperine*, $C_{24}H_{16}ON_2$, brown crystals, m. p. $282-284^\circ$; the *hydrochloride*, $C_{24}H_{16}ON_2 \cdot HCl$, crystallises in brown prisms; 10-*hydroxy-10-benzylphthaloperine*, $C_{25}H_{18}ON_2$, crystallises in rhombohedra, m. p. $258-259^\circ$, and, when boiled with acetic anhydride, yields 10-*benzylidenephthaloperine*, $C_{25}H_{16}N_2$, crystallising in purplish-red nodules, m. p. 191° .

o-Perimidylbenzoic acid, $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{C} \cdot C_6H_4 \cdot CO_2H$, is formed when the condensation of phthalic anhydride with 1:8-naphthylenediamine is carried out in various solvents; also when phthaloperinone is heated with concentrated hydrochloric acid. It is obtained as yellow flakes, and does not possess a definite m. p.

11-(or 14-)*Nitro-10-phthaloperinone*, $C_{18}H_9O_3N_3$, prepared by heating the diamine with 3-nitrophthalic acid at $185-200^\circ$, forms dark red crystals, m. p. $210-215^\circ$. 12-(or 13-)*Nitro-10-phthaloperinone*,



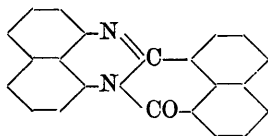
prepared similarly by using 4-nitrophthalic acid, forms red crystals, m. p. $278-280^\circ$; the acid anhydride and the diamine unite in ethereal solution, yielding 4-*nitro-2-perimidylbenzoic acid*,



a pale brick-red powder, which loses water at 205° and passes into the anhydro-derivative.

Dichlorophthaloperinone, $C_{18}H_8ON_2Cl_2$, prepared by heating dichlorophthalic acid with the diamine, has m. p. $235-237^\circ$; it yields a *dibromo-derivative*, $C_{18}H_6ON_2Cl_2Br_2$, reddish-violet crystals, m. p. 224° , and a *dinitro-derivative*, $C_{18}H_6O_5N_4Cl_2$, a yellowish-brown substance decomposing at $213-215^\circ$. Dichlorophthalic anhydride and the diamine combine in ethereal solution, yielding *perimidyl-dichlorobenzoic acid*, $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{C} \cdot C_6H_2Cl_2 \cdot CO_2H$, yellowish-red crystals, which lose water at 180° .

Naphthaloperinone, annexed formula, prepared by heating the diamine with naphthalic anhydride at $180-200^\circ$, forms long, dark red crystals, m. p. 253° ; the *dinitro-derivative*,



$C_{22}H_{10}O_5N_4$,

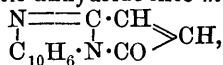
forms red crystals, decomposing at $300-310^\circ$; the *diamino-derivative*, $C_{22}H_{14}ON_4$, is a

bluish-violet powder, decomposing above 300° ; the *dibromo-derivative*, $C_{22}H_{10}ON_2Br_2$, crystallises in nodules of red needles, m. p. 261° . The parent substance is converted by alcoholic potassium hydroxide into 8-*perimidyl-naphthoic acid*, $C_{11}H_7N_2 \cdot C_{10}H_6 \cdot CO_2H$, a brown substance, which passes into the anhydride at 180° .

Succinic anhydride and 1:8-naphthylenediamine interact in toluene, yielding *perimidylpropionic acid*, $C_{11}H_7N_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, a yellowish.

grey substance, m. p. 253°, which, when heated at this temperature, passes into *succinoperinone*,
$$\begin{array}{c} \text{N}=\text{C}\cdot\text{CH}_2 \\ | \\ \text{C}_{10}\text{H}_6\cdot\text{N}-\text{CO} \end{array} > \text{CH}_2$$
, m. p. 158°.

Perimidylacrylic acid, $\text{C}_{11}\text{H}_7\text{N}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, is obtained as a brownish-red precipitate, decomposing at 210°, by the action of maleic anhydride on 1:8-naphthylenediamine in glacial acetic acid; it is converted by boiling acetic anhydride into *maleinoperinone*,



m. p. 161°.

IV. 1:8-Naphthylenediamine and Carbonic Acid Derivatives.—*Dihydro-2-perimidone* (1:8-naphthylenecarbamide),



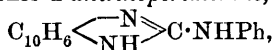
may be prepared by the action of carbonyl chloride, ethyl chloro-carbonate, ethyl carbonate, or hydrocyanic acid on the diamine; it forms glistening, white crystals, m. p. 304—305°. *2-Ethoxyperimidine*, $\text{C}_{10}\text{H}_6 < \begin{array}{c} \text{NH} \\ \text{N} \end{array} > \text{C}\cdot\text{OEt}$, is obtained by heating the diamine with ethyl orthocarbonate at 140—180°; it crystallises in almost colourless needles, m. p. 125°, and is converted by hot concentrated hydrochloric acid into the dihydroperimidone just described; the *hydrochloride*, $\text{C}_{10}\text{H}_{12}\text{ON}_2\cdot\text{HCl}$, forms white crystals, decomposing at 300°; the *sulphate* crystallises in white needles, m. p. 192°. Dihydro-2-perimidone, when heated with phosphoryl chloride under pressure at 130°, yields *2-chloroperimidine*, $\text{C}_{10}\text{H}_6 < \begin{array}{c} \text{N} \\ \text{NH} \end{array} > \text{CCl}$, crystallising in greyish-green leaflets, m. p. 194°. *2-Thiodihydroperimidone*,



prepared by acting on the diamine with carbon disulphide or potassium xanthate, crystallises in large, glistening leaflets, which sublime without melting.

V. 1:8-Naphthylenediamine with Compounds containing Sulphur or Selenium.—*2-Aminoperimidine*, $\text{C}_{10}\text{H}_6 < \begin{array}{c} \text{N} \\ \text{NH} \end{array} > \text{C}\cdot\text{NH}_2$, formed together with the dihydrothioperimidone just described by the action of ammonium thiocyanate on the diamine, is a yellowish-white substance, m. p. 239°; the *sulphate*, *acetate*, *nitrate*, *hydrochloride*, m. p. 282°, *picrate*, red leaflets, and *platinichloride* were prepared.

Phenyl-8-aminonaphthylthiocarbamide, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$, prepared by acting on the diamine with phenylthiocarbimide in cold benzene, is a yellowish-white substance, m. p. 238°. When the solution of these components in benzene is boiled for twelve hours, a substance is obtained which is either *2-anilinoperimidine*,

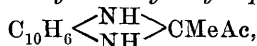


or *phenyl-1:8-naphthyleneguanidine*, $\text{C}_{10}\text{H}_6 < \begin{array}{c} \text{NH} \\ \text{NH} \end{array} > \text{C}\cdot\text{NPh}$; it crystallises in glistening, white leaflets, m. p. 245°; the *picrate* is red.

The following compounds are prepared by similar methods: *o*-Tolyl-8-aminonaphthylthiocarbamide, $C_7H_7 \cdot NH \cdot CS \cdot NH \cdot C_{10}H_6 \cdot NH_2$, an almost white substance, m. p. 229° ; 2-*o*-toluidinoperimidine, $C_{18}H_{15}N_3$, m. p. $240-241^\circ$. *p*-Tolyl-8-aminonaphthylthiocarbamide, $C_{18}H_{17}N_3S$, m. p. 259° ; 2-*p*-toluidinoperimidine, $C_{18}H_{15}N_3$, m. p. 247° . Allyl-8-aminonaphthylthiocarbamide, $C_{14}H_{15}N_3S$, yellowish-white needles, which commence to decompose at 170° , m. p. 300° ; allyl-8-aminonaphthylcarbamide, $C_{14}H_{15}ON_3$, is obtained by treating an alcoholic solution of the latter substance with mercuric oxide; it has m. p. 225° . Phenyl-8-aminonaphthylcarbamide, $C_{17}H_{15}ON_3$, crystallises in white leaflets with a red tinge, m. p. 304° .

Thionyl chloride, when boiled with a solution of the diamine in benzene, yields a substance having the formula $C_{10}H_6 \langle \begin{smallmatrix} NH \\ NH \end{smallmatrix} \rangle SO$ or $C_{10}H_6 \langle \begin{smallmatrix} N \\ N \end{smallmatrix} \rangle S, H_2O$. Selenious acid reacts with the diamine dissolved in 50% acetic acid, yielding a substance, $C_{10}H_6 \langle \begin{smallmatrix} N \\ N \end{smallmatrix} \rangle Se$, obtained as a black, infusible precipitate.

VI. Action of Ketones, Diketones, and Ketocarboxylic Acids on 1:8-Naphthylenediamine.—2-Acetyl-2-methyldihydroperimidine,



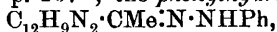
is prepared by acting on the diamine with diacetyl in alcoholic solution, and forms colourless crystals, m. p. $181-183^\circ$; the phenylhydrazone, $C_{12}H_{11}N_2 \cdot CMe : N \cdot NHPh$, crystallises in white, fan-shaped needles, sinters at 145° , m. p. $147-149^\circ$; the oxime, $C_{12}H_{11}N_2 \cdot CMe : NOH$, crystallises in yellow needles decomposing at about 300° ; the semicarbazone, $C_{12}H_{11}N_2 \cdot CMe : N \cdot NH \cdot CO \cdot NH_2$, has m. p. $224-226^\circ$; the azine, $(C_{12}H_{11}N_2 \cdot CMe)_2N_2$, forms pink crystals, m. p. 229° (decomp.); the benzylidene derivative, $C_{12}H_{11}N_2 \cdot CO \cdot CH : CHPh$, is obtained as the hydrochloride by acting on a solution of the perimidine in alcohol with benzaldehyde in the presence of hydrogen chloride; the hydrochloride is a brownish-yellow powder without a sharp m. p.

1:8-Naphthylenediamine condenses with isatin, forming a substance, $C_{10}H_6 \langle \begin{smallmatrix} NH \\ NH \end{smallmatrix} \rangle C \langle \begin{smallmatrix} CO \\ C_6H_4 \end{smallmatrix} \rangle NH$, which sinters at 170° , m. p. 181° , and, when heated further, yields another substance, crystallising in long needles, m. p. 254° . The condensation product of the diamine with alloxan has the formula $C_{10}H_6 \langle \begin{smallmatrix} NH \\ NH \end{smallmatrix} \rangle C \langle \begin{smallmatrix} CO \cdot NH \\ CO \cdot NH \end{smallmatrix} \rangle CO$; it crystallises in slender, white needles.

Ethyl acetoacetate reacts with the diamine at the ordinary temperature with the formation of ethyl 2-methyldihydroperimidylacetate, $C_{10}H_6 \langle \begin{smallmatrix} NH \\ NH \end{smallmatrix} \rangle CMe \cdot CH_2 \cdot CO_2Et$, white, glistening needles, m. p. 97° ; the sulphate, yellow needles decomposing above 260° , and oxalate, m. p. 241° , were prepared. The substance decomposes when heated at $150-160^\circ$, yielding ethyl acetate and 2-methylperimidine.

Acetonylperimidine, $C_{10}H_6 \langle \begin{smallmatrix} N \\ NH \end{smallmatrix} \rangle C \cdot CH_2 \cdot COMe$, is formed when

the diamine is boiled with ethyl acetoacetate; it crystallises in glistening, yellow needles, m. p. 267°; the *phenylhydrazone*,



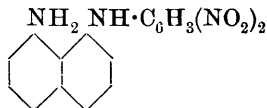
forms yellow crystals, m. p. 195°. When the same substances are heated together with dilute hydrochloric acid, they interact, yielding ethyl acetate and 2-methylperimidine.

Methyl acetoacetate reacts in the same manner with the diamine; *methyl 2-methyldihydroperimidylacetate*, $\text{C}_{15}\text{H}_{16}\text{O}_2\text{N}_2$, crystallises in glistening, white needles, m. p. 145°. *Ethyl 2-methyldihydroperimidylpropionate*, $\text{C}_{10}\text{H}_8\text{N}_2 \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, prepared from the diamine and ethyl laevulate, crystallises in white needles, m. p. 102°.

1 : 8-Naphthylenediamine (1 mol.) reacts with acetylacetone (1 mol.), yielding 2-methylperimidine and acetone; 2 : 2-dimethyldihydroperimidine, $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CMe}_2$, long needles, m. p. 117°, is also formed when an excess of the diketone is employed. Benzoylacetone (1 mol.) reacts with the diamine (1 mol.), yielding at first 2-methylperimidine and acetophenone; the latter substance interacts with another molecule of the diamine, yielding 2-phenyl-2-methyldihydroperimidine, $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CMePh}$, obtained as a white precipitate.

Benzenesulphonyl chloride reacts with the diamine dissolved in benzene in the presence of potassium carbonate, yielding *dibenzenesulphonyl-1 : 8-naphthylenediamine*, $\text{C}_{22}\text{H}_{18}\text{O}_4\text{N}_2\text{S}_2$, m. p. 192·5°, which couples with diazobenzenesulphonic acid in alkaline solution, forming an *azo-dye*; the latter substance when reduced yields *dibenzenesulphonyl-1 : 4 : 8-triaminonaphthalene*, $\text{C}_{22}\text{H}_{19}\text{O}_4\text{N}_3\text{S}_2$, a white, crystalline substance, m. p. 200° (decomp.).

2' : 4'-Dinitro-8-aminophenyl naphthylamine, annexed formula, prepared by boiling the diamine with chlorodinitrobenzene in alcoholic solution in the presence of sodium acetate, forms red crystals, m. p. 203·5—204°.



W. H. G.

Reduction of cycloAmine-ones. II. Diacridyl. HERMAN DECKER and GEORGES DUNANT (*Ber.*, 1909, 42, 1176—1178).—By the reduction of 10-methylacridone (Abstr., 1906, i, 901) a yellow precipitate is obtained in addition to methylacridonium hydroxide and methyldihydroacridine. This yellow compound is regarded as dimethyldiacridine, $\text{NMe} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} : \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{NMe}$, and the crystalline product obtained by the action of nitric acid as *dimethyldiacridylium nitrate*, $\text{NO}_3 \cdot \text{NMe} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} : \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{NMe} \cdot \text{NO}_3$. This nitrate forms large, glistening plates, only sparingly soluble in hot water, and is not molten at 330°. When reduced with zinc dust and acetic acid, it yields 10-methylacridonium hydroxide. Solutions of the salt do not yield precipitates with sodium hydroxide solution, but give precipitates with solutions of other salts. The *chromate* is a crystalline, yellow precipitate; the *sulphate* forms sparingly soluble, yellow

crystals; the *picrate*, $C_{40}H_{28}O_{14}N_8$, crystallises from alcohol in yellow crystals, m. p. 300° (decomp.); and the *iodide* forms glistening, red crystals, which lose methyl iodide readily at $245\text{--}270^\circ$, yielding *diacridyl*, $N \begin{array}{c} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{array} C \cdot C \begin{array}{c} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{array} N$, as a colourless, crystalline base, m. p. above 350° .

J. J. S.

Question of the Attachment of the Purine Bases in the Nucleic Acid Molecule. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1909, 60, 69—78).—According to Burian (Abstr., 1904, i, 354), purine bases and iminazoles which are not substituted in position 7 react with diazobenzenesulphonic acid, yielding coloured compounds, which were regarded as diazoamino-compounds. The products of reduction of these coloured compounds indicate that the compounds are azo-dyes with the $\cdot N:NR$ group attached to carbon number 8.

Theophylline combines with *p*-dichlorodiazobenzene chloride, yielding a dye which crystallises from alcohol or acetic acid in brilliant red needles. When reduced with sodium hyposulphite, it yields 8-aminotheophylline (compare D.R.-P. 156900) and dichloro-aniline. The same aminotheophylline is obtained when Burian's theophylline diazobenzenesulphonate is reduced. It can be diazotised, and then forms dyes with R-salt, but it does not combine with diazo-compounds.

Xanthine reacts with *p*-dichlorodiazobenzene chloride, yielding a brownish-red dye, which gives 8-aminoxanthine when reduced. This amino-compound can be diazotised, and yields the *anhydro*-compound, $CO \begin{array}{c} \diagup NH \cdot CO \cdot C \text{---} N \cdot N \\ \diagdown NH \text{---} C \cdot N \cdot C \cdot N \end{array}$, which crystallises in yellow masses of needles similar to tyrosine. It explodes at 150° , couples with an alkaline solution of R-salt, and when evaporated to dryness several times with 20% hydrochloric acid yields uric acid.

Guanine and *p*-dichlorodiazobenzene chloride yield a dark red dye, which forms 8-aminoguanine (2:8-diamino-6-pyrimidone) when reduced. 8-Aminoguanine sulphate, $2C_5H_7ON_6 \cdot H_2SO_4 \cdot 2H_2O$, crystallises in long needles, and loses its water of hydration at $120\text{--}130^\circ$. The amino-compound does not couple with diazo-compounds, but can be diazotised itself at 40° , and then reacts with an alkaline solution of R-salt, yielding a violet dye.

The conclusion is drawn that in nucleic acids the phosphorus atom is attached to the purine bases in positions 7 or 8 (compare Burian, Abstr., 1904, i, 358).

J. J. S.

Physico-chemical and Chemical Investigations on the Behaviour of Uric Acid in Solution. F. GUDZENT (*Zeitsch. physiol. Chem.*, 1909, 60, 25—37. Compare His and Paul, Abstr., 1900, i, 591; Gudzent, Abstr., 1908, i, 704).—The following constants have been determined for uric acid at 37° . Solubility in water, 1 in 15,505 parts, or 1 litre of solution contains 0.0649 gram of acid. Specific electrical conductivity, 0.000013, and molecular conductivity, 33.92. Degree of ionisation of saturated solution, 0.075. Dissociation constant, $K = 0.000233$. Heat of solution, -8954 cal.

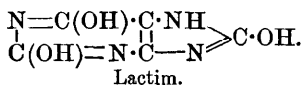
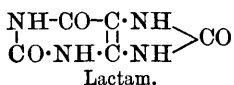
When shaken with water, uric acid decomposes, so that the solubility tends to increase with the time. The increase is only noticed at the end of twenty-four hours, and then rises rapidly, so that at the end of ten days the solubility is eleven times as great as at the end of a few hours, and in the same time the electrical conductivity of the solution has increased some fifty-five times.

An increase in the electrical conductivity is also observed when a saturated solution of the acid is kept in the absence of solid uric acid. Platinum has an accelerating effect on this change, and the curves obtained by plotting the conductivities against the time show that the reaction has a logarithmic course, indicating that a state of equilibrium has reached.

J. J. S.

Physico-chemical Researches on the Behaviour of Urates in Solution. F. GUDZENT (*Zeitsch. physiol. Chem.*, 1909, 60, 38—68. Compare Abstr., 1908, i, 704).—As the result of a series of investigations, the following conclusions are drawn.

(1) Uric acid forms two series of primary metallic salts (monosodium, potassium, and ammonium urates), which differ as regards solubility. The salts of the *a*-series cannot be obtained pure, as at the moment of their formation in water they tend to pass over into salts of the *b*-series. The probable cause of this change is an intramolecular rearrangement, so that the two series correspond with the two tautomeric forms of uric acid:



The unstable *a*-series are probably lactam urates, and the stable *b*-series, lactim urates.

(2) The *a*-salts have solubilities and specific conductivities which at 18° are some 33·4%, or at 37° 33·9%, greater than the corresponding values for the more stable *b*-salts.

(3) The transformation is practically complete, and the velocity of transformation is rapid in a homogeneous system, but much slower in a heterogeneous system, and depends on the amount of solid and of solvent present.

(4) The following constants at 18° and 37° are given in the original for the *a*- and *b*-modifications of the monosodium, monopotassium, and monoammonium salts, and also for mixtures of the two forms such as are usually met with in the ordinary commercial preparations of urates: solubility, molecular conductivity, conductivity at v_{∞} , migration values of the anions, time required to obtain a saturated solution, concentration of free hydroxyl ions, and degree of hydrolysis.

(5) The *a*- and *b*-forms of any one salt appear to be isomorphous.

J. J. S.

Isomeric Azoxy-compounds. ARNOLD REISSERT (*Ber.*, 1909, 42, 1364—1371).—Up to the present time no cases of isomeric azoxy-compounds have been observed in which the isomerism is undoubtedly due to a constitutional or steric difference in the azoxy-

groups (compare Janovsky and Reimann, Abstr., 1889, 392, 865; Bamberger, Abstr., 1900, i, 531; 1902, i, 505; Kekulé and Hidegh, *Ber.*, 1870, 3, 235).

On treating nitrosobenzene at low temperatures with aqueous-alcoholic sodium hydroxide, instead of alcoholic potassium hydroxide (compare Bamberger, Abstr., 1902, i, 279), the author obtains the known azoxybenzene together with a small quantity of an isomeric compound, to which he gives the name *iso*azoxybenzene; similarly, *o*-nitrosotoluene yields *o*-azoxytoluene and *o-iso*azoxytoluene, the latter in this case forming the main product. *p*-Nitrosotoluene yields *p*-azoxytoluene, together with a substance of high and indefinite m. p., which is evidently not a simple azoxy-compound. In the condensation of β -phenylhydroxylamine with nitrosobenzene, no trace of *iso*azoxybenzene is formed.

The two *iso*azoxy-compounds obtained are almost colourless, and when heated pass into the isomeric azoxy-compounds, the transformation not taking place at any definite temperature, but increasing in velocity as the temperature is raised. They are stable compounds, but a small quantity of bromine added to a chloroform solution of *iso*azoxytoluene converts the latter into azoxytoluene, probably by way of an intermediate additive bromine derivative (compare Wohl, Abstr., 1904, i, 201).

No specific chemical difference has been demonstrated between the isomeric azoxy-compounds. Phenylhydrazine acts on neither of the azoxytoluenes, whilst hydroxylamine converts the *iso*-compound partly into the normal form.

*iso*Azoxybenzene, $C_6H_5 \cdot N_2O \cdot C_6H_5$, crystallises from aqueous-methyl alcohol in slender needles, m. p. 84° if rapidly heated; if slowly heated, the compound begins to liquefy at 81° , at which temperature gradual change into azoxybenzene takes place.

*o-iso*Azoxytoluene, $C_7H_7 \cdot N_2O \cdot C_7H_7$, separates from light petroleum in faintly yellow, spear-like crystals, from aqueous methyl alcohol in needles, and from benzene in compact prisms, m. p. 82° (rapid), $80-81^\circ$ (slow heating).

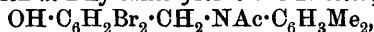
Bromo-o-azoxytoluene, $C_7H_6Br \cdot N_2O \cdot C_7H_7$, prepared from *o*-azoxytoluene or *o-iso*azoxytoluene, crystallises from 96% alcohol in almost colourless needles, m. p. 68.5° ; it is a derivative of *o*-azoxytoluene and not of the *iso*-compound, since the latter is converted into its isomeride by bromine (*vide supra*).

The substance, $C_{21}H_{19}O_2N_3 (= 3C_7H_7ON - H_2O)$, obtained together with *p*-azoxytoluene by the action of aqueous-alcoholic sodium hydroxide on *p*-nitrosotoluene, liquefies at $183-190^\circ$, but the liquid becomes clear only at about 250° .
T. H. P.

Influence of Substituents on the Capacity for Migration of Acid Residues. KARL AUWERS (*Annalen*, 1909, 365, 278-290).—A continuation of the investigation on the intramolecular transformations of acylated compounds (this vol., i, 222). The results obtained by the author in conjunction with Hirt, von Heyden, Hannemann, and Dannehl are discussed fully in this paper (compare following abstracts).

The migration of the acid radicle is not prevented by the presence of

two ortho-substituents, since 3:5-dibromo-2-acetoxybenzyl bromide when condensed with *m*-2-xylydine yields the *N*-ester,



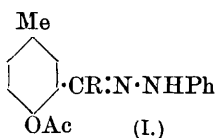
crystallising in needles.

The reduction of a very large number of derivatives of benzeneazo-*p*-tolyl acetate has been studied, and it is found that the migration of the acetyl group which takes place with the parent substance is totally prevented by the introduction of the most varied groups into the molecule with but one remarkable exception; the introduction of a methyl group in the para-position does not hinder the migration of the acid radicle (compare Auwers, Abstr., 1908, i, 228).

The introduction of various groups in the phenylhydrazine residue has a great influence on the capacity for migration of the acyl group in the *O*-acetates and *O*-benzoates of the substituted phenylhydrazones of salicylaldehyde.

The *O*-acetates and *O*-benzoates of the condensation products of salicylaldehyde with phenylhydrazine, *o*-tolylhydrazine, *o*-anisylhydrazine, *p*-chlorophenylhydrazine, *p*-bromophenylhydrazine, and *m*-2-xylylhydrazine, when heated with glacial acetic acid, pass into the isomeric *N*-acyl derivatives. The acetates, but not the benzoates, of the derivatives of *o*-chlorophenylhydrazine, *o*-bromophenylhydrazine, and *m*-nitrophenylhydrazine undergo the same transformation. Neither the acetates nor the benzoates undergo rearrangement when *o*-nitrophenylhydrazine and *p*-nitrophenylhydrazine are condensed with salicylaldehyde. It is evident, therefore, that the chemical nature of the substituent has a great influence on the stability of the hydrazone. The nitro-group is the only group of those investigated which is capable of preventing the migration of the acetyl group, and only then when in the ortho- or para-position to the imino-group; in the meta-position it only prevents the wandering of the heavier benzoyl group. Chlorine and bromine in the ortho-position also prevent the migration of the benzoyl group, but not when they occupy the para-position.

In the cases just cited it is evident that the steric, as compared with the chemical, influence of the ortho-substituents is quite negligible. However, steric influences have been detected in the intramolecular



transformations of the *O*-esters of the phenylhydrazones of *o*-hydroxy-ketones. The migration of the acyl group in compounds of type (I) does not occur when *R* represents a phenyl group, but does so when *R* is either hydrogen or methyl. In this connexion, it is also found that the imino-

hydrogen atom in phenylhydrazones of the type $\text{CPhR} \cdot \text{N} \cdot \text{NHPh}$ is replaced only with great difficulty and occasionally not at all by acid radicles when *R* is a heavy group. Even the phenylhydrazones of benzophenone and acetophenone may be obtained unchanged after boiling for some time with acetic anhydride, whereas the hydrazone derivatives of salicylaldehyde and its substituted products are, generally speaking, acetylated with great readiness.

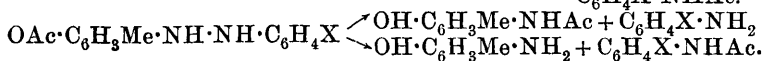
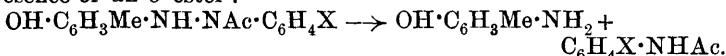
The same difference is encountered in the condensation of various aldehydes and ketones with *as*-phenylhydrazines. Aldehydes, likewise acetophenone and its derivatives, condense readily with *as*-acylphenyl-

hydrazines, whilst benzophenone and many of its derivatives do not yield condensation products with the same *as*-phenylhydrazine.

W. H. G.

Acylated *o*-Hydroxyazo-substances and Their Reduction.

KARL AUWERS [with W. HIRT and FRIEDRICH VON DER HEYDEN] (*Annalen*, 1909, 365, 291—313. Compare preceding abstract).—The hydroxyazo-compounds described later were prepared by coupling the phenol with the diazo-salt in very dilute aqueous solution. The acetates were obtained by heating the hydroxyazo-compound with acetic anhydride and sodium acetate. The reduction of the acetyl derivatives to the corresponding hydrazo-compounds was accomplished by means of zinc dust and acetic acid, less frequently by sodium amalgam and acetic acid. The position of the acyl group in the molecule was determined by reducing the compound and testing the products formed for the free base, $C_6H_4X \cdot NH_2$, the isolation of which indicated the presence of an *O*-ester:



The following are the new compounds described:

3-Benzeneazo-*m*-4-xylénol, $C_{14}H_{14}ON_2$, glistening, dark red needles, m. p. 90° (compare Grevingk, *Abstr.*, 1886, 348); the *acetate*, $C_{16}H_{16}O_2N_2$, crystallises in bright red, glistening needles, m. p. 68°; *O*-acetylbenzenehydrazo-*m*-4-xylénol, $C_{16}H_{18}O_2N_2$, is obtained as a pale yellow powder, m. p. 103°.

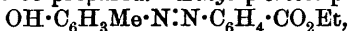
3-Benzeneazo-*o*-4-xylénol crystallises in glistening, dark orange-red needles, m. p. 130°; the *acetate* forms orange-yellow, pearly leaflets, m. p. 113°; *O*-acetylbenzenehydrazo-*o*-4-xylénol has m. p. 84—85°. Benzene-

azocresol, $\begin{matrix} CH & \text{---} & CMe & \text{---} & CH \\ & | & & & | \\ & C(OMe) \cdot C(OH) : C \cdot N : NPh \end{matrix}$, crystallises in red leaflets, m. p.

112°; the *acetate* crystallises in slender, glistening, red needles, m. p. 114°; the corresponding *O*-acetylhydrazo-derivative forms white leaflets, m. p. 102°; *O*-acetyl-3-benzenehydrazo-5-bromo-*p*-cresol, $C_{15}H_{15}O_2N_2Br$, forms slender, white leaflets, m. p. 91°.

3-*o*-Tolueneazo-*p*-tolyl acetate, $C_{16}H_{16}O_2N_2$, crystallises in small, red needles, m. p. 59°; the *O*-acetylhydrazo-compound, $C_{16}H_{18}O_2N_2$, forms white leaflets, m. p. 89°. 3-*m*-Tolueneazo-*p*-tolyl acetate forms compact, dark red crystals, m. p. 61—63°; the *O*-acetylhydrazo-compound crystallises in colourless leaflets, m. p. 92—95°. *N*-Acetyl-3-*p*-toluenehydrazo-*p*-cresol, $C_{16}H_{18}O_2N_2$, prepared by reducing 3-*p*-tolueneazo-*p*-tolyl acetate with sodium amalgam (compare Goldschmidt and Pollak, *Abstr.*, 1892, 974), crystallises in white leaflets, m. p. 102°. *o*-4-Xyleneazo-*p*-cresol, $C_{15}H_{16}ON_2$, is a brownish-yellow, crystalline powder, m. p. 131—132°; the *acetate*, $C_{17}H_{18}O_2N_2$, crystallises in orange-yellow leaflets and flat needles, m. p. 106—106.5°, and when reduced yields the *O*-acetylhydrazo-compound. *p*-Anisylazo-*p*-cresol, $C_{14}H_{14}O_2N_2$, crystallises in small, red needles, m. p. 94—95°; the *acetate*, $C_{16}H_{16}O_3N_2$, forms slender, yellowish-red, felted needles, m. p. 60—61°; the corresponding *N*-acetyl-*O*-benzoate, $C_{22}H_{19}O_3N_2Cl$, forms slender, white, felted needles, m. p. 175—176°. *p*-Nitrobenzeneazo-*p*-tolyl acetate, $C_{15}H_{13}O_4N_3$,

crystallises in slender, felted, red needles, m. p. 184° ; the hydrazo-compound could not be prepared. *Ethyl p-cresol-p-azobenzoate*,



forms small, red leaflets, m. p. $96-97^{\circ}$; the *acetate* forms red leaflets, m. p. 81° ; the *O-acetylhydrazo*-compound, $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_2$, forms white leaflets, m. p. $118-119^{\circ}$.

α -Naphthaleneazo-p-cresol, $\text{C}_{17}\text{H}_{14}\text{ON}_2$, forms small, brownish-violet crystals, m. p. $102-104^{\circ}$; the *acetate* is a light red, crystalline powder, m. p. $109-111^{\circ}$; the *O-acetylhydrazo*-derivative, $\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_2$, is a brown, crystalline powder, m. p. $139-141^{\circ}$. *β -Naphthaleneazo-p-cresol* forms yellow crystals, m. p. 167° ; the *acetate*, $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$, is a yellowish-red, crystalline powder, m. p. $95-96^{\circ}$; the *O-acetylhydrazo*-compound is a white powder.

W. H. G.

Migration of Acid Residues in the Phenylhydrazones of Acylated *o*-Hydroxyaldehydes. KARL AUWERS [with K. HANNEMANN] (*Annalen*, 1909, 365, 314-342. Compare preceding abstracts).—The hydrazones described in this paper were prepared by the action of the hydrazine on the aldehyde in alcoholic solution. The *O*-acetyl derivatives were usually obtained by treating the hydrazone in pyridine with acetyl chloride; in some cases they were more readily obtained from the acetyl-aldehyde. The diacetates, prepared by heating the hydrazone with acetic anhydride and sodium acetate, yield on partial hydrolysis with alcoholic alkali hydroxide the corresponding *N*-acetyl derivatives. The benzoates were prepared by condensation of the hydrazine with the aldehyde-benzoate; a few were prepared from the hydrazone by benzylation in pyridine. Boiling with excess of benzoyl chloride yielded the dibenzoates, which, when warmed with alcoholic alkali, were transformed into the *N*-benzoyl compounds.

The transformation of the *O*-esters into the corresponding *N*-acyl compounds was performed generally by boiling gently with ten times the quantity of glacial acetic acid. The values given in brackets later represent the times required to effect this change completely, unless otherwise stated. In some cases, the conversion of the *O*-acyl compound into the *N*-compound is accompanied by other reactions. For example, *O*-benzoylsalicylaldehyde-*p*-chlorophenylhydrazone is not only converted into the *N*-benzoyl compound, but is also split by the acetic acid into benzoylsalicylaldehyde and *p*-chlorophenylhydrazine; the *N*-benzoyl compound is similarly decomposed. As a result, the various substances interact, and the product of the transformation is a mixture of the *O*-benzoate, *N*-benzoyl compound, dibenzoate, and *p*-chlorophenylhydrazine. The following are the new compounds described.

Salicylaldehydephenylhydrazone-*O*-acetate is converted completely in three hours into the *N*-acetyl compound, $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$, prisms, m. p. $158-159^{\circ}$. The *O*-benzoate requires seven hours for its conversion into the *N*-benzoyl derivative, $\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_2$, white, felted needles, m. p. 169° .

Salicylaldehyde-*o*-tolylhydrazone, $\text{C}_{14}\text{H}_{14}\text{ON}_2$, yellow needles, m. p. $110-111^{\circ}$; *O*-acetate, $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$, pale yellow needles, m. p. 111.5° (three hours); *N*-acetyl derivative, white, rhombic crystals, m. p. $121-122^{\circ}$; *O*-benzoate, $\text{C}_{21}\text{H}_{20}\text{O}_2\text{N}_2$, yellow, silky needles, m. p.

157—158° (eight hours); *N*-benzoyl derivative, small, white needles, m. p. 184°.

Salicylaldehyde-o-anisylhydrazone, $C_{14}H_{14}O_2N_2$, yellow needles, m. p. 93—94°; *O*-acetate, $C_{16}H_{16}O_3N_2$, yellow needles, m. p. 112—113° (three hours); *diacetate*, $C_{18}H_{18}O_4N_2$, white needles, m. p. 155—156°; *N*-acetyl derivative, small, white needles, m. p. 120°; *O*-benzoate, $C_{21}H_{18}O_3N_2$, lemon-yellow needles, m. p. 157—158° (sixteen hours); *N*-benzoyl derivative, slender, white needles, m. p. 158—159°; *di*-benzoate, slender, white needles, m. p. 178°.

Salicylaldehyde-o-chlorophenylhydrazone, $C_{17}H_{11}ON_2Cl$, compact tetrahedra, m. p. 123°, the *O*-acetate, m. p. 105—106°, passes with great readiness into the *N*-acetyl derivative, m. p. 153—154°; the *O*-benzoate, $C_{20}H_{15}O_2N_2Cl$, white needles, m. p. 164°, is recovered unchanged after heating for sixteen hours with acetic acid.

Salicylaldehyde-m-chlorophenylhydrazone, stellate groups of light brown needles, m. p. 163—164°; *O*-benzoate, tufts of lemon-yellow, sword-shaped needles, m. p. 142—143°, partly converted in seven hours by boiling acetic acid into the *N*-benzoyl derivative, compact, granular crystals, m. p. 168—170°.

Salicylaldehyde-p-chlorophenylhydrazone, pale yellow leaflets, m. p. 169—170°; the *O*-benzoate, long, flexible, silky, yellow needles, m. p. 176—177°, is not converted completely, even after twenty hours, into the *N*-benzoyl derivative, white, felted needles, m. p. 166—167°.

Salicylaldehyde-p-bromophenylhydrazone *O*-acetate, $C_{15}H_{13}O_2N_2Br$, pale yellow, rhombohedral leaflets, m. p. 119—120° (three hours); *N*-acetyl derivative, tufts of light brown, pointed crystals, m. p. 148—149°; *diacetate*, $C_{17}H_{15}O_3N_2Br$, white needles, m. p. 152°; the *O*-benzoate, $C_{20}H_{15}O_2N_2Br$, yellow, silky needles, m. p. 186°, is converted into the *N*-benzoyl derivative, white needles, m. p. 163—164°, when boiled with glacial acetic acid, but other reactions take place simultaneously; the *dibenzoate*, $C_{27}H_{19}O_3N_2Br$, forms long, white needles, m. p. 156°.

Salicylaldehyde-o-bromophenylhydrazone, $C_{18}H_{11}ON_2Br$, yellow, pointed crystals, m. p. 111—112°; *O*-acetate, white needles, m. p. 114° (three to four hours); *N*-acetyl derivative, rosettes of pointed crystals, m. p. 142—143°; the *O*-benzoate, pale yellow, glistening leaflets, m. p. 164°, remains unchanged when boiled with acetic acid for twenty hours.

Salicylaldehyde-o-nitrophenylhydrazone *O*-acetate, $C_{15}H_{13}O_4N_3$, crystallises in soft, flexible, light red needles, m. p. 160°; it does not change into the *N*-acetyl derivative.

Salicylaldehyde-m-nitrophenylhydrazone *O*-acetate, red, ellipsoidal needles, m. p. 165° (seven hours); the *N*-acetyl derivative crystallises in lemon-yellow, compact needles, m. p. 164°, and white, felted needles, m. p. 162—163°; the *diacetate*, $C_{17}H_{15}O_5N_3$, forms white leaflets, m. p. 149—150°; the *O*-benzoate, $C_{20}H_{15}O_4N_3$, long, yellow needles, m. p. 177°, does not change into the *N*-benzoyl derivative.

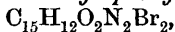
The *O*-acetate of salicylaldehyde-*p*-nitrophenylhydrazone crystallises in red needles, m. p. 185—186°, and with $\frac{1}{2}C_6H_6$ in yellow needles, m. p. 185—186°; the *O*-benzoate forms soft, yellow, felted needles, m. p. 207—208°; neither of these esters undergoes transformation into

the corresponding *N*-derivative; the *diacetate* forms small, white, felted needles, m. p. 164·5°.

Salicylaldehyde-o-cyanophenylhydrazone, $C_{14}H_{11}ON_3$, small, yellow needles, m. p. 163°; the *O*-benzoate, $C_{21}H_{15}O_2N_3$, light yellow needles, m. p. 164—165°, is decomposed when boiled with glacial acetic acid.

Salicylaldehyde-m-2-xylylhydrazone O-benzoate, $C_{22}H_{20}O_2N_2$, yellow needles, m. p. 100° (eight hours); *N*-benzoyl derivative, colourless needles, m. p. 179°.

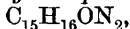
3 : 5-Dibromo-2-hydroxybenzaldehydophenylhydrazone *O*-acetate,



yellow, felted prisms, m. p. 166—167° (fourteen hours); the *N*-acetyl derivative, m. p. 188°, was incorrectly described by Rossing as the *O*-acetate (Abstr., 1885, 388); the *diacetate* has m. p. 164—165°; Rossing gives m. p. 158° (*loc. cit.*); the *O*-benzoate, $C_{20}H_{14}O_2N_2Br_2$, forms slender, yellow prisms, m. p. 211—212° (twelve hours); the *N*-benzoyl derivative forms slender, white prisms, m. p. 174°.

o-Nitrosalicylaldehydophenylhydrazone *O*-benzoate, light brown needles, m. p. 204—205° (eight hours); *N*-benzoyl derivative, yellow, felted needles, m. p. 199—200°. The *O*-benzoate of the corresponding *p*-nitro-compound forms light red needles, m. p. 230° (eight hours); *N*-benzoyl derivative, white needles, m. p. 260°. W. H. G.

Capacity for Transformation of Acyl Derivatives of the Phenylhydrazones of *o*-Hydroxyketones. KARL AUWERS [with H. DANNEHL] (*Annalen*, 1909, 365, 343—352. Compare preceding abstracts).—2-Hydroxy-5-methylacetophenonephenylhydrazone,

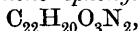


prepared from *o*-acetyl-*p*-cresol and phenylhydrazine, forms compact, glistening, pale yellow plates, m. p. 152·5°; the crystalline *O*-acetate, $C_{17}H_{18}O_2N_2$, has m. p. 99°, and is converted when boiled for eight hours with glacial acetic acid into the *N*-acetyl derivative, compact, straw-yellow prisms, m. p. 105°; the *O*-benzoate, $C_{22}H_{20}O_2N_2$, forms soft, yellow needles, m. p. 154°, and when boiled with glacial acetic acid for three to four hours, yields *o*-acetyl-*p*-cresol and acetylbenzoylphenylhydrazine, thus: $OBz \cdot C_6H_3Me \cdot CMe \cdot N \cdot NPh \longrightarrow$



2-Hydroxy-5-methylbenzophenonephenylhydrazone, $C_{20}H_{18}ON_2$, crystallises in pale yellow prisms, m. p. 135·5°; the crystalline *O*-acetate, $C_{22}H_{20}O_2N_2$, has m. p. 107—108°, and is not converted by boiling glacial acetic acid into the *N*-derivative. Attempts to prepare the latter directly were unsuccessful. The hydroxy-compound is converted by acetic anhydride and sodium acetate into what is probably a *diacetate*, m. p. 107—108°, which is hydrolysed by cold alcoholic alkali, yielding the *N*-acetyl derivative (?), m. p. 147—148°.

2-Hydroxy-5-methoxybenzophenonephenylhydrazone *O*-acetate,



forms compact, yellow prisms, m. p. 134°, and is not changed by hot glacial acetic acid; all attempts to prepare the *N*-derivative were fruitless. W. H. G.

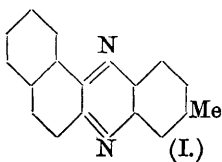
Reduction Products of β -Naphthaquinonehydrazones [2-Benzeneazo- α -naphthols]. EMILIO NOELTING, EUGÈNE GRANDMOUGIN, and H. FREIMANN (*Ber.*, 1909, 42, 1377—1386).—Noelting and Grandmougin (*Abstr.*, 1891, 1076) arrived at the conclusion that β -naphthaquinonehydrazones must be regarded as 2-azo-derivatives of α -naphthol, and that the ethers of these hydrazones are true oxygen ethers, since reduction by means of stannous chloride and hydrochloric acid yields, besides ethers of aminonaphthols, aniline, and not an alkylated aniline. These reductions are, however, more complicated than the above results indicate, the ethyl and methyl ethers and the acetyl derivative of 2-benzeneazo- α -naphthols always yielding a considerable proportion of a base, $C_{16}H_{14}N_2$, which is probably 2-amino-1-anilinonaphthalene; the latter may be formed from the 2-benzeneazo- α -naphthol derivative by a re-arrangement somewhat similar to the benzidine conversion with simultaneous displacement of the hydroxyl group. The product obtained by Harden (*Abstr.*, 1890, 630) by the action of phenylhydrazine on nitroso- β -naphthylamine, and described by him as 2-amino-1-anilinonaphthalene, probably has some other constitution. It is strange that this base is not obtained by reduction of 2-benzeneazo- α -naphthol itself. The reductions of the ethers and of the acetyl derivative give also other compounds, the constitutions of which have not been determined; thus, the acetyl derivative yields a crystalline base, m. p. 124—125°, in small quantity.

2-Amino-1-anilinonaphthalene (?), $NH_2 \cdot C_{10}H_6 \cdot NPh$, separates from benzene or alcohol in granular crystals, m. p. 170°, and with organic solvents gives solutions exhibiting faint blue fluorescence. Its *sulphate*, $2(C_{16}H_{14}N_2) \cdot H_2SO_4$, *chloride*, $C_{16}H_{14}N_2 \cdot HCl$, *acetyl* derivative, $C_{18}H_{16}ON_2$, m. p. 200°, and *benzoyl* derivative, m. p. 239°, were prepared. By the action of nitrous acid, the base is converted into an *azoimide*, $C_{16}H_{11}N_3$, which separates from light petroleum in large crystals, m. p. 77°. When distilled with lead oxide, 2-amino-1-anilinonaphthalene yields phenonaphthazine, m. p. 142°, also yielded by the isomeric 1-amino-2-anilinonaphthalene, whilst when boiled with benzil in acetic acid solution it yields the corresponding azonium base, m. p. 215°.

The methyl ether of 2-benzeneazo- α -naphthol has m. p. 102—103°: McPherson (*Abstr.*, 1900, i, 123) gave 95°. On reduction, this ether gives 2-amino-1-anilinonaphthalene, aniline, and 2-amino-1-methoxynaphthalene, $NH_2 \cdot C_{10}H_6 \cdot OMe$, which crystallises in readily volatile, shining leaflets, m. p. 48—49°, forms with organic solvents solutions showing blue fluorescence, and yields an *acetyl* derivative, $C_{13}H_{13}O_2N$, m. p. 132°.

The ethyl ether of 2-benzeneazo- α -naphthol, obtained by Meldola and Hanes (*Trans.*, 1894, 65, 834) as a viscid, red oil, forms crystals, m. p. 44°. On reduction, it yields 2-amino-1-anilinonaphthalene, aminonaphthol, aniline, and 2-amino-1-ethoxynaphthalene, $NH_2 \cdot C_{10}H_6 \cdot OEt$, which forms volatile, white leaflets, m. p. 48—49°, and yields an *acetyl* derivative, m. p. 147—148°.

The *acetyl* derivative of β -naphthaquinone-*p*-tolylhydrazone (2-*p*-tolueneazo- α -naphthol), m. p. 102°, gives, on reduction with stannous chloride



and hydrochloric acid, a base, m. p. 118°, which, when distilled with lead oxide, yields a new *tolunaphthazine* (formula I), m. p. 179°, showing the characteristic azine reactions. T. H. P.

Acylazoaryl Compounds and Behaviour of Certain Diazo-salts towards Ethers. GIACOMO PONZIO and G. CHARRIER (*Atti R. Accad. Sci. Torino*, 1909, **44**, 295—313).—The oxidation of the hydrazo-group in compounds such as α -benzoyl- β -phenylhydrazine, with formation of the corresponding azo-derivative, can be readily effected by passing nitrous anhydride into ether containing the hydrazo-compound in suspension, the liquid being kept cold and well shaken. The acylazoaryl compounds thus obtained are readily crystallisable, red or brown substances, which are reduced easily, and in the cold, by phenylhydrazine, giving the hydrazo-compounds from which they are prepared: $R \cdot CO \cdot N : NAr + NHPh \cdot NH_2 = R \cdot CO \cdot NH \cdot NHAr + C_6H_6 + N_2$.

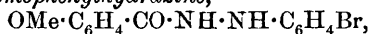
Benzoylazobenzene, $NBz : NPh$, which crystallises from alcohol in large, red prisms, m. p. 30° (decomp.), was obtained by Fischer (*Abstr.*, 1878, 302) as an impure liquid by oxidising α -benzoyl- β -phenylhydrazine in chloroform solution by means of mercuric oxide, and was named by him diazobenzene benzoate.

Anisoylazobenzene, $OMe \cdot C_6H_4 \cdot CO \cdot N_2Ph$, crystallises from alcohol in amethyst-red plates, m. p. 40°, and, in alcoholic solution, is reduced to α -anisoyl- β -phenylhydrazine by means of zinc dust and acetic acid.

p-Toluylazobenzene, $C_6H_4Me \cdot CO \cdot N_2Ph$, crystallises from alcohol in large, red prisms, m. p. 41°.

Anisoylazo-p-bromobenzene, $OMe \cdot C_6H_4 \cdot CO \cdot N_2 \cdot C_6H_4Br$, crystallises from alcohol in garnet-red, flattened needles, m. p. 72°.

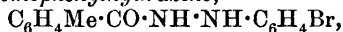
β -Anisoyl- α -p-bromophenylhydrazine,



obtained as hydrochloride by the interaction of *p*-bromophenylhydrazine (2 mols.) and anisoyl chloride (1 mol.) in ethereal solution, crystallises from alcohol in white laminae, m. p. 183° (decomp.).

p-Toluylazo-p-bromobenzene, $C_6H_4Me \cdot CO \cdot N_2 \cdot C_6H_4Br$, crystallises from alcohol in brown laminae, m. p. 98°.

β -p-Toluyal- α -p-bromophenylhydrazine,

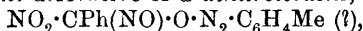


prepared from *p*-bromophenylhydrazine and *p*-toluyl chloride, crystallises from alcohol in shining, white needles, m. p. 202° (decomp.).

It has been found previously (*Abstr.*, 1908, i, 482) that the diazobenzene derivative of ω -dinitrotoluene, dissolved in moist ether, undergoes intramolecular rearrangement, yielding ω -benzeneazo- ω -dinitrotoluene, and (this vol., i, 338) that, under similar conditions, the *p*-bromodiazobenzene derivative of ω -dinitrotoluene is transformed into benzoylazo-*p*-bromobenzene. The authors now describe experiments made with a view to ascertain the influence exerted on this reaction by the nature of the diazo-derivative employed. It is found that, whilst the *o*-diazotoluene, *o*-chlorodiazobenzene, and *o*-bromodiazobenzene derivatives of ω -dinitrotoluene are transformed into the isomeric ω -*o*-tolueneazo-, ω -*o*-chlorobenzeneazo-, and ω -*o*-bromobenzeneazo-derivatives of ω -dinitrotoluene, the isomeric *p*-compounds are converted into the benzoylazo-derivatives of *p*-toluene, *p*-chloro-

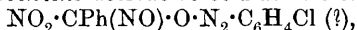
and *p*-bromo-benzene, losing two atoms of nitrogen and three of oxygen in the form of nitrous compounds (compare this vol., i, 338).

The *o*-diazotoluene derivative of ω -dinitrotoluene,



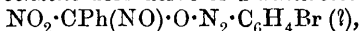
prepared from *o*-diazotoluene acetate and the potassium derivative of ω -dinitrotoluene, is obtained as a yellow powder, m. p. 58° (decomp.), dissolves in concentrated sulphuric acid, giving an emerald-green solution, and, when heated with alcohol, is partly oxidised to acet-aldehyde with evolution of nitrogen and partly transformed into ω -*o*-tolueneazo- ω -dinitrotoluene, $\text{CPh}(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Me}$, which is also formed in a moist ethereal solution of the preceding compound and separates in shining, red needles, m. p. 137° (decomp.).

The *o*-chlorodiazobenzene derivative of ω -dinitrotoluene,



is a yellow powder, m. p. 56° (decomp.), gives an emerald-green solution with concentrated sulphuric acid, and, when heated with alcohol, is partly oxidised with evolution of nitrogen and partly transformed into ω -*o*-chlorobenzeneazo- ω -dinitrotoluene, $\text{CPh}(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Cl}$, which is deposited in shining, orange-red laminae, m. p. 140° (decomp.).

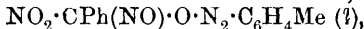
The *o*-bromodiazobenzene derivative of ω -dinitrotoluene,



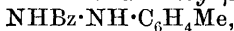
is a yellow powder m. p. 65° (decomp.).

ω -*o*-Bromobenzeneazo- ω -dinitrotoluene, $\text{CPh}(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Br}$, separates in orange-coloured laminae, m. p. 140° (decomp.).

The *p*-diazotoluene derivative of ω -dinitrotoluene,



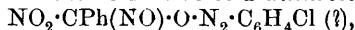
is a yellow powder, m. p. 74° (decomp.). When dissolved in moist ether, it is converted into *benzoylazo-p*-toluene, which could not be crystallised, and, on reduction with zinc and acetic acid in alcoholic solution, is converted into α -*benzoyl-p*-tolylhydrazine,



crystallising from benzene in shining, white laminae, m. p. 145 — 146° , and obtainable also by the interaction of *p*-tolylhydrazine (2 mols.) and benzoyl chloride (1 mol.) in ethereal solution.

ω -*p*-Tolueneazo- ω -dinitrotoluene, $\text{CPh}(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Me}$, prepared by heating the *p*-diazotoluene derivative of ω -dinitrotoluene with alcohol, crystallises from chloroform in orange-red laminae, m. p. 153 — 154° (decomp.).

The *p*-chlorodiazobenzene derivative of ω -dinitrotoluene,



is a yellow powder, m. p. 61° (decomp.), and, when dissolved in moist ether, is converted into *benzoylazo-p*-chlorobenzene, $\text{NBz} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Cl}$, which crystallises from light petroleum in orange-yellow laminae, m. p. 73° .

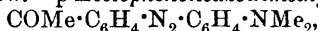
α -Benzoyl- β -*p*-chlorophenylhydrazine, $\text{NHBz} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl}$, prepared by reducing the preceding compound or by the interaction of *p*-chlorophenylhydrazine (2 mols.) and benzoyl chloride (1 mol.), crystallises from benzene in white laminae, m. p. 153° . When suspended in anhydrous ether and oxidised by means of nitrous anhydride, it is transformed into benzoylazo-*p*-chlorobenzene.

ω -*p*-Chlorobenzeneazo- ω -dinitrotoluene, $\text{CPh}(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Cl}$, crystal-

lises from chloroform in shining, orange-yellow needles, m. p. 161° (decomp.).
T. H. P.

Some Azo-dyes from *p*-Aminoacetophenone. HENRY A. TORREY and WARREN MACPHERSON (*J. Amer. Chem. Soc.*, 1909, 31, 579—583).—As very few azo-dyes derived from *p*-aminoacetophenone have hitherto been described, some of these compounds have now been prepared. The aminoazo-compounds obtained have been found to change from yellow to red on the addition of acids. Determinations of the sensitiveness of *p*-acetophenoneazo-diphenylamine, -dimethylaniline, and -diethylaniline, and the oxime of the last, by a method similar to that of Salm's (*Abstr.*, 1906, ii, 218) showed that the hydrogen ion concentration at which the change in colour occurs is about 5×10^{-5} in the case of *p*-acetophenoneazo-diethylaniline, whilst the other compounds are less sensitive, *p*-acetophenoneazodiphenylamine being the least so. In preparing *p*-acetophenoneazodiphenylamine, the diazotised solution was added to a solution of diphenylamine in a large quantity of glacial acetic acid. This method is recommended for the preparation of phenylaminoazobenzene and other azo-compounds of weak bases which are not readily soluble in dilute mineral acids.

p-Acetophenoneazoresorcinol, $\text{COMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{OH})_2$, m. p. $215-220^{\circ}$ (decomp.), crystallises in deep orange-red needles, and dissolves in dilute alkali hydroxide to form a deep red solution which dyes silk bright yellow. *p*-Acetophenoneazodimethylaniline,



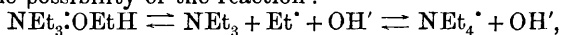
m. p. $203-204^{\circ}$, forms red crystals, and yields a purple hydrochloride; its oxime, m. p. $242-243^{\circ}$, forms orange-red crystals. *p*-Acetophenoneazodiethylaniline, $\text{COMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NEt}_2$, m. p. $162-163^{\circ}$, dissolves in dilute acids to form a crimson solution, which dyes silk deep orange-red; the oxime melts at $199-200^{\circ}$. *p*-Acetophenoneazodiphenylamine, $\text{COMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NHPh}$, m. p. $184-185^{\circ}$, crystallises in long, red prisms and gives a bright purple solution with acids, which dyes silk and wool a poor shade of orange-yellow. *p*-Acetophenoneazo- β -naphthol, m. p. $181-183^{\circ}$, forms small, red prisms, and is insoluble in aqueous alkali (compare Klingel, *Abstr.*, 1886, 61); its oxime was prepared.
E. G.

***p*-Nitrobenzenediazonium Chloride.** CARL G. SCHWALBE (*Ber.*, 1909, 42, 1425. Compare *Abstr.*, 1905, i, 952).—A criticism of the statements and conclusions of Bucherer and Wolff (this vol., i, 272) as to the stability and use of "nitrosoamine paste" for preparing a nitrous acid-free solution of *p*-nitrodiazobenzene.

J. V. E.

Constitution of Diazonium and Ammonium Salts. JOHN C. CAIN (*Ber.*, 1909, 42, 1208—1211. Compare this vol., i, 70).—Polemical. It is pointed out in reply to Hantzsch (this vol., i, 193) that: (1) benzenediazonium chloride and *p*-benzoquinone chloroimide are exceedingly similar in their properties; (2) diazo-salts and

quinones behave similarly towards bromine. It is possible that the diazo-perbromides are analogous in constitution to benzoquinone dibromide; (3) the reduction of azobenzene to hydrazobenzene is not accompanied by separation of the nitrogen atoms, and, therefore, a substance having the formula given by the author to benzenediazonium chloride need not necessarily yield a diamine when reduced. (4) The Blomstrand formulation does not account for the formation of a diazo-salt from *ar*-naphthylamine and the non-formation of a diazo-compound from *ac*-naphthylamine. The reason of this different behaviour, according to the author's theory, is due to the fact that only in the former case is the formation of a quinonoid system possible. (5) Although ethyl alcohol and triethylamine do not combine under ordinary conditions, this is no argument against the possibility of the reaction:



since ethyl alcohol, under ordinary conditions, does not exist in the dissociated state.

W. H. G.

Hydrolysis of Crystallised Albumin from the Hen's Egg.

THOMAS B. OSBORNE, D. BREESE JONES, and CHARLES S. LEAVENWORTH (*Amer. J. Physiol.*, 1909, 24, 252—262).—Estimations of the products of acid hydrolysis were made, the total yield accounting for 50% of the protein. Glucosamine was present to the extent of 1.23%. The other figures are not widely different from those given by Abderhalden and Pregl, but estimations of diamino-acids are given which were omitted in the work of these observers. The figures obtained by Hugounenq and Morel, who used baryta as the hydrolysing agent, are widely different in most cases from those recorded in the present paper.

W. D. H.

Partial Hydrolysis of Edestin. ZDENKO H. SKRAUP and A. WÖBER (*Monatsh.*, 1909, 30, 289—309).—Proteins, such as egg-albumin, casein, edestin, and serum globulin, dissolve in a mixture of equal volumes of fuming hydrochloric and acetic acids. When such solutions are diluted and nearly neutralised with ammonia, amorphous precipitates are obtained, which diminish in amount the more the action of the concentrated acids is prolonged.

One hundred parts of edestin yield thirteen parts of insoluble compound *A*, and twenty-seven parts of the soluble albumose peptone mixture *B*. These substances give different colour reactions from the original edestin. When edestin is converted into substance *A*, not only the proportion of glutamic acid, but also that of tyrosine, phenylalanine, leucine, alanine, glycine, and even arginine diminishes, whereas in the partial hydrolysis of albumin (compare Skraup and Hummelberger, this vol., i, 711) the reverse is the case. In substance *B* as compared with *A* the amount of histidine is distinctly, and that of arginine and glutamic acid largely, increased.

When treated with sodium hydroxide, edestin yields fractions differing in solubility, designated as protalbic and lysalbic acids and lysalbin-peptone. The former gives the same colour reactions as

substance *A*, the later two behave similarly to *B*. In the case of edestin apparently the carbohydrate group remains in the sparingly soluble fraction, whereas in albumin it is found in the most soluble fraction.

E. F. A.

Hydrolysis of Casein with Hydrochloric and with Sulphuric Acid. ZDENKO H. SKRAUP and W. TÜRK (*Monatsh.*, 1909, 30, 287—288).—Air-dry casein, hydrolysed either by boiling with fuming hydrochloric acid or with 33% sulphuric acid, yielded 22·3% and 20·3% of crude glutamic acid hydrochloride respectively. This is partly racemised; $[\alpha]_D + 21\cdot7^\circ$. Kutscher's statement that much less glutamic acid is obtained on hydrolysis with sulphuric acid is therefore to be corrected.

E. F. A.

Depression of Freezing Point Due to Caseinates in Solution. T. BRAILSFORD ROBERTSON and THEO. C. BARNETT (*J. Biol. Chem.*, 1909, 6, 105—114).—Neutral (to litmus) and basic (neutral to phenolphthalein) caseinates of potassium, lithium, ammonium, and calcium, when dissolved in water, depress the freezing point to a definite measurable degree. The results indicate that casein behaves towards bases as a monobasic acid, possessing, when combined with bases in solutions neutral to phenolphthalein, a molecular weight of about 1400, and when combined with bases in solutions neutral to litmus, a molecular weight of about 2000.

W. D. H.

Nucleo-protein from the Gastric Mucosa. ARCHIBALD E. OLPP (*Proc. Amer. Soc. Biol. Chem.*, 1908, 1; *J. Biol. Chem.*, 6).—Dilute alkali extracts from the mucous membrane of the stomach a nucleo-protein which is precipitable by acids. The product obtained is free from mucin. A relationship between it and pepsinogen is suggested.

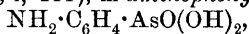
W. D. H.

Nucleic Acids. W. A. JACOBS and PHÆBUS A. LEVENE (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxxvi—xxxvii; *J. Biol. Chem.*, 6).—On acid hydrolysis of inosic acid, the lævorotatory solution became dextro-rotatory, and from this a reducing crystalline barium salt of a pentose-phosphoric acid was isolated. On alkaline hydrolysis, phosphoric acid was split off without the appearance of free hypoxanthine or sugar in the solution; from this solution a silver compound of a pentose-hypoxanthine complex was obtained; this is not reducing. It is thus proved that the phosphoric acid is bound to one of the hydroxyls of the pentose, and hypoxanthine is linked to the aldehyde group in a glucoside arrangement.

It is considered probable that nucleic acids are built up of "nucleotides," groups similar in composition to that of inosic acid, which are joined together as the phosphoric acid radicles in polyphosphoric acids. From yeast-nucleic acid a substance was isolated as a tetranucleotide, in which the sugar is pentose, and the bases adenine, guanine, uracil, and cytosine.

W. D. H.

Preparation of *m*-Aminophenylarsinic Acid (*m*-Arsanilic Acid). FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 206344).—From the nitrophenylarsinic acid formerly obtained by Michaelis (Abstr., 1902, i, 411), *m*-aminophenylarsinic acid,



colourless prisms, m. p. $212-214^\circ$, is obtained by reduction, either with sodium amalgam or ammonium sulphide. In the former case the reduction is effected in methyl-alcoholic solution, and the product precipitated as its zinc salt. In the latter, the aqueous solution of ammonium sulphide is evaporated to dryness, the residue extracted with dilute hydrochloric acid to remove the intermediate products, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsS}_2$ and $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsS}$, which, after desulphurisation with copper sulphate in alkaline solution, yields an alkali salt of *m*-aminophenylarsinic acid.

F. M. G. M.

Preparation of an α -Naphtholarsinic Acid [4-Hydroxynaphthalenearsinic Acid]. WILHELM ADLER (D.R.-P. 205775).—4-Aminonaphthalenearsinic acid (prisms, m. p. $173-175^\circ$) is prepared by heating α -naphthylamine (4 parts) and arsenic acid (3 parts) at 190° until quantitative tests show that the condensation has reached its maximum. The product is extracted with cold aqueous alkali hydroxide and reprecipitated with mineral acids, diazotised in cold 15% hydrochloric acid, and the solution heated to boiling.

The sodium salt of 4-hydroxynaphthalenearsinic acid, colourless needles or leaflets, is precipitated by means of alcohol. The free acid, which is sparingly soluble in water and dissolves readily in alcohol, has an intense action on the skin, and may accordingly be employed in dermatology.

F. M. G. M.

Formation of Peroxides in the Oxidation of Organo-magnesium Compounds. HENRI WUYTS (*Compt. rend.*, 1909, 148, 930—931).—The action of oxygen on an ethereal solution of magnesium phenyl bromide leads, not only to the formation of phenol (Bodroux, Abstr., 1903, i, 249), but also to the formation of other phenolic compounds with diphenyl, *p*-diphenylbenzene, phenylethylcarbinol, and ethyl alcohol. The formation of alcohols is explained by the equation: $\text{PhMgBr} + \text{OEt}_2 + \text{O} = \text{CHMePh} \cdot \text{OH} + \text{OEt} \cdot \text{MgBr}$.

Probably, however, a peroxide is first formed, since it has been found that a toluene solution of magnesium phenyl bromide, which has been exposed to the action of dry oxygen at a low temperature, is capable of liberating iodine from potassium iodide solutions. Further experiments are described which confirm this supposition.

W. O. W.

Organic Chemistry.

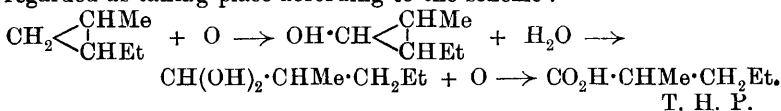
Catalytic Reactions at High Temperatures and Pressures.
XVII. Reduction of Fatty Compounds with an Ethylene Linking in Presence of Cupric Oxide. WLADIMIR IPATIEFF (*Ber.*, 1909, 42, 2089—2092. Compare Sabatier and Senderens, *Abstr.*, 1905, i, 333).—Ethylene is reduced to ethane by hydrogen at 180° under 60 atmospheres' pressure, cupric oxide being used as the catalyst. With nickel oxide, a part of the ethane is always broken down to methane.

β -Methyl- Δ^2 -butylene, $\text{CMe}_2\text{:CHMe}$, is reduced at 300° under 100 atmospheres to isopentane, a little *tert.*-amyl alcohol being also formed. The reduction at the ordinary pressure in presence of nickel does not take place in such cases, it being necessary that the double linking should be attached to a methylene group.

Under similar conditions, oleic acid yields stearic acid. *cyclo*-Hexene remains unaltered. C. H. D.

Researches in the Hexene and Heptene Series. E. S. PRSCHEVALSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 464—469).—According to Welt (*Abstr.*, 1897, i, 452), *n*-heptylene may be obtained by Kraft's method, namely, by heating corresponding esters of high molecular weight. The author finds, however, that by heating heptyl palmitate, the hydrocarbon obtained is not a definite individual, since on oxidation it yields an acid, the silver salt of which contains more silver than corresponds with silver hexoate. The removal of hydrogen iodide from α -iodo- β -methyl-*n*-pentane results in the formation of a closed-ring compound (compare Zelinsky and Prschevalsky, *Abstr.*, 1908, i, 845).

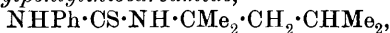
Reduction of methyl *n*-propyl ketone and treatment of the alcohol thus obtained with hydrochloric acid in a sealed tube at 110—120° yields the chloride, $\text{CHMePr}^\alpha\text{Cl}$, b. p. 96—97°/746 mm., D_4^{15} 0.8753, D_4^{20} 0.8704, $n_D^{19.5}$ 1.4062; for this compound, Wagner and Saytzeff (*Abstr.*, 1876, i, 547) gave the constants: b. p. 103—105°, D_4^0 0.912, D_4^{21} 0.891. Treatment of this chloride with magnesium and then with trioxymethylene gives β -methyl-*n*-pentyl alcohol, which, by means of iodine and phosphorus, is converted into α -iodo- β -methyl-*n*-pentane, $\text{CHMePr}^\alpha\text{CH}_2\text{I}$, b. p. 72—73°/32 mm., D_4^{15} 1.4496, D_4^{20} 1.4430, n_D^{19} 1.4938. The action of alcoholic potassium hydroxide on this iodide yields 1-methyl-2-ethylcyclopropane, $\text{CH}_2\text{<}\begin{smallmatrix} \text{CHMe} \\ \text{CHEt} \end{smallmatrix}$, b. p. 61.5—62.5°/736 mm., D_4^{15} 0.6867, D_4^{20} 0.6820, n_D^{20} 1.3928. Oxidation of this hydrocarbon by permanganate yields formic, acetic, propionic, butyric, and isohexic acids. The formation of the last-named acid is regarded as taking place according to the scheme:



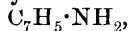
$\beta\delta$ -Dimethylpentane and its Occurrence in Caucasian Naphtha. G. W. CHONIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 327—344).—Part of this paper has been already published (Abstr., 1905, i, 729; *J. Russ. Phys. Chem. Soc.*, 1908, 40, 731; compare also Konowaloff, Abstr., 1906, i, 129).

Nitration of $\beta\delta$ -dimethylpentane yields mainly the tertiary nitro-derivative, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NO}_2$, which on reduction gives the corresponding amine, $\text{C}_7\text{H}_{15}\cdot\text{NH}_2$, b. p. 121—122.2°/753 mm. (compare Konowaloff, Abstr., 1908, i, 241); the *hydrochloride* of the latter, $\text{C}_7\text{H}_{15}\cdot\text{NH}_2\cdot\text{HCl}$, m. p. 208—209° (decomp.), and the *platinichloride*, $(\text{C}_7\text{H}_{15}\cdot\text{NH}_2)_2\cdot\text{H}_2\text{PtCl}_6$, decomposing at 183°, were prepared.

Phenyl- $\beta\delta$ -diethylpentylthiocarbamide,



prepared by the action of phenylthiocarbimide on the amine,



crystallises from methyl alcohol in colourless, rhombic plates, m. p. 111—112°.

The occurrence of $\beta\delta$ -dimethylpentane in Caucasian naphtha is demonstrated by the preparation from the latter of the above tertiary nitro-derivative, the corresponding amine, and phenyl- $\beta\delta$ -dimethyl-pentylthiocarbamide.

T. H. P.

Dipropargyl, its Magnesium Derivative, and $\Delta^{\beta\epsilon}$ -Hexadiene- $\alpha\zeta$ -dicarboxylic Acid. ROBERT LESPIEAU and VAVON (*Compt. rend.*, 1909, 148, 1331—1333).—When treated with iodine, the copper derivative of dipropargyl yields *aa $\beta\epsilon\zeta\zeta$ -hexa-iodo- $\Delta^{\beta\epsilon}$ -hexadiene*, $\text{Cl}_2\cdot\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Cl}\cdot\text{Cl}_2$, m. p. 155—156°. When the *magnesium* derivative of this substance is treated with carbon dioxide it forms *$\Delta^{\beta\epsilon}$ -hexadi-ene- $\alpha\zeta$ -dicarboxylic acid*, $\text{CO}_2\text{H}\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CO}_2\text{H}$, m. p. 190° (decomp.). This acid undergoes reduction to suberic acid when treated in alcoholic solution with hydrogen in the presence of platinum-black.

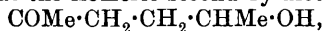
W. O. W.

The Action of Alcohol, its Impurities, and its Denaturing Agents on the Ordinary Metals. RENÉ P. DUCHEMIN (*Bull. Assoc. Chim. suc. dist.*, 1909, 26, 1076—1078).—The metals iron, tin, zinc, copper, and brass were exposed for three months at 18° to the action of pure ethyl and methyl alcohols (95°), and to mixtures of these with 50% of water, with 10% of acetaldehyde, 10% of ethyl acetate, and 10% of amyl acetate respectively in the case of ethyl alcohol, and with 10% of acetone and 10% of methyl acetate in the case of methyl alcohol. The liquids were evaporated, and a table of the weights of the solid remaining is given. Examination of this table shows that addition of acetaldehyde, amyl acetate, and water augments the attack on all the metals, particularly iron and zinc in the latter case, whilst the presence of ethyl acetate increases the action on iron, tin, and zinc, but not on copper or brass. Addition of water to methyl alcohol accelerates the attack on iron, tin, and zinc, of acetone that on tin and copper, and of methyl acetate that on tin and zinc. These results are in accordance with Lindet's work (*ibid.*, 1904—1905, 370).

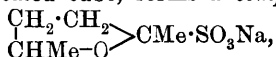
The conclusions are drawn that ethyl and methyl alcohols have a comparable action on metals, and that it is the presence of impurities which causes serious disadvantages in the use of denatured alcohol.

E. H.

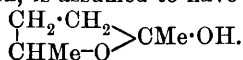
Hexan-6-one-β-ol. ANDREAS LIPP and E. SCHELLER (*Ber.*, 1909, 42, 1960—1967).—The interaction of propylene bromide and ethyl sodioacetoacetate (Perkin and Stenhouse, *Trans.*, 1892, 61, 67) has been re-examined. A brominated intermediate compound, analogous to that formed in the case of trimethylene bromide (*Abstr.*, 1886, 218), cannot be detected, and the ethyl 2-acetyl-1-methylcyclopropane-2-carboxylate and ethyl dimethyldehydropentanecarboxylate, which are formed in approximately equal quantities, yield by heating with dilute hydrochloric acid, not acetoisobutyl alcohol as Perkin and Stenhouse assume, but the isomeric secondary alcohol,



the constitution of which is proved by its oxidation to acetylacetone by sodium dichromate and sulphuric acid. The alcohol has b. p. 201—205°/270 mm., reduces warm ammoniacal silver nitrate and Fehling's solutions, yields an *anhydride*, b. p. 70°, when heated at 230° in a sealed tube, forms a *compound*,



with sodium hydrogen sulphite, an oily *oxime*, a *semicarbazone*, m. p. 149—150°, and *esters* of benzoic and acetic acids. Since the esters do not react with hydroxylamine or sodium hydrogen sulphite, the ketol, in alkaline solution, is assumed to have the constitution:



C. S.

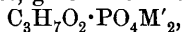
Oxidation of Polyhydric Alcohols by a Peroxydase System. E. DE STOECKLIN and E. VULQUIN (*Compt. rend.*, 1909, 148, 1404—1406. Compare this vol., i, 196, 198).—It has been shown previously that polyhydric alcohols are not attacked in presence of the system hydrogen peroxide—tannin—iron; when quinol, however, is substituted for tannin, somewhat profound oxidation takes place. The action of this peroxydase system has been studied in connexion with the following alcohols, and in each case the product shows the presence of a ketone or aldehyde. Ethylene glycol is converted into glycollaldehyde. Glycerol forms glyceraldehyde and dihydroxyacetone. Mannitol forms mannose together with a ketone, of which the *osazone* has m. p. 188°. The products of oxidation of dulcitol contain an aldehydic sugar and yield dulcitosazone. In the case of sorbitol, sorbosazone has been isolated from the product together with an unknown osazone crystallising in lamellæ.

W. O. W.

Preparation of Glycerylphosphates, Particularly Crystallisable Sodium Glycerylphosphates. LES ÉTABLISSEMENTS POULENC FRÈRES (D.R.-P. 208700).—On heating glycerol in a vacuum with

k k 2

the metallic or ammonium phosphates of the general formula $M'H_2PO_4$, the diglyceryl ester, $(C_3H_7O_2)_2PO_4M'$, is produced, and this, on treatment with alkali hydroxides, gives rise to the glyceryl ester,



of which the sodium salt is crystallisable.

F. M. G. M.

Preparation of Sulphonic Acids of the Aliphatic Series.

ALEXANDER E. ARBUSOFF and P. S. PISHTSCHIMUKI (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 451—454).—The authors find that for the preparation of Strecker's compounds, from which the corresponding sulphonic acids may be readily obtained, it is unnecessary to heat the mixture of alkyl halide and potassium or sodium sulphite in sealed tubes at 140° , as the reaction takes place at the ordinary temperature. It is found, too, that hydrolysis of ethyl sulphite and its homologues by alkali hydroxides yields the alkali sulphites.

The following Strecker's salts were prepared: (1) $4Et \cdot SO_3K, KI$, by hydrolysing ethyl sulphite by means of potassium hydroxide in presence of ethyl iodide; (2) $4Me \cdot SO_3K, KI$, from ethyl sulphite, potassium hydroxide, and methyl iodide; and (3) $4C_3H_5 \cdot SO_3K, KI$, from ethyl sulphite, potassium hydroxide, and allyl iodide. In all these cases, after removal of the sulphonate from the solution, the latter contained no sulphite, so that the reaction between the alkyl iodide and the sulphite is complete.

T. H. P.

Constitution of Certain Mercuric Compounds with Complex Cations. III. VINCENZO BORELLI (*Gazzetta*, 1909, 39, i, 455—477. Compare Abstr., 1908, ii, 1039).—In this paper the author discusses previous work on complex salts formed by mercuric sulphide, and describes *sulphidomercury acetate*, $Hg_2S(OAc)_2$, and *sulphidomercury basic acetate*, $(Hg_2S \cdot Hg_2O)(OAc)_4$.

Dissolution of mercuric sulphide in mercuric acetate solution causes depressions of the freezing point in amount more than double the theoretical elevations, so that considerable diminution in the concentration of the molecular complexes occurs. Conductivity measurements of these solutions indicate an increase of the specific conductivity, and hence an increase in the number of ions. An explanation is given of these two apparently contradictory observations. Electrolysis of the solutions shows that the mercuric sulphide exists in the form of complex ions, which move towards the cathode under the influence of the current.

General conclusions are drawn from these results and those given in the two preceding papers (Abstr., 1908, i, 515; 1908, ii, 1039).

T. H. P.

Action of Finely Divided Metals on Aliphatic Acids.

ALPHONSE MAILHE (*Bull. Soc. chim.*, 1909, [iv], 5, 616—623).—Zinc dust decomposes acetic acid, producing hydrogen, carbon dioxide, acetone, and some acetaldehyde. This type of action also takes place with finely divided cadmium, iron, aluminium, lead, and copper, but the temperature at which the reaction commences varies with each metal, as does also the vigour of the action and the relative extent to

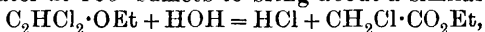
which the various products are formed. With nickel, the chief product of the action is the corresponding lower saturated hydrocarbon, no ketone being produced. When acetic acid vapour is passed over heated zinc dust, it begins to be decomposed at 250° , yielding hydrogen and zinc acetate, and if the action is continued at $250-280^{\circ}$, hydrogen is replaced by carbon dioxide, and acetone accompanied by some acetaldehyde distils over. After a time all action ceases, and the acid is no longer decomposed. If the temperature is now raised to 420° , the zinc oxide remaining in the tube begins to form acetone and carbon dioxide from the acetic acid vapour catalytically (compare Senderens, Abstr., 1908, i, 494). Under the same conditions and at a temperature of $280-290^{\circ}$, propionic, butyric, isobutyric, isovaleric, hexoic, octoic, and nonoic acids are decomposed by zinc dust, yielding, like acetic acid, the corresponding aldehyde and symmetrical ketone. Finely divided cadmium reacts with acetic acid vapour in much the same way as zinc dust. At 315° the gas evolved is about 92% carbon dioxide and 8% hydrogen, and the ratio of acetaldehyde to acetone in the distillate is 1:7. The residue in the tube at the end of the experiments consists mainly of unchanged metal with a little cadmium oxide. The higher homologues of acetic acid already mentioned are also decomposed by finely divided cadmium, the symmetrical ketone in each case being the chief product of the reaction.

With finely divided nickel at 230° , propionic acid yields a little acetaldehyde, but ethane and carbon dioxide are the chief products, and, similarly, butyric and isobutyric acids yield each a little of the corresponding aldehyde, but the chief product in each case is propane.

With finely divided copper, reaction sets in at $380-400^{\circ}$, and a little of the symmetrical ketone, corresponding with the acid, is formed, accompanied by saturated hydrocarbons. With iron the action commences at 240° , and the sole products are the corresponding ketone and carbon dioxide. With aluminium, action takes place normally at 380° , a little aldehyde being formed in addition to the ketone, and with lead, action begins at 300° , becomes rapid at 350° , and is quite normal.

T. A. H.

Production of Alkyl Chloroacetates from Dihalogenated Vinyl Ethers. GEORGES IMBERT UND CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 209268).—Dihalogenated vinyl ethers and alcohol interact, forming ethyl chloride and alkyl monohalogenated acetate, $C_2HCl_2 \cdot OEt + EtOH = EtCl + CH_2Cl \cdot CO_2Et$. It has now been found that water at 100° suffices to bring about a similar change:



and in this way ethyl chloroacetate is produced from ethyl dichlorovinyl ether.

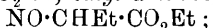
F. M. G. M.

True Nitroso-derivatives of the Esters of Aliphatic Carboxylic Acids. JULIUS SCHMIDT and KARL TH. WIDMANN (*Ber.*, 1909, 42, 1886—1902. Compare this vol., i, 134).—By the action of the nitrous gases from arsenious oxide and nitric acid, it has been found possible to replace an acetyl by a nitroso-group in the following compounds provided a solvent is not used: Ethyl diacetylsuccinate, and the

ethyl esters of methyl-, ethyl-, and butyl-acetoacetic acids. The compounds thus formed are the esters of nitroso-derivatives of aliphatic acids, e.g., $\text{Ac}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et} \rightarrow \text{O}\cdot\text{N}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$.

The compounds obtained are blue or bluish-green liquids with a penetrating odour. The depth of colour and also the stability of the compound increases with the complexity of the alkyl group present. When kept for some time at the ordinary temperature, or more quickly when shaken with water or alkalis, the blue colour disappears. This is partly due to conversion into the corresponding colourless oximino-derivatives and partly to polymerisation. They all give the Liebermann nitroso-reaction, and decompose when distilled under reduced pressure. When reduced, they yield esters of amino-acids, and when oxidised, esters of nitro-aliphatic acids. The latter are pale yellow oils which cannot be distilled under reduced pressure; when strongly heated they explode.

The following compounds have been prepared: *ethyl α -nitroso-propionate*, $\text{NO}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$; *ethyl α -nitroso-n-butyrate*,



ethyl α -nitrosohexoate, $\text{NO}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}_2\text{Et}$, D_{41}^{18} 1.24, n_D^{18} 1.6251; the corresponding nitro- and amino-derivatives; *ethyl α -nitroso- β -acetylsuccinate*, $\text{CO}_2\text{Et}\cdot\text{CH}(\text{NO})\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$. J. J. S.

Petroselic Acid. A New Acid of the Oleic Acid Series. EDUARD VONGERICHTEN and A. KÖHLER (*Ber.*, 1909, 42, 1638—1639).—The *fat*, $\text{C}_3\text{H}_5(\text{C}_{18}\text{H}_{33}\text{O}_2)_3$, isolated from oil of parsley seeds has m. p. 32° , solidifies at 16.5° , has n_D^{40} 1.4619, saponification number 191.2, iodine number 84.3, and is hydrolysed by alcoholic potassium hydroxide, yielding *petroselic acid*, $\text{C}_{18}\text{H}_{34}\text{O}_2$, m. p. $33-34^\circ$, solidifying at 27° , D^{40} 0.8681, n_D^{40} 1.4533, of which the *amide*, $\text{C}_{17}\text{H}_{33}\cdot\text{CO}\cdot\text{NH}_2$, has m. p. 76° , and the *lead*, *barium*, *zinc*, *magnesium*, and *silver* salts are mentioned. The new acid has iodine number 89.9, Köttstorfer's index 198.6, acetyl number 0, yields with a trace of nitrous acid an *acid*, $\text{C}_{18}\text{H}_{34}\text{O}_2$, m. p. 54° , analogous to elaidic acid, and combines with bromine to form a *dibromide*, which, with methyl-alcoholic potassium hydroxide under pressure, yields an *analogue* of stearolic acid, $\text{C}_{18}\text{H}_{32}\text{O}_2$, m. p. 54° , which is converted by Baruch's method into a *ketonic acid*, $\text{C}_{18}\text{H}_{34}\text{O}_3$, m. p. 80° , the oxime of which by fission, after undergoing the Beckmann transformation, yields lauric and pimelic acids and undecylamine. Petroselic acid is oxidised by alkaline potassium permanganate to a *dihydroxystearic acid*, m. p. 122° , and forms an ozonide which yields lauric acid by decomposition. The results indicate that petroselic acid has the constitution $\text{CH}_3\cdot[\text{CH}_2]_{10}\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$. C. S.

Crotonic Anhydride. ANDREAS LUNIAK (*Ber.*, 1909, 42, 1854).—The crotonic anhydride described by the author as new (this vol., i, 284) has been previously prepared by Clover and Richmond (*Abstr.*, 1903, i, 397). C. H. D.

Gluconic Acid from an Efflorescence on the Walls of a Sugar Magazine. VLADIMIR STANÉK (*Zeitsch. Zuckerind. Böhm.*, 1909, 33, 547—551).—The efflorescence which had formed during

several years was a brown substance, in some places mixed with moulds. It contained: water, 13.60; insoluble organic matter, 5.15; sand, 3.25; Fe_2O_3 and Al_2O_3 , 0.25; CaO , 8.35; MgO , 0.22; alkalis, 2.50, and soluble organic matter, 66.68%. One kilo. of the substance when extracted with water yielded 450 grams of basic calcium gluconate, from which the lactone (m. p. 132°) was obtained and analysed. The substance was further identified by means of the zinc salt and the phenylhydrazide.

The production of gluconic acid is attributed to the action of micro-organisms, *Micrococcus oblongus* (Boutroux, *Compt. rend.*, 1880, 91, 236) or *Bacterium xylinum* (Beyerinck, *ibid.*, 1884, 98, 995), on glucose.
N. H. J. M.

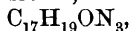
Preparation of Ketonesulphoxylates. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 207846).—*Sodium acetone-sulphoxylate*, $\text{C}_3\text{H}_6\text{O}\cdot\text{NaHSO}_2\cdot\text{H}_2\text{O}$, colourless needles, easily soluble in water and also in alcohol, is obtained by adding zinc dust to an aqueous solution of acetone and sodium hydrogen sulphite. The reduction may also be effected by powdered iron and acetic acid.

Sodium methyl-ethyl-ketone-sulphoxylate is similarly prepared from methyl ethyl ketone, the yield being 80–90%. These ketone-sulphoxylates are less stable than the formaldehydesulphoxylates, and reduce indigotin and naphthylamine Bordeaux even in the cold.

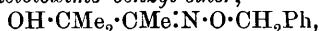
F. M. G. M.

Action of Alkali Dichromates on Agaricic Acid. J. D. RIEDEL (*Chem. Zentr.*, 1909, i, 1403; from *Gesch. Ber.*, 1909, 9–10).—Methyl heptadecyl ketone, $\text{C}_{17}\text{H}_{35}\cdot\text{CO}\cdot\text{CH}_3$ (Abstr., 1908, i, 4), has been prepared in a high state of purity and in good yield (60–70%) from agaricic acid by dissolving it in glacial acetic acid and warming with an alkali dichromate. Thus prepared, it forms colourless crystals, m. p. 55.5° , and gives an oxime, m. p. 76.5 – 77.5° .
J. V. E.

Ethers of Oximinoketones. OTTO DIELS and FRITZ TER MEER (*Ber.*, 1909, 42, 1940–1945).—The behaviour of oximinoketones and their ethers towards Grignard reagents recalls that towards aldehydes and ketones (Abstr., 1905, i, 509; 1907, i, 466); the ethers alone react. The interaction of magnesium methyl iodide and diacetylmonoxime methyl ether in cold ethereal solution leads to the formation of *trimethylketoloxime methyl ether*, $\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}\cdot\text{NOMe}$, b. p. 153 – 154° (decomp.) or 50 – $52.5^\circ/15$ mm., D^{20}_D 0.9646, a colourless, mobile liquid with a characteristic odour, which reacts with phenylcarbimide to form the *phenylurethane*, $\text{NHPh}\cdot\text{CO}\cdot\text{O}\cdot\text{CMe}_2\cdot\text{CMe}\cdot\text{NOMe}$, m. p. 138° . *Diacetylmonoxime benzyl ether*, $\text{COMe}\cdot\text{CMe}\cdot\text{N}\cdot\text{O}\cdot\text{CH}_2\text{Ph}$, b. p. $130^\circ/12$ mm., D^{20}_D 1.0564, prepared from sodium ethoxide, benzyl chloride, and diacetylmonoxime in boiling alcohol, forms a *phenylhydrazone*,



m. p. 73° , and reacts with ethereal magnesium methyl iodide to yield ultimately *trimethylketoloxime benzyl ether*,



b. p. $143^\circ/12$ mm. (decomp.), D^{20}_D 1.0365, which does not react with

phenylcarbimide. Attempts to hydrolyse the ether by nitrous acid result in complete decomposition, benzaldehyde, benzoic acid, nitric oxide, benzyl nitrate, and benzyl nitrite being produced. C. S.

Condensation of Formaldehyde. OSCAR LOEW (*Pflüger's Archiv*, 1909, 128, 282).—A question of priority arising out of Grube's statement (this vol., ii, 328) that H. and A. Euler were the first to obtain sugar by the condensation of formaldehyde in a practically neutral solution. The author had performed similar experiments twenty years earlier. W. D. H.

Birotation of Dextrose. II. YUKICHI OSAKA (*Mem. Coll. Sci. Eng. Kyōto*, 1908, 1, 304—319. Compare Abstr., 1900, i, 127).—The author has studied the influence of temperature, the influence of sodium chloride, both alone and in the presence of hydrochloric acid, and the action of a weak acid on the mutarotation of dextrose. From experiments carried out at 15°, 20°, and 25°, the ratio of the velocities at 25° and 15° is found to be 2·7:1, whilst the velocity constant calculated by Arrhenius' formula for 20° from the constants for 15° and 25° agrees with the observed value (compare Levy, Abstr., 1895, i, 586). In confirmation of the observations of Levy (*loc. cit.*) and Trey (Abstr., 1897, ii, 299), the author finds that the velocity of the mutarotation is diminished by sodium chloride when present to the extent of one-tenth gram-molecule per litre or in greater concentrations. It is found that sodium chloride has no effect on the mutarotation by *N*/15 hydrochloric acid when present to the extent of one-tenth gram-molecule per litre, but that at greater concentrations the catalytic action of the acid is increased (compare Trey).

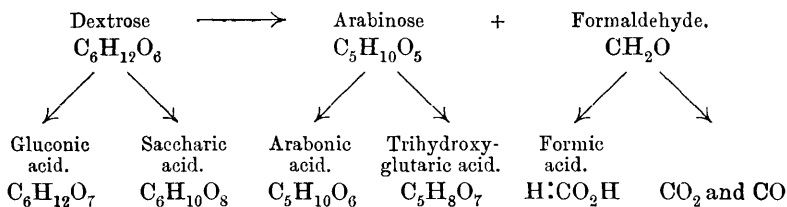
It seemed probable that the catalytic action of an acid being mainly due to hydrogen ions, its presence having diminished the concentration of the hydroxyl ions, a gradual diminution in the concentration of the acid would produce a state in which the action of the hydrogen ions was no longer significant, whilst the concentration of the hydroxyl ions was still far less than in aqueous solution. In such a state the acid would retard the velocity of the mutarotation, whilst further dilution by increasing the concentration of the hydroxyl ions would increase the velocity. A minimum velocity of this nature is actually observed with acetic acid, in *N*/150 solution, and with succinic acid, in *N*/300 solution. E. H.

The Scission of Sugars. III. Electrolysis of Dextrose. WALTHER LÖB (*Biochem. Zeitsch.*, 1909, 17, 132—144. Compare Abstr., 1908, i, 715, 764).—The question under investigation was whether synthesis and decomposition of sugar are chemically as well as biologically reversible processes. The electrolysis of dextrose was carried out in dilute sulphuric acid solution in the cold, precautions being adopted to prevent a rise of temperature during electrolysis. Lead electrodes were used, and in presence of an excess of dextrose it was possible to regulate the current so as to have very little gas production at the anode.

After electrolysis, in addition to unaltered dextrose, the solutions contained formaldehyde, formic acid, *d*-arabinose, *d*-arabonic acid,

trihydroxyglutaric acid, gluconic and saccharic acids. Products such as glyceraldehyde, dihydroxyacetone, and lactic acid could not be identified.

The following is considered the most probable scheme to explain the formation of these products :



here the primary process is the decomposition of the dextrose and the secondary process the oxidation to the acids.

E. F. A.

Crystallised *l*-Ribose. WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 373—375. Compare Abstr., 1908, i, 9).—Crystallised *l*-ribose has been isolated by converting the ribose syrup obtained by reduction of *l*-ribonolactone into its *p*-bromophenylhydrazone (m. p. 165°), and treatment of this substance with benzaldehyde to liberate *l*-ribose. After the lapse of two months, the syrup thus obtained crystallised. It has m. p. 87°, and $[\alpha]_D$ in 1.5% aqueous solution = +18.8°. Mutarotation is not exhibited by solutions of this concentration.

A. J. W.

The Action of Sulphuric and Nitric Acids in the Nitration of Cellulose. C. NAPIER HAKE and MARCUS BELL (*J. Soc. Chem. Ind.*, 1909, 28, 457—464. Compare Hake and Lewis, Abstr., 1905, i, 512).—The action of mixtures of concentrated sulphuric and nitric acids on cellulose (filter paper) at 10—20° has been studied. In each case a large excess of the acid mixture was used, the ratio of acid mixture to cellulose being usually 50:1 by weight, and after nitration the products were immersed in a large excess of cold water and washed in cold running water until neutral.

Variations of temperature within the limits 0° and 25° and variations in the excess of acid mixture to cellulose (within limits 20—200 of acid to 1 of cellulose) have little or no influence on the formation of sulphuric esters. Similarly, variations in the amount of water show that, within the limits 4—8%, the water contents of the acid have practically no effect. With mixtures of the two acids, a certain amount of sulphuric acid is always found combined in the final product, and the amount increases as the ratio of sulphuric/nitric acid is increased, for example, when the ratio is 1/3 the % combined sulphuric acid in the product is 0.37, and this increases gradually to 6.5 as the ratio is raised to 10/1.

The formation of mixed esters is due to delayed nitration. The cellulose is first partly dissolved or gelatinised by the sulphuric acid and subsequently nitrated.

The nature of the products formed varies with the density of the cellulose; with thick papers, the ratio N/SO₄ in the product is con-

siderably less than when Swedish filter paper is used, and the ratio in this is less than that in the product from cotton wool. J. J. S.

Morphotrophy of Some Synthetic Compounds. V. ROSICKÝ (*Zeitsch. Kryst. Min.*, 1909, 46, 357—376).—The ethylenediammonium double salts of iron, manganese, and cadmium described by Grossmann and Schück (Abstr., 1906, i, 630) have been examined goniometrically. The crystals are all triclinic pinakoidal. $(\text{Fe}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [$a : b : c = 0.54737 : 1 : 0.42196$; $\alpha = 91^\circ 15\frac{1}{2}'$, $\beta = 94^\circ 18\frac{1}{3}'$, $\gamma = 93^\circ 22'$]. $(\text{Mn}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [$a : b : c = 0.54646 : 1 : 0.42512$; $\alpha = 91^\circ 28\frac{1}{6}'$, $\beta = 94^\circ 53\frac{1}{2}'$, $\gamma = 93^\circ 19\frac{1}{2}'$]. $(\text{Cd}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [$a : b : c = 0.54594 : 1 : 0.43076$; $\alpha = 91^\circ 30\frac{2}{3}'$, $\beta = 94^\circ 31\frac{1}{2}'$, $\gamma = 93^\circ 32\frac{5}{8}'$].

Since ethylenediammonium manganosulphate, in the magnitude of its molecular volume and topic axes, comes between the iron and the cadmium salts, the three salts afford an instance in which the crystallographic properties are not periodic functions of the atomic weights of the mutually substituting metals (compare Tutton, Abstr., 1907, ii, 688).

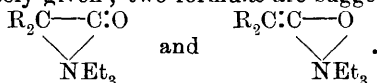
Ethylenediammonium cuprisulphate, $(\text{Cu}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, D 2.128, forms monoclinic prisms [$a : b : c = 0.86397 : 1 : 0.87847$; $\beta = 94^\circ 46'$]. The rhombic, pyramidal crystals of the molybdenum compounds, $[\text{Mo}(\text{SCN})_6, \text{H}_2\text{O}]\text{K}_3 \cdot \text{C}_2\text{H}_4\text{O}_2$, D 1.893, and $[\text{Mo}(\text{SCN})(\text{H}_2\text{O})(\text{NH}_3)_3]\text{H}_3 \cdot \text{C}_2\text{H}_4\text{O}_2$, D 1.654, have been described by Maas and Sand (Abstr., 1908, i, 397). Ammonium orthosulphovanadate, $(\text{NH}_4)_3\text{VS}_4$, forms monoclinic crystals [$a : b : c = 1.1634 : 1 : 1.0165$; $\beta = 90^\circ 27'$]. Nef's ethyl 3:6-dimethoxybenzene-1:2:4:5-tetracarboxylate has D 1.276, and forms monoclinic prisms [$a : b : c = 0.64084 : 1 : 0.39365$; $\beta = 105^\circ 15\frac{1}{3}'$]. Dihydroxytriphenylacetic acid, $\text{C}_6\text{H}_5(\text{OH})_2 \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, D 1.293, is also monoclinic [$a : b : c = 1.11430 : 1 : 0.81194$; $\beta = 120^\circ 26\frac{2}{3}'$]. Cuminylnitroline, $\text{C}_6\text{H}_4\text{Pr} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, m. p. 36° , D 1.108, triclinic [$a : b : c = 1.5279 : 1 : 1.2793$; $\alpha = 122^\circ 11\frac{2}{3}'$, $\beta = 113^\circ 42\frac{2}{3}'$, $\gamma = 78^\circ 41\frac{1}{6}'$]. C. S.

Lipo-proteins and their Significance in Fatty Degeneration of Cells. II. Lipo-peptides, their Significance, Synthesis, and Properties. S. BONDI (*Biochem. Zeitsch.*, 1909, 17, 543—552).—The author discusses the possibility of the formation in the organism of condensation products of higher fatty acids and amino-acids. He has prepared lauryl-glycine by condensation of lauryl chloride and glycine, and lauryl-alanine by condensation of lauryl chloride and alanine. The former melted at 117.5° , and the latter not quite sharply at 103 — 104° . The glyceryl condensation products are stronger acids than lauric acid itself, as the sodium salts undergo less hydrolytic dissociation; they diffuse through parchment membranes more rapidly than sodium laurate. The condensation products have properties similar to the lipo-proteins, being less soluble than lauric acid, and showing similar staining action with Soudan or Scharlach. S. B. S.

Lipo-proteins and their Significance in Fatty Degeneration of Cells. III. Synthesis of Palmityl-glycine and Palmityl-alanine. S. BONDI and TH. FRANKL (*Biochem. Zeitsch.*, 1909, 17, 553—554).—Preparation similar to corresponding lauryl compounds (see preceding abstract). Palmityl-glycine has m. p. 121°, and palmityl-alanine, m. p. 106° (not quite sharp). S. B. S.

Lipo-proteins and their Significance in Fatty Degeneration of Cells. IV. The Behaviour of Lipo-peptides towards Ferments. S. BONDI and TH. FRANKL (*Biochem. Zeitsch.*, 1909, 17, 555—561).—The sodium salts of lauryl-glycine and lauryl-alanine were used for experiments. Pepsin, trypsin, and the juice from a pancreatic fistula were without action. The action of extracts of several organs (from rabbit) was investigated. Only two of these extracts caused hydrolysis of the peptides, namely, those of liver and of kidneys; the latter were the most active. S. B. S.

Ketenium Compounds. EDGAR WEDEKIND and MORIZ MILLER (*Ber.*, 1909, 42, 1269—1275).—It was observed that in the preparation of 1:3-diketotetramethylcyclobutane, an oil having a characteristic odour and b. p. above 185° was simultaneously produced (Abstr., 1906, i, 437). This oil has been now obtained in larger quantity, the only difference from the original directions for the preparation being to add a further quantity of triethylamine towards the end of the reaction. From the mixture, *dimethylketen-triethylium*, $\text{CMe}_2\text{:CO,NEt}_3$, has been isolated as a pale yellow oil, which soon becomes colourless in sunlight, b. p. 192—193°, D^{18}_D 0.892, n_D 1.440. It has an odour resembling menthol, and a determination of its molecular weight in benzene showed it to be unimolecular. *Chlorophenylketentriethylium*, CClPh:C:O,NEt_3 , obtained by the interaction of phenylchloroacetyl chloride and triethylamine in light petroleum, the viscous, yellowish-brown mass being distilled at 138—142°/0.1 mm., separates from methyl alcohol as a colourless, crystalline powder, m. p. 51°, and is unimolecular. Both these compounds differ from Staudinger's keten bases (Abstr., 1907, i, 424) in (1) that he found that the ketens unite with cyclic bases and not with bases of the fatty series; (2) these new compounds contain 1 mol. keten: 1 mol. base, whereas the others have 2 mols. keten: 1 mol. cyclic base; (3) the triethylium compounds are surprisingly stable, neither boiling dilute acids or alkalis, or even water at 160°, decomposing them; hydrochloric acid at 130°, however, hydrolyses them with formation of triethylamine hydrochloride and isobutyric acid and mandelic acid respectively. The constitution of these compounds cannot yet be definitely given; two formulæ are suggested:



W. R.

Thioformamide. RICHARD WILLSTÄTTER and THEODOR WIRTH (*Ber.*, 1909, 42, 1908—1922).—*Thioformamide*, CH_3NS , may be

obtained from formamide and phosphorus pentasulphide by working with small quantities of the materials in the absence of a solvent. With water it forms a *hydrate*, $\text{CH}_3\text{NS}\cdot\text{H}_2\text{O}$, which is soluble in ether and can thus be separated readily from unaltered formamide. To obtain the anhydrous compound the ethereal solution is treated with phosphoric oxide, filtered, concentrated, cooled to -15° , and mixed with light petroleum. It forms a brilliant white, crystalline mass, m. p. $28-29^\circ$, but is unstable, and turns yellow in the course of an hour, ultimately yielding a brownish-red syrup. It has a characteristic odour, which becomes more intense as decomposition proceeds, and also has a bitter taste. It appears to react in the tautomeric forms: $\text{HS}\cdot\text{CH}\cdot\text{NH} \rightleftharpoons \text{S}\cdot\text{CH}\cdot\text{NH}_2$, and is distinctly acid to litmus. When boiled with water, it yields hydrogen sulphide, with cold alkali, ammonia, and with concentrated sulphuric acid, hydrogen sulphide and sulphur dioxide. It reduces Fehling's solution in the cold, and with silver nitrate yields a precipitate of silver sulphide. It gives precipitates with many salts, and forms additive compounds with bromine and phosphorus trichloride.

With concentrated potassium cyanide solution, it yields crystals of chrysean (Hellsing, Abstr., 1899, i, 563), and with benzophenone chloride it gives Tschugaeff's reaction. When heated under reduced pressure, the amide gives dimolecular hydrogen cyanide (iminoformyl cyanide: Nef, Abstr., 1896, i, 71). *Thioformamide hydrochloride*, $\text{CH}_3\text{NS}\cdot\text{HCl}$, is obtained as a white, crystalline precipitate by passing hydrogen chloride into a dry ethereal solution of the amide. It is extremely hygroscopic, and, when heated, yields hydrogen sulphide, hydrogen chloride, hydrogen cyanide, carbon disulphide, and carbon monoxide, but no carbon monosulphide.

The amide reacts with chloroacetaldehyde, yielding thiazole (Hantzsch and Popp, Abstr., 1888, 1269), and when an aqueous solution of the platinichloride of this base is warmed, it yields a crystalline precipitate of tetrachlorodithiazole platinum.

A small amount of *thiazoline*, $\begin{array}{c} \text{CH}_2-\text{S} \\ | \quad \diagup \\ \text{CH}_2\cdot\text{CH} \end{array} \text{N}$, is formed when the amide is heated with bromoethylamine hydrobromide. It is a colourless oil with an odour recalling those of pyridine and thiophen, and has b. p. $138-139^\circ$ (corr.).

Alkylated thioformamides have been prepared by the action of phosphorus pentasulphide on alkylated formamides, using Hantzsch's method (Abstr., 1889, 723). *Dimethylthioformamide*, $\text{S}\cdot\text{CH}\cdot\text{NMe}_2$, is a pale yellow, strongly refractive oil, b. p. $96.5-97^\circ/12$ mm. or $227-228^\circ/760$ mm. (corr.), and has $D_4^{20} 1.047$. It is neutral to litmus, and is not decomposed when heated with phosphoric oxide or zinc chloride. The *methiodide*, $\text{CHNMe}_2\cdot\text{S}\cdot\text{MeI}$, forms colourless needles, m. p. $122-123^\circ$. *Diethylthioformamide*, $\text{S}\cdot\text{CH}\cdot\text{NEt}_2$, has b. p. $116-117^\circ/14$ mm. and m. p. below 0° ; the *methiodide* has m. p. $111-112^\circ$.

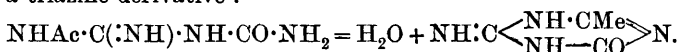
Thioformylpiperidine, $\text{CHS}\cdot\text{C}_5\text{NH}_{10}$, has b. p. $148-149^\circ/11-12$ mm., and the corresponding *methiodide* crystallises in needles, m. p. $119-120^\circ$. *Diphenylthioformamide*, $\text{CHS}\cdot\text{NPh}_2$, forms lemon-yellow plates, m. p. $108-109^\circ$; the *methiodide*, $\text{C}_{14}\text{H}_{14}\text{NSI}$, has no definite m. p., but decomposes when heated.

J. J. S.

Tetra-acetamide Compound of Calcium Chloride. P. I. KUSNETZOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 379—382).—When a mixture of calcium chloride (1 mol.) and acetamide (about 6 mols.) is heated and subsequently cooled, it deposits rosette-shaped aggregates of slender, hatched plates having the composition $\text{CaCl}_2 \cdot 4\text{COMe} \cdot \text{NH}_2$ and decomposing at 71—72°. The existence of this compound, which is analogous and similar in appearance to the β -tetrahydrate of calcium chloride, was not indicated by the results of Menschutkin (this vol., i, 89). T. H. P.

Condensation of Ethyl Carbamate with Acid Esters. OTTO DIELS (*Ber.*, 1909, 42, 1853).—The condensation of ethyl carbamate with acid esters (Ruhemann and Priestley, *Trans.*, 1909, 95, 449) has already been applied by Hantzsch (*Abstr.*, 1894, 363) and by Diels (*Abstr.*, 1903, i, 324; 1905, i, 174), and many acylcarbamates have been prepared in this way. C. H. D.

New Derivatives of Guanylcabamide. ADRIANO OSTROGOVICH (*Gazzetta*, 1909, 39, i, 540—549).—The interaction of acetyl chloride and guanylcabamide in a sealed tube at 100° yields *acetylguanylcabamide hydrochloride*, $\text{NHAc} \cdot \text{C}(\text{NH}) \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2 \cdot \text{HCl}$, which crystallises from water in deep yellow, flattened needles, m. p. 227—228° (decomp.). Attempts to convert the hydrochloride into the free acetylguanylcabamide result in the conversion of the latter into a triazine derivative:



The change affords a new and excellent method of obtaining triazine bases, which can be synthesised from their elements by way of calcium carbide, calcium cyanamide, cyanoguanidine, guanylcabamide, acetylguanylcabamide, and methyliminoketotriazine.

Guanylcabamide picrate crystallises from water in aggregates of yellow laminae, which melt at 280° (decomp.) if plunged into a bath previously heated to that temperature.

Guanylcabamide aurichloride, $(\text{C}_2\text{H}_6\text{ON}_4 \cdot \text{HCl})_2 \cdot \text{AuCl}_3$, and two *auribromides*, $(\text{C}_2\text{H}_6\text{ON}_4 \cdot \text{HBr})_2 \cdot \text{AuBr}_3$ and $\text{C}_2\text{H}_6\text{ON}_4 \cdot \text{HBr} \cdot \text{AuBr}_3$, were also prepared.

The action of benzaldehyde on a concentrated sulphuric acid solution of guanylcabamide sulphate yields benzylideneguanylcabamide sulphate, which, with ammonia or sodium carbonate, gives *benzylideneguanylcabamide* (?), $\text{NH} \begin{array}{c} \text{CHPh} \cdot \text{NH} \\ \text{CO} \rightarrow \text{NH} \end{array} \text{C} : \text{NH}$, in the form of minute, colourless scales or needles, m. p. 183—184° (decomp.). *Benzylideneguanylcabamide picrate*, m. p. 211—212° (decomp.), was also prepared.

Benzylidenebiuret can be obtained pure and in theoretical yield by the action of benzaldehyde on a solution of biuret hydrate in concentrated sulphuric acid (compare Biginelli, *Abstr.*, 1894, i, 374, and Schiff, *Abstr.*, 1896, i, 529). T. H. P.

Crystallographic Examination of Some Thiocyanocompounds. H. STEINMETZ (*Zeitsch. Kryst. Min.*, 1909, 46, 377—379. Compare Maas and Sand, *Abstr.*, 1908, i, 11, 397).—The compound

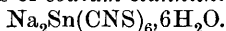
$[\text{Mo}(\text{SCN})_6(\text{H}_2\text{O})(\text{NH}_3)_3]\text{H}_3, 3\text{H}_2\text{O}$ forms brownish-red, twinned, rhombic crystals $[a:b:c = 0.6134:1:0.8943]$. The compound $[\text{Mo}(\text{SCN})_6(\text{H}_2\text{O})]\text{K}_3, 4\text{H}_2\text{O}$ forms brown or yellow, ψ -hexagonal crystals $[a:c = 1:0.6749]$. The compound

$[\text{Cr}(\text{SCN})_6(\text{H}_2\text{O})(\text{NH}_3)_3]\text{H}_3, \text{C}_2\text{H}_4\text{O}_2$ forms small, dark red, rhombic crystals $[a:b:c = 0.72:1:0.6334]$.

C. S.

Comparative Crystallographic Examination of Cyanuric Acid and the Acid Product of the Synthesis of Biuret by Ethyl Cyanoacetate, and of their Salts. E. BILLOWS (*Zeitsch. Kryst. Min.*, 1909, 46, 481—483; from *Riv. Min. Crist. ital.*, 1907, 33, 87—94).—Cyanuric acid forms monoclinic prisms $[a:b:c = 1.3694:1:1.8502; \beta = 106^\circ 4\frac{1}{2}']$, whilst its calcium salt crystallises in the triclinic system $[a:b:c = 1.0928:1:0.5986; \alpha = 81^\circ 10', \beta = 87^\circ 16', \gamma = 103^\circ 38']$. The acid product of the synthesis of biuret by ethyl cyanoacetate closely resembles cyanuric acid in its composition and behaviour, but differs greatly in its crystalline form; it belongs to the triclinic system $[a:b:c = 0.9850:1:0.5552; \alpha = 92^\circ 11', \beta = 114^\circ 1', \gamma = 76^\circ 6\frac{1}{2}']$, whilst its calcium salt is monoclinic, the crystals, however, being too small for measurement. C. S.

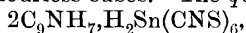
Stannithiocyanates. RUDOLF WEINLAND and ERNST BAMES (*Zeitsch. anorg. Chem.*, 1909, 62, 250—264).—The only thiocyanates of a quadrivalent metal known, other than those containing oxygen, are the platinithiocyanates. It is now found that sodium stannichloride, $\text{Na}_2\text{SnCl}_6, 6\text{H}_2\text{O}$, reacts with sodium thiocyanate in alcohol, forming colourless prisms of *sodium stannithiocyanate*,



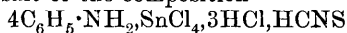
The salt may also be prepared in aqueous solution. The *potassium* salt, $\text{K}_2\text{Sn}(\text{CNS})_6, 4\text{H}_2\text{O}$, forms colourless plates or prisms. The *magnesium* salt, $\text{MgSn}(\text{CNS})_6, 6\text{H}_2\text{O}$, hygroscopic leaflets; *calcium* salt, $\text{CaSn}(\text{CNS})_6, 7\text{H}_2\text{O}$, tablets, and *strontium* salt, $\text{SrSn}(\text{CNS})_6, 12\text{H}_2\text{O}$, glistening needles, are also described.

The organic salts are prepared either by dissolving stannichlorides of organic bases in 10% thiocyanic acid solution, or by mixing solutions of sodium stannichloride and sodium thiocyanate with a nitric acid solution of the organic base.

Pyridine stannithiocyanate, $2\text{C}_5\text{NH}_5, \text{H}_2\text{Sn}(\text{CNS})_6$, may be recrystallised from acetone in colourless cubes. The *quinoline* salt,



forms a white, microcrystalline powder; the *dimethylaniline* salt, $2\text{C}_6\text{H}_5\text{NMe}_2, \text{H}_2\text{Sn}(\text{CNS})_6$, forms pale yellow, quadratic leaflets. The *pyridine sodium* salt, $2\text{C}_5\text{NH}_5, \text{H}_2\text{Sn}(\text{CNS})_6, \text{NaCNS}$, forms microscopic cubes. An *aniline* salt of the composition



is obtained in colourless, double pyramids when aniline stannichloride is dissolved in thiocyanic acid.

The new salts are more readily decomposed by water than the stannichlorides. Silver nitrate precipitates the whole of the thiocyanate from their aqueous solutions. The co-ordination number of the simpler salts is 6; the proper formulation of the more complex aniline and pyridine sodium salts is still undetermined. C. H. D.

Reaction between Ferric Chloride and Potassium Ferri-cyanide. YOGORO KATO (*Mem. Col. Sci. Eng. Kyōto*, 1908, i, 352—374).—Although ferric chloride and potassium ferrocyanide only give a reddish-brown colour when mixed in dilute aqueous solution, it has been shown by Spring (*Bull. Acad. Roy. Belg.*, 1892, [iii], 34, 255) that a deep blue precipitate, with evolution of chlorine, is produced when very concentrated solutions of ferric chloride are used, and he ascribed this to a change in the stability of ferric chloride with change of concentration. It is now shown that a blue colour is produced even in dilute solutions of the reagents when the reaction takes place in concentrated solutions of many salts, and various explanations of this observation are suggested and tested.

The salts of metals having the same valency have, in solutions of equal concentration, nearly equal capacity for promoting the reaction, but it takes place in a more dilute solution in the case of the salts of metals of higher valency. It is not probable that the reaction is connected with the elimination of chlorine according to the equation: $2\text{FeCl}_3 = 2\text{FeCl}_2 + \text{Cl}_2$, as ferric nitrate and sulphate behave very like ferric chloride. Neither is the suggestion of Spring, that the decomposition potential of ferric chloride into ferrous chloride and chlorine varies with the concentration, an adequate explanation of the observations, as experiment shows that the decomposition potential of ferric chloride does not vary greatly with the concentration. The final conclusion is drawn that the reaction is connected with the precipitation of colloidal Prussian blue by the salts. G. S.

Action of Hydrogen Sulphide on Imino-ethers. MOROOKI MATSUI (*Mem. Coll. Sci. Eng. Kyōto*, 1908, 1, 285—289).—The action of hydrogen sulphide on imino-ethers is found to be analogous to that of water on their hydrochlorides (Pinner, *Abstr.*, 1883, 730), and to that of hydrogen sulphide on the substituted amidines (Berntsen, *Abstr.*, 1878, 70), the imide group being replaced by sulphur and a β -thiocarboxylic ester formed. When dry hydrogen sulphide is passed into an ethereal solution of ethyl iminoacetate (Pinner, *Abstr.*, 1883, 1089), there is formed *ethyl β -thionacetate*, $\text{CH}_3\cdot\text{CS}\cdot\text{OEt}$, a yellow, mobile liquid having a very unpleasant odour, which reacts violently with concentrated nitric acid, forming ethyl acetate, but does not yield the thio-acid on saponification. If the ethereal solution into which hydrogen sulphide has been passed is kept, the thionacetate is completely transformed into thioacetamide. *Ethyl β -thionpropionate*, prepared similarly, is a yellow liquid, b. p. 128—130°, having a very disagreeable odour and similar properties to those of ethyl β -thionacetate, except that it does not form thiopropionamide.

By passing dry hydrogen sulphide into an ethereal solution of ethyl iminobenzoate, thiobenzamide and *ethyl β -thionbenzoate*, $\text{C}_6\text{H}_5\cdot\text{CS}\cdot\text{OEt}$, are formed. The latter is a yellow liquid having a very disagreeable odour, and properties analogous to those of the other two thio-esters. It changes into thiobenzamide when kept in contact with alcoholic ammonia. E. H.

Reactions of Ethyl Diazoacetate. ANTON LOOSE (*J. pr. Chem.*, 1909, 79, 505—510).—I. Ethyl diazoacetate reacts slowly with boiling *d*-pinene, yielding a *substance*, $\text{C}_{14}\text{H}_{22}\text{O}_2$, obtained as a colourless

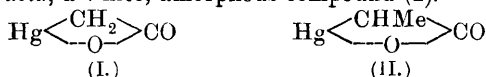
liquid, b. p. 140—150°/15 mm. It is converted by boiling 15% aqueous sodium hydroxide into another *substance*, obtained as a colourless liquid, b. p. 170—180°/15 mm., having a pine-like odour.

II. Ethyl diazoacetate decomposes when its solution in light petroleum (b. p. 98—100°) is warmed in the presence of platinum, mercury, or aluminium, yielding ethyl pyrazoline-3:4:5-tricarboxylate. When copper-bronze (Kahlbaum's naturkupfer C) is employed, however, 70% of the product of the reaction is ethyl fumarate. The condensation product of pinene with ethyl diazoacetate just described is more rapidly obtained by using copper-bronze as a catalyst.

W. H. G.

Preparation of Iron Salts of Arsenitartaric and Arsenicitric Acids. CARL SORGER (D.R.-P. 208711).—The double alkali ferrous salts of arsenitartaric and arsenicitric acids are soluble substances, and are thirty-five times less poisonous than arsenious acid. *Ferrous arsenitartarate*, greyish-white powder soluble in cold dilute sodium hydroxide, is prepared by adding successively arsenic acid and ferrous sulphate to a solution of sodium tartrate and sodium carbonate. *Ferrous arsenicitrate* is similarly prepared by using ferric chloride instead of ferrous sulphate; the corresponding ferric salts are produced. *Sodium ferric arsenitartarate*, a deep yellow salt, is precipitated by adding ferric chloride to a concentrated solution of tartaric and arsenic acids dissolved in excess of sodium carbonate. F. M. G. M.

[Preparation of the Mercury Derivatives of Fatty Acids.] WALTHER SCHOELLER and WALTHER SCHRAUTH (D.R.-P. 208634).—When methyl malonate and mercuric oxide are suspended in water and shaken together for twelve hours, a white compound, *methyl mercuridimalonate*, $\text{Hg}[\text{CH}(\text{CO}_2\text{Me})_2]_2$, results. This substance, when shaken with aqueous sodium hydroxide, undergoes further change, and the solution, when acidified, gives rise to the *anhydride* of *hydroxy-mercuriacetic acid*, a white, amorphous compound (I).



Methyl methylmalonate gives the corresponding *anhydride* of *hydroxymercuripropionic acid* (II). The corresponding *hydroxy-mercuributyric acid* is formed from mercuric oxide and methyl ethylmalonate.

F. M. G. M.

Crystalline Forms of Some Benzene Derivatives. E. REPOSSI (*Zeitsch. Kryst. Min.*, 1909, 46, 402—407).—The following data are given:

2:5-Dibromonitrobenzene: triclinic [$a:b:c = 1.3854:1.07879$; $\alpha = 87^\circ 29'$, $\beta = 114^\circ 35'$, $\gamma = 83^\circ 26'$]. 2-Chloro-5-bromonitrobenzene: triclinic [$a:b:c = 1.3823:1.08196$; $\alpha = 86^\circ 30'$, $\beta = 114^\circ 29'$, $\gamma = 82^\circ 20'$]. 5-Chloro-2-bromonitrobenzene: triclinic [$a:b:c = 1.4159:1.08157$; $\alpha = 87^\circ 17'$, $\beta = 113^\circ 47'$, $\gamma = 82^\circ 25'$]. 2:5-Dichloronitrobenzene: triclinic [$a:b:c = 1.4385:1.08223$; $\alpha = 87^\circ 18'$, $\beta = 114^\circ 17'$, $\gamma = 82^\circ 37'$]. 3-Bromo-2-iodonitrobenzene: monoclinic [$a:b:c = 0.6342:1.05680$; $\beta = 105^\circ 4' 30''$]. 2:3-Dibromonitrobenzene: monoclinic [$a:b:c =$

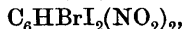
1.0309 : 1 : 0.2824 ; $\beta = 99^{\circ}51'30''$]. 1 : 2 : 3-Tribromobenzene : monoclinic [$a : b : c = 1.5490 : 1 : 1.8516$; $\beta = 113^{\circ}7'30''$]. The first four compounds are isomorphous. C. S.

Crystalline Forms of Some Benzene Derivatives. ETTORE ARTINI (*Zeitsch. Kryst. Min.*, 1909, 46, 407—414).—The following crystallographic data are given :

4 : 6-Di-iodo-1 : 3-dinitrobenzene : rhombic, bipyramidal [$a : b : c = 2.1859 : 1 : 0.7084$]. 3 : 5-Dichloro-1 : 2-dinitrobenzene : ditetragonal, bipyramidal [$a : c = 1 : 1.9767$]. 2-Bromo-6-nitroaniline : monoclinic, prismatic [$a : b : c = 1.2799 : 1 : 0.3809$; $\beta = 111^{\circ}54'$]. 2-Bromo-5-nitroacetanilide : monoclinic, prismatic [$a : b : c = 3.3702 : 1 : 1.2522$; $\beta = 102^{\circ}57'$]. 2 : 4-Dichloro-5-nitroaniline : monoclinic, prismatic [$a : b : c = 2.1321 : 1 : 3.0222$; $\beta = 106^{\circ}33'$]. 2-Chloro-4-bromo-5-nitroaniline : monoclinic, prismatic [$a : b : c = 2.1367 : 1 : 3.0297$; $\beta = 107^{\circ}10'$]. 4-Chloro-2-bromo-5-nitroaniline : monoclinic, prismatic [$a : b : c = 2.1525 : 1 : 2.9625$; $\beta = 105^{\circ}44'$]. 2 : 4-Dibromo-5-nitroaniline : monoclinic, prismatic [$a : b : c = 2.1598 : 1 : 3.0212$; $\beta = 106^{\circ}9'$]. 2 : 4-Dichloroacetanilide : monoclinic, prismatic [$a : b : c = 0.8252 : 1 : 0.6773$; $\beta = 102^{\circ}34'$]. 2-Chloro-4-bromoacetanilide : monoclinic, prismatic [$a : b : c = 0.8152 : 1 : 0.6669$; $\beta = 103^{\circ}18'$]. 4-Chloro-2-bromoacetanilide : monoclinic, prismatic [$a : b : c = 0.8230 : 1 : 0.7088$; $\beta = 102^{\circ}11'$]. 2 : 4-Dibromoacetanilide : monoclinic, prismatic [$a : b : c = 0.8135 : 1 : 0.6903$; $\beta = 103^{\circ}5'$].

C. S.

2-Bromo-1 : 3 : 5-tri-iodo-4 : 6-dinitrobenzene. CHARLES LORING JACKSON and H. E. BIGELOW (*Ber.*, 1909, 42, 1868—1869).—2-Bromo-1 : 3 : 5-tri-iodobenzene, $C_6H_2BrI_3$, obtained from *s*-tri-iodoaniline, has m. p. 139° , and reacts with fuming nitric acid, yielding the dinitro-derivative, $C_6BrI_3(NO_2)_2$, m. p. 292° . When the dinitro-compound is left in contact with an alcoholic solution of ethyl sodiomalonate, the chief product is 2-bromo-1 : 3-di-iodo-4 : 6-dinitrobenzene,



m. p. 187° , ethyl ethanetetra-carboxylate being also formed. The behaviour of the nitro-compound is thus analogous to that of 1 : 3 : 5-tri-iodo-4 : 6-dinitrobenzene (*Abstr.*, 1904, i, 861). J. J. S.

Preparation of Benzenesulphonyl Chloride. RUDOLF PUMMERER (*Ber.*, 1909, 42, 1802—1804).—Benzenesulphonyl chloride is conveniently prepared by the action of chlorosulphonic acid on benzene. It is advisable to work up large quantities in one operation at a low temperature, and use a large excess of chlorosulphonic acid. The acid is cooled to -15° , stirred, and benzene allowed to drop in slowly during three to four hours ; the mixture is poured on to ice, the oil separated, and distilled in a vacuum. E. F. A.

Preparation of Benzenesulphonyl Chloride. FRITZ ULLMANN (*Ber.*, 1909, 42, 2057—2058).—In the preparation of benzenesulphonyl chloride from benzene and chlorosulphonic acid, the low yield obtained by Pummerer (preceding abstract) is due to the

employment of too low a temperature. At 15—20° a yield of 62% is obtained. After an hour, the mass is poured on to ice, extracted with ether, and the residue, after evaporation of the ether, distilled under reduced pressure. The chloride passes over, leaving a residue of sulphobenzide. C. H. D.

Catalytic Reactions at High Temperatures and Pressures. XVIII. Reduction of Fluorene, Acenaphthene, and Retene in Presence of Nickel Oxide. WLADIMIR N. IPATIEFF (*Ber.*, 1909, 42, 2092—2096).—Polynuclear aromatic hydrocarbons, which are only incompletely reduced by the ordinary methods, undergo complete reduction with hydrogen under high pressure in presence of nickel oxide. Fluorene is reduced in two stages when heated at 285° under 120 atmospheres, the first product being decahydrofluorene, which is afterwards converted into perhydrofluorene, $C_{13}H_{22}$. Similarly, acenaphthene yields tetra- and deca-hydroacenaphthene.

Retene first yields dodecahydroretene, and, on further reduction, *perhydroretene*, $C_{18}H_{32}$, an oil, b. p. 300—315°. It is not identical, as had been suspected, with fichtellite, the hydrocarbon found together with retene in Bavarian peat (Bamberger, *Abstr.*, 1889, 714).

C. H. D.

2:6-Dinitro-4-amino-*m*-xylene. RAFFAELE MALTESE (*Gazzetta*, 1909, 39, i, 517—520).—2:6-Dinitro-4-benzoylamino-*m*-xylene, $NHBz \cdot C_6HMe_2(NO_2)_2$, obtained by nitrating 2-nitro-4-benzoylamino-*m*-xylene (*Abstr.*, 1904, i, 307), forms small, shining laminae, m. p. 244°.

2:6-Dinitro-4-amino-*m*-xylene, $NH_2 \cdot C_6HMe_2(NO_2)_2$, crystallises from aqueous alcohol in orange-yellow needles, and from alcohol in hard, dark red prisms, m. p. 145°.

T. H. P.

Imino-chlorides of Oxalic Acid. II. RUDOLPH BAUER (*Ber.*, 1909, 42, 2111—2118).—It has been shown previously (*Abstr.*, 1907, i, 603) that diphenyl- and the three ditolyl-oxalimino-chlorides are converted by concentrated sulphuric acid into isatin and methylisatins respectively. The object of the present investigation was to prepare methoxyisatins by similar means, but it is found that di-*p*-anisylloxalimino-chloride is converted only to a very slight extent, whilst the *o*-compound is not converted at all, into the corresponding methoxyisatins; in both cases the chief product is an oxaloanisididedisulphonic acid.

Heating phenol ethers with *N*-hydrochloric acid under pressure at 175—180° is recommended as a good method of hydrolysing these compounds.

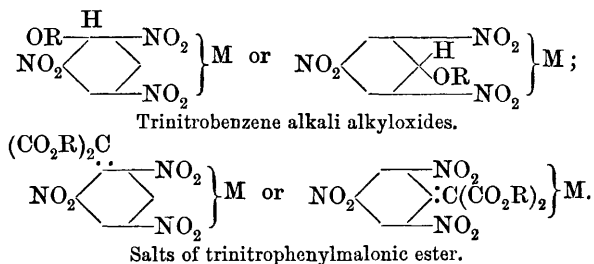
Di-p-anisylloxalimino-chloride, $C_2Cl_2 \cdot (N \cdot C_6H_4 \cdot OMe)_2$, prepared by treating a solution of oxalo-*p*-anisidide in benzene with phosphorus pentachloride, crystallises in yellow needles, m. p. 150°. When treated with concentrated sulphuric acid, it yields oxalo-*p*-anisididedi-*o*-sulphonic acid, $C_2O_2[NH \cdot C_6H_3(SO_3H) \cdot OMe]_2$, which crystallises with $8H_2O$ in slender, white needles and prisms, m. p. 261° (decomp.), and is converted by boiling 30% sulphuric acid into 4-amino-1-methoxybenzene-

2-sulphonic acid (compare this vol., i, 470). 5-Methoxyisatin-3-phenylhydrazone, $C_{15}H_{13}O_2N_3$, crystallises in dark yellow, hair-like needles, m. p. 219° .

The following compounds are prepared by methods similar to those just described. *Di-o-anisylloxalimino-chloride*, $C_{16}H_{14}O_2N_2Cl_2$, crystallises in small, yellow, rhombic plates, m. p. 101° . *Oxalo-o-anisididedi-sulphonic acid*, $C_{16}H_{16}O_{10}N_2S_2$, forms colourless, hair-like needles, m. p. 271° (decomp.); the ammonium salt, $C_{16}H_{22}O_{10}N_4S_2 \cdot 2H_2O$, crystallises in white prisms.

It is shown in conclusion that the methylisatin derived from di-*m*-tolylloxalimino-chloride (*loc. cit.*) is identical with that described by Findelee (Abstr., 1906, i, 43); further, this compound is 6-methylisatin, since it is oxidised by chromic acid to *m*-homoisatoic acid. 6-Methylisatin has m. p. 182° , and not 165° as given previously; the phenylhydrazone, $C_{15}H_{13}ON_3$, forms golden-yellow, hair-like needles, m. p. 236° . 6-Methylisatoxime, $C_9H_8O_2N_2$, crystallises in yellow leaflets, m. p. 235° .
W. H. G.

The Chromophore of Salts from Polynitrobenzene Derivatives. ARTHUR HANTZSCH and NORMAN PICTON (*Ber.*, 1909, 42, 2119—2128).—Although 2:4:6-trinitrobenzene, ethyl 2:4-dinitrophenylmalonate, and ethyl 2:4:6-trinitrophenylmalonate are practically colourless, nevertheless the compounds of the first-named substance with alkali alkylloxides and the salts of the two esters are intensely coloured, and give absorption spectra which are extremely similar, from which fact the conclusion is drawn that they all possess the same chromophoric group. Since the salts obtained by the addition of potassium methoxide to mononitro-compounds, such as nitroanthracene, are colourless, it is evident that the colour of the salts derived from the polynitro compounds is due to the combined action of two nitro-groups. Definite structural formulæ cannot yet be assigned to these substances, but omitting ethylene linkings they may be represented by the following formulæ:

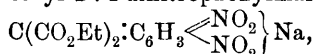


In agreement with the view that the chromo-salts have the above quinonoid formulæ is the fact that the deep brownish-red silver salt of ethyl trinitrophenylmalonate yields with ethyl iodide a brown, oily, unstable ester, which undoubtedly contains the analogous chromophoric group, $C_6 \begin{array}{c} \text{NO}_2 \\ \diagdown \quad \diagup \\ \text{NO}_2 \end{array} \text{Et}$, and passes slowly into a crystalline, orange-coloured, stable isomeride. This stable ester, since it is

coloured, cannot be the true ethyl ester of trinitrophenylethylmalonic acid, $C_6H_2(NO_2)_3 \cdot C(Et)(CO_2Et)_2$, but is undoubtedly the ethyl derivative of the enolic form of the ester, $C_6H_2(NO_2)_3 \cdot C(CO_2Et) : C(OEt)_2$.

2 : 4 : 6-Trinitrobenzene can be obtained as snow-white leaflets; the compound with sodium methoxide yields with acetone the *substance*, $C_6H_3(NO_2)_3 \cdot MeONa, \frac{1}{2} COMe_2$, which crystallises in small, dark green needles.

The *sodium* salt of ethyl 2 : 4-dinitrophenylmalonate,



crystallises in long, reddish-brown prisms; the *silver* salt is very unstable.

The *potassium* salt of ethyl 2 : 4 : 6-trinitrophenylmalonate crystallises in small, brownish-red needles. The *silver* salt, $C_{12}H_{12}O_{10}N_3Ag$, is a reddish-brown powder, and when treated with ethyl iodide yields the *chromo-ester*, $C(CO_2Et)_2 \cdot C_6H_2(NO_2)_3 \left\langle \begin{smallmatrix} NO_2 \\ NO_2 \end{smallmatrix} \right\rangle Et$, a brown oil which passes slowly into the *oxygen ester*, $C_6H_2(NO_2)_3 \cdot C(CO_2Et) : C(OEt)_2$, orange-yellow crystals, m. p. 81° .

All attempts to prepare the ester, $C_6H_2(NO_2)_3 \cdot C(Et)(CO_2Et)_2$, were unsuccessful.

W. H. G.

Combination of Picric Acid and β -Naphthol. LOUIS PELET-JOLIVET and TH. HENNY (*Bull. Soc. chim.*, 1909, [iv], 5, 623—626).—Sisley has shown that picric acid combines with certain hydrocarbons and with β -naphthol more readily in presence of acids than in neutral solution, and similarly that certain dyes, which will not dye silk in dilute solution, do so if acid is added, and argues from analogy that if the formation of picrate of β -naphthol is a chemical combination, so also must be the fixation of dye by a tissue (*Bull. Soc. chim.*, 1908, October).

In the present paper it is shown (1) that more β -naphthol picrate is formed in acid than in neutral solution; (2) that the quantity formed depends on the number of H-ions present, and (3) that in neutral solution the formation of some picrate is due to the β -naphthol becoming positively charged, due to the H-ions present. These results show that the combination of picric acid with β -naphthol takes place according to the law of adsorption. Adsorption may be the result of partial dissociation of a chemical compound in aqueous solution.

T. A. H.

Oxidation of Quinol by the Catalysis of Carbon. MOTOOKI MATSUI (*Mem. Coll. Sci. Eng. Kyōto*, 1908, 1, 386—390. Compare Hofmann, *Ber.*, 1874, 7, 530; Cazeneuve, *Abstr.*, 1890, 690; Freundlich, *Abstr.*, 1907, ii, 155).—When charcoal and quinol moistened with water are rubbed together in a mortar, or when a small quantity of charcoal is added to a 3% aqueous or alcoholic solution of quinol, oxidation takes place, and green crystals of quinhydrone separate. In ethereal solution only a slight oxidation occurs, whilst in aqueous and alcoholic solution it proceeds at about equal rates. The oxidation is not due to the oxygen contained in the

charcoal, since it does not occur in the absence of air, and the view that it is due to the oxygen of the air is supported by the observation that the greater the surface of the quinol solution the greater is the effect. The rate of oxidation is increased by raising the temperature, particularly in ethereal solution.

The purest form of animal charcoal (from Merck) was used, whilst finely powdered wood charcoal was found to have a similar, but very feeble, catalytic action. E. H.

Bismuth Salts of Brominated Catechols. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 207544).—Bismuth tribromophenoxide employed medicinally under the name of "Xeroform" is neither tasteless nor odourless, and a more satisfactory medicament is obtained by employing brominated catechols.

The *bismuth* derivative of tetrabromocatechol, a yellow powder, is produced by adding an acid solution of bismuth nitrate to alkaline tetrabromocatechol or by introducing precipitated bismuth hydroxide into an alcoholic solution of catechol. Similar products are obtainable from di- and tri-bromocatechols. F. M. G. M.

New Derivatives of Catechol. Preparation of Phenylethylenecatechol. I. LAZENNEC (*Bull. Soc. chim.*, 1909, [iv], 5, 509—511. Compare this vol., i, 488).—Moureu found (Abstr., 1899, i, 494) that *o*-hydroxyphenoxyacetal could be dehydrated by the usual agents, such as phosphoric anhydride, yielding ethylenecatechol, but this method is not available in the case of *o*-hydroxyphenoxyacetophenone, which is, however, readily dehydrated by careful heating under reduced pressure. The product of this reaction is *phenylethylenecatechol*, $C_6H_4 \begin{smallmatrix} \diagup O \cdot CH \\ | \\ O \cdot CPh \end{smallmatrix}$, m. p. 73°, which crystallises in colourless lamellæ from methyl alcohol. The dibromide could not be isolated in a free state, but on heating during eight hours in water with calcium carbonate is decomposed, yielding phenylglyoxal and catechol, which from analogy to Moureu's results (*loc. cit.*) establishes the constitution of the parent substance. T. A. H.

Preparation of Pyrogallol from 2:6-Dichloro-4-sulphonic Acid. AKTIEN-GESELLSCHAFT FÜR ANILINFABRIKATION (D.R.-P. 207374).—2:6-Dichlorophenol-4-sulphonic acid when heated with 40% aqueous potassium hydroxide at 150—160° yields potassium pyrogallol-5-sulphonate, which on heating at 200° in slightly acidified solution gives rise to pyrogallol. F. M. G. M.

Crystallographic Examination of Some Organic Additive Compounds. GIOVANNI BOERIS (*Zeitsch. Kryst. Min.*, 1909, 46, 472—474. From *Mem. Accad. Sci. Bologna*, 1907, (vi, a), 4, 343).—The additive compound, m. p. 76—77°, of *iso*apiole and *s*-trinitrobenzene separates from a mixture of alcohol and ether in monoclinic crystals [$a:b:c=0.9090:1:0.4194$; $\beta=90^\circ 57'$]; The additive compound, m. p. 152°, of naphthalene and *s*-trinitrobenzene forms monoclinic crystals [$a:b:c=2.3170:1:4.0961$; $\beta=96^\circ 36'$], isomorphous with

the additive compound of naphthalene and picric acid. Naphthalene and picryl chloride form an additive compound, $C_{10}H_8 \cdot C_6H_2(NO_2)_3Cl$, m. p. 95—96°, which crystallises in the triclinic system [$a:b:c = 0.4940:1:0.4455$; $\alpha = 100^\circ 59'$, $\beta = 93^\circ 54'$, $\gamma = 85^\circ 28'$]. Isomorphous with this is the additive compound of naphthalene and trinitrotoluene [$a:b:c = 0.4891:1:0.4839$; $\alpha = 99^\circ 16'$, $\beta = 94^\circ 35'$, $\gamma = 85^\circ 35'$]. The methyl group and the halogen apparently exert the same crystallographic influence; Jaeger uses the same conception to explain the isomorphism of 2:3:5- and of 3:4:5-tribromotoluene. C. S.

Action of Aromatic Mercaptides on Ethyl α -Chloroacetoacetate. HERMANN FINGER and O. HEMMETER (*J. pr. Chem.*, 1909, 79, 449—451).—Sodium phenylmercaptide and ethyl α -chloroacetoacetate interact in equivalent quantities in alcoholic solution, yielding diphenyl disulphide and ethyl diacetylsuccinate, thus: $2PhSNa + 2CMeO \cdot CHCl \cdot CO_2Et = 2NaCl + PhS \cdot SPh + \begin{matrix} CHAc \cdot \overset{\text{CH}}{\underset{\text{CH}}{\text{CO}_2Et}} \\ CHAc \cdot \overset{\text{CH}}{\underset{\text{CH}}{\text{CO}_2Et}} \end{matrix}$

Sodium *p*-tolylmercaptide and ethyl α -chloroacetoacetate interact in an analogous manner. W. H. G.

4-Amino-1-methoxybenzene-2-sulphonic Acid. RUDOLF BAUER (*Ber.*, 1909, 42, 2106—2111).—4-Amino-1-methoxybenzene-2-sulphonic acid has been prepared for purposes of identification (compare this vol., i, 466).

Dipotassium 4-benzylidene-amino-1-phenol-2-sulphonate,



prepared by the condensation of benzaldehyde and potassium 4-amino-phenol-2-sulphonate in alcoholic solution, crystallises in greenish-yellow needles and leaflets. It is converted by carbon dioxide in aqueous solution into the *potassium* salt, $CHPh \cdot N \cdot C_6H_3(OH) \cdot SO_3K$, which crystallises in yellowish-white prisms. Both salts are instantly decomposed by acids into benzaldehyde and aminophenolsulphonic acid.

Potassium benzylidene-p-anisidine-2-sulphonate, $C_{14}H_{12}O_4NSK \cdot H_2O$, is obtained by the action of methyl sulphate on an alkaline solution of the dipotassium salt just described; it crystallises in yellowish-white leaflets, and when decomposed by acids yields 4-amino-1-methoxybenzene-2-sulphonic acid, $\begin{matrix} CH \cdot C(OMe) \cdot C \cdot SO_3H \\ | \\ CH \cdot C(NH_2) \cdot CH \end{matrix}$, which crystallises with

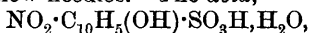
$2H_2O$ in long, colourless prisms and needles, and commences to carbonise at 320° . The latter substance when diazotised yields 4-diazoanisole-2-sulphonic acid, $OMe \cdot C_6H_3 \cdot \begin{matrix} SO_2 \\ \diagup \quad \diagdown \\ N \quad N \end{matrix} \cdot O$, which crystallises in almost colourless, rectangular plates and prisms, and explodes slightly at 191° without melting.

Large quantities of 4-amino-1-methoxybenzene-2-sulphonic acid are best prepared by sulphonating *p*-anisidine with fuming sulphuric acid.

W. H. G.

Naphthol Yellow-S. HERMANN FINGER [with E. BRETSCH and W. ZEH] (*J. pr. Chem.*, 1909, 79, 441—445).—It is shown that the com-

pound obtained by reducing naphthol yellow-S with stannous chloride and hydrochloric acid (compare Lauterbach, Abstr., 1882, 63) is 2-nitro-4-amino- α -naphthol-7-sulphonic acid. When treated with aqueous-alcoholic hydrochloric acid and amyl nitrite, it yields the corresponding *diazo*-derivative, $\text{OH}\cdot\text{C}_{10}\text{H}_4(\text{NO}_2)\text{N}=\text{N}\text{SO}_3$, obtained as small, brown crystals, which, when boiled with absolute alcohol and copper powder and subsequently with water, yields *copper 2-nitro- α -naphthol-7-sulphonate*, $[\text{NO}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{SO}_3]_2\text{Cu}\cdot 5\text{H}_2\text{O}$, crystallising in small, greenish-yellow needles. The *acid*,



crystallises in slender, lemon-yellow needles, and is reduced by stannous chloride and hydrochloric acid to 2-amino- α -naphthol-7-sulphonic acid, $\text{NH}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{SO}_3\text{H}\cdot 2\text{H}_2\text{O}$, crystallising in colourless needles. An alkaline solution of the latter substance becomes green when exposed to the air; the *sodium* salt, when acted on by nitroso-*m*-dimethylaminophenol hydrochloride in aqueous solution, yields an *oxazine* dye, which forms small, brass-yellow crystals, and dyes wool, but not cotton, an intense blue.

W. H. G.

Modifications of Anthesterol and its Benzoate. TIMOTHÉE KLOBB (*Compt. rend.*, 1909, 148, 1272—1274. Compare Abstr., 1902, i, 165).—Like certain other cholesterol, anthesterol exists in several modifications; these are prepared by hydrolysis of the corresponding benzoates. The α -benzoate, m. p. 284—286° (*loc. cit.*), has $[\alpha]_D + 64\cdot 36^\circ$ in carbon tetrachloride. On hydrolysis it gives α -anthesterol, m. p. 221—223°, $[\alpha]_D + 54\cdot 1^\circ$ in xylene. The β -benzoate, m. p. 230—235°, crystallises in lamellæ, and has $[\alpha]_D + 68\cdot 8$ —71·7° in carbon tetrachloride. On hydrolysis it forms β -anthesterol. When heated on the Maquenne block this melts at 160—164°, then solidifies, and again melts at 190—195°. It has $[\alpha]_D + 48\cdot 3^\circ$ in xylene, and 56·8° in ethylene dibromide. The γ -benzoate crystallises with $\frac{1}{2}\text{H}_2\text{O}$ in spherical aggregates, m. p. 240—250°, $[\alpha]_D + 66\cdot 7^\circ$. Boiling alcohol transforms it into the β -benzoate.

Both α - and β -anthesterol spontaneously change into a more stable modification, δ -anthesterol, m. p. 150—160°; $[\alpha]_D + 44\cdot 7^\circ$ in xylene.

W. O. W.

Polynaphthenic Acids. II. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 345—353. Compare this vol., i, 154).—Oxidation of the fraction of naphtha, b. p. 164—166°/753 mm., by means of air in presence of powdered sodium hydroxide yields an *acid*, $\text{C}_{24}\text{H}_{34}\text{O}_4$, D 1·025, containing two hydroxyl groups and one carboxyl group.

Oxidation in a similar manner of synthetic heptanaphthene (dimethylcyclopentane), obtained by reducing toluene by means of hydriodic acid in a sealed tube at 240—260°, yields a syrupy acid, the character of which was not determined.

No definite oxidation products were obtained with the fractions of Grosny naphtha: (1) b. p. 144—146°, D 0·765, containing trimethyl-

and methylethyl-*cyclohexanes*; and (2) b. p. 128—129°, which should correspond with one of the octanaphthenes.

The main product of the oxidation of cymene by means of air in presence of alkali consists of cuminic acid. Menthane apparently yields a mixture of naphthenic and polynaphthenic acids.

These results are discussed in relation to the structure of the benzene nucleus (compare Obermiller, *Abstr.*, 1907, i, 200; Vidal, *Abstr.*, 1907, i, 1020). T. H. P.

Catalytic Reactions at High Temperatures and Pressures.

XIX. Reduction of Aromatic Acids in Presence of Nickel Oxide and Cupric Oxide. WLADIMIR N. IPATIEFF (*Ber.*, 1909, 42, 2097—2102).—Since aromatic acids are not reduced by hydrogen in presence of cupric oxide, whilst ethylene linkings are so reduced (this vol., i, 499), it should be possible to reduce a double linking in the side-chain of an aromatic acid in this way. This is confirmed by experiments with cinnamic acid. Sodium cinnamate is reduced in presence of nickel oxide at 300° to β -*cyclohexylpropionic* acid, whilst in presence of cupric oxide, β -phenylpropionic acid is obtained quantitatively. With copper as the catalyst, the reaction is incomplete, the product being a mixture of cinnamic and β -phenylpropionic acids.

The naphthoic acids require a higher temperature than benzoic acid. β -Naphthoic acid at 360° yields chiefly tetrahydro- β -naphthoic acid with nickel oxide as catalyst. When the reaction is repeated, a mixture of decahydro- β -naphthoic acid and decahydronaphthalene is obtained. α -Naphthoic acid yields tetrahydronaphthalene.

C. H. D.

Action of Iodine on Silver Benzoate and Salicylate.

NIKOLAI N. BUNGE (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 455—460).—It has been shown by Simonini (*Abstr.*, 1893, i, 391) that at temperatures below 70° the interaction of iodine and the silver salt of a fatty acid gives rise to a compound of the anhydride of the acid with silver hypoiodite, thus: $2R\cdot CO_2Ag + I_2 = AgI + (R\cdot CO)_2O, AgIO$.

The author finds that silver benzoate and iodine yield a similar compound, $Bz_2O, AgIO$, which was isolated in an almost pure condition. This compound is only formed in entire absence of water, which decomposes it into benzoic acid and silver iodide and iodate. On heating, it decomposes rapidly, with evolution of carbon dioxide and organic products, silver iodide with a small admixture of silver being found in the residue.

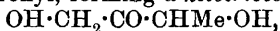
With silver salicylate, no such compound was obtainable.

T. H. P.

Dimethylketol. II. Conversion into a Ketotriose.

OTTO DIELS and ERICH STEPHAN (*Ber.*, 1909, 42, 1787—1792. Compare *Abstr.*, 1907, i, 1000).—The benzoyl derivative of dimethylketol can be brominated without difficulty so as to introduce one or two atoms of bromine; both these enter the same methyl

group, forming the compounds (1) $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{O}\cdot\text{COPh}$ and (2) $\text{CHBr}_2\cdot\text{CO}\cdot\text{CHMe}\cdot\text{O}\cdot\text{COPh}$. When cautiously hydrolysed with ice-cold dilute alkali, the benzoyl group is eliminated and the bromine atoms replaced by hydroxyl, forming a *ketotriose*,



and an *osone*, $\text{CHO}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{OH}$. Both these yield the same osazone, identical with that derived from methylglyceraldehyde (compare Wohl and Franck, *Abstr.*, 1902, i, 532). This behaviour establishes the above formula for the dibromide.

Bromobenzoyldimethylketol, prepared by bromination in chloroform solution in sunlight, crystallises in well formed, colourless prisms, m. p. 72—73°, and has a pleasant aromatic odour.

Dibromobenzoyldimethylketol, prepared by bromination with excess of bromine in chloroform solution and warming, forms similar crystals to the monobromo-derivative, and has m. p. 49°.

Dihydroxymethylacetone is obtained as a clear, yellow syrup, which showed signs of crystallising after a time. It tastes, like other methylated sugars, both bitter and sweet, reduces Fehling's solution in the cold, and reacts with phenylhydrazine, forming the osazone, $\text{OH}\cdot\text{CHMe}\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$, m. p. 174°, to a yellow liquid crystallising in especially regularly formed, quadrate, golden crystals. The *acetylbenzoyl* derivative of dihydroxymethylacetone, $\text{OBz}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OAc}$, is obtained by the interaction of bromobenzoyldimethylketol with potassium acetate; it forms stellar aggregates of colourless, pointed needles, m. p. 54.5°.

E. F. A.

Aromatic Compounds with Labile Halogen. FRITZ ULLMANN (*Annalen*, 1909, 366, 79—118).—Investigation of the compounds derived from picryl chloride by replacing a nitro-group by a carboxyl, benzoyl, or sulfoxyl group shows that the mobility of the chlorine atom is not hindered by the introduction of these groups.

It is also found that substituted dinitrohydroxydiphenylamines, like trinitrohydroxydiphenylamine (compare Turpin, *Trans.*, 1891, 59, 72), give rise to derivatives of phenoxazine only, however, when the position 6 is occupied by a substituent; for example, compounds of the annexed type, where $\text{X}=\text{NO}_2$, HSO_3 , or CO_2H , are not converted into phenoxazine derivatives when acted on by alkalis, although 2 : 6 - dinitro - 6' - hydroxydiphenylamine, when similarly treated, yields 5-nitrophenoxazine.

Derivatives of phenothiazine may be prepared in the manner originally employed by Kehrman (Abstr., 1900, i, 61).

The formation of an azine could only be realised in one case, namely, the preparation of 4-aminophenazine by the reduction of 2 : 4-dinitro-6'-aminodiphenylamine-6-carboxylic acid.

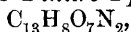
[With GADIENT ENGL.]—I. 2-Chloro-3 : 5-dinitrobenzoic Acid.—3 : 5-Dinitro-2-methylaminobenzoic acid, $\text{C}_8\text{H}_7\text{O}_6\text{N}_3$, prepared by the action of methylamine on 2-chloro-3 : 5-dinitrobenzoic acid, crystallises in orange-yellow needles, m. p. 233°. 3 : 5-Dinitro-2-dimethylamino-

benzoic acid, $C_9H_5O_6N_3$, obtained by similar means, crystallises in long, orange-yellow, prismatic needles, m. p. 185° . The chlorodinitrobenzoic acid, when heated with aniline in alcohol, yields the *aniline salt* of 2:4-dinitrodiphenylamine-6-carboxylic acid, $C_{19}H_{16}O_6N_4$, crystallising in red needles, m. p. 192° ; it readily passes into the yellow modification. 4-Nitro-2-aminodiphenylamine-6-carboxylic acid, $C_{13}H_{11}O_4N_3$, prepared by reducing the corresponding 2:4-dinitro-compound with the calculated quantity of ammonium sulphide, crystallises in glistening, reddish-brown needles, m. p. 221° . It is converted by sodium nitrite and acetic acid into 4-nitrophenaziminobenzene-6-carboxylic acid, $C_{13}H_9O_4N_4$, m. p. 273° .

2:4-Diaminodiphenylamine-6-carboxylic acid, $C_{13}H_{13}O_2N_3$, obtained by reducing the dinitro-compound with excess of ammonium sulphide, forms glistening, yellowish-brown crystals, m. p. $237-238^\circ$ (decomp.).

3:5-Dinitro-2-methoxybenzoic acid, $\begin{matrix} C(NO_2) \cdot CH : C \cdot CO_2H \\ | \\ CH \cdot C(NO_2) : C \cdot OMe \end{matrix}$, prepared by

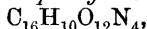
the action of sodium methoxide in methyl alcohol on the chlorodinitrobenzoic acid, crystallises in white, glistening needles, m. p. 165° . The corresponding *ethyl* compound, $C_9H_5O_7N_2$, prepared in a similar manner, has m. p. 133° . 3:5-Dinitro-2-phenoxybenzoic acid,



prepared by heating the chlorodinitrobenzoic acid with sodium phenoxide at $140-165^\circ$, forms colourless crystals, m. p. 150° . It is converted by the action of phosphorus pentachloride in benzene into the *chloride*, which, when treated with aluminium chloride, yields

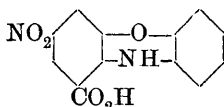
2:4-dinitroanthone, $C_6H_4 \begin{matrix} \diagup CO \\ \diagdown O \end{matrix} C_6H_2(NO_2)_2$, crystallising in pale yellow needles, m. p. 206° .

Methyl 4:6:4':6'-tetranitrodiphenyl-2:2'-dicarboxylate,



prepared by treating methyl 2-chloro-3:5-dinitrobenzoate with copper at $115-140^\circ$, crystallises in almost colourless needles, m. p. 176° ; the *acid*, $C_{14}H_6O_{12}N_4$, crystallises in colourless needles, m. p. about 284° (decomp.).

2:4-Dinitro-2'-hydroxydiphenylamine-6-carboxylic acid, $C_{13}H_9O_7N_3$, obtained by the condensation of 2-chloro-3:5-dinitrobenzoic acid with *o*-aminophenol in the presence of sodium acetate, crystallises in glistening, reddish-brown needles, m. p. 213° . When warmed with aqueous sodium hydroxide, it yields 3-nitrophenoxazine-5-carboxylic



acid (annexed formula), crystallising in orange-red needles, m. p. 295° (decomp.); the *sodium salt*, $C_{13}H_7O_5N_2Na$, forms brownish-red needles; the *ammonium salt* crystallises in glistening, bright red needles.

2:4-Dinitro-2'-aminodiphenylamine-6-carboxylic acid, $C_{13}H_{10}O_6N_4$, obtained by the condensation of 2-chloro-3:5-dinitrobenzoic acid with *o*-phenylenediamine, crystallises in red needles, and is converted by stannous chloride and hydrochloric acid into 4-aminophenazine, m. p. $290-291^\circ$; Fischer gives m. p. 274° (Abstr., 1896, i, 628).

[With NICOLAS WOSNESSENSKY.]—II. 4-Chloro-3:5-dinitrobenzoic

Acid.—The following compounds were obtained by methods similar to those employed in the preparation of the isomeric 2-chloro-compounds.

Methyl 4-chloro-3:5-dinitrobenzoate has m. p. 105° and not 175° as given by Ullmann and Bielecke (Abstr., 1901, i, 586); the *ethyl* ester, $C_9H_7O_6N_2Cl$, has m. p. 83°.

3:5-Dinitro-4-methylaminobenzoic acid, $C_8H_7O_6N_3$, crystallises in yellow needles, m. p. 218°. The corresponding dimethylamino-compound, $C_9H_9O_6N_3$, forms orange-yellow needles, m. p. 246°. 2:6-Dinitro-2'-hydroxydiphenylamine-4-carboxylic acid, $C_{13}H_9O_7N_3$, crystallises in red needles with a metallic lustre, m. p. 216°; it is converted by aqueous sodium hydroxide into 5-nitrophenoxazine-3-carboxylic acid, $C_{13}H_9O_5N_2$, crystallising in violet needles.

4-Chloro-3:5-dinitrobenzoic acid condenses with *o*-aminothiophenol, yielding 2:6-dinitro-2'-thio-oxydiphenylamine-4-carboxylic acid, which crystallises in yellow needles, m. p. 254°, and is converted by a dilute solution of sodium hydroxide into 5-nitrophenothiazine-3-carboxylic acid,

$C_6H_4 \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} C_6H_2(NO_2)_2 \cdot CO_2H$, dark violet, felted needles, m. p. about 316°; the sodium salt forms violet crystals.

4-Chloro-3:5-dinitrobenzophenone, $C_{13}H_7O_5N_2Cl$, prepared by treating a solution of 4-chloro-3:5-dinitrobenzoic acid in benzene with phosphorus pentachloride and subsequently with aluminium chloride, crystallises in yellow rhombohedra, m. p. 118°; it is converted (1) by an aqueous alcoholic solution of sodium hydroxide into 3:5-dinitro-4-hydroxybenzophenone, $C_{13}H_8O_6N_2$, almost colourless needles, m. p. 136°; (2) by aqueous ammonia into 3:5-dinitro-4-aminobenzophenone, $C_{13}H_9O_5N_3$, long, pale-yellow needles, m. p. 148°; (3) by aniline in alcohol into 2:6-dinitro-4-benzoyldiphenylamine, $C_{19}H_{13}O_5N_3$, orange-yellow needles, m. p. 211°; (4) by condensation with *o*-aminophenol into 2:6-dinitro-2'-hydroxy-4-benzoyldiphenylamine, $C_{19}H_{13}O_6N_3$, brick-red crystals, m. p. 220° (decomp.), which is converted by dilute aqueous sodium hydroxide into 5-nitro-3-benzoylphenoxazine,

$C_{19}H_{12}O_4N_2$, glistening, red leaflets, m. p. 216°; (5) by condensation with *o*-aminothiophenol into 2:6-dinitro-4-benzoyl-1-anilino-2'-thiophenol, $C_{19}H_{13}O_5N_3S$, yellow crystals, m. p. 200° (decomp.), which, when treated with dilute alcoholic sodium hydroxide, yields 5-nitro-3-benzoylphenothiazine, $C_{19}H_{12}O_3N_2S$, reddish-violet needles, m. p. 200° (decomp.).

[With EMIL KUHN].—III. 4-Chloro-3:5-dinitrobenzenesulphonic Acid. —Potassium 4-chloro-3:5-dinitrobenzenesulphonate, $C_6H_2O_7N_2SClK$, crystallises in white, glistening scales, m. p. 293°; the sulphonyl chloride, $C_6H_2O_6N_2SCl_2$, forms colourless prisms, m. p. 89°, and is converted by aniline into 2:6-dinitrodiphenylamine-4-sulphonanilide, $C_{18}H_{14}O_6N_4S$, red, felted needles, m. p. 200°. The latter substance is converted by hot dilute aqueous sodium hydroxide into 2:6-dinitrophenol-4-sulphonanilide, $C_{12}H_9O_7N_2S$, crystallising in leaflets with a bronzy reflex, m. p. 177°. The potassium salt above mentioned is converted by dilute aqueous ammonia into potassium 2:6-dinitroaniline-4-sulphonate, $C_6H_4O_7N_3SK$, thin, yellow leaflets, which explode slightly when heated. Potassium 4-chloro-3:5-dinitrobenzenesulphonate reacts with aniline,

yielding *aniline 2:6-dinitrodiphenylamine-4-sulphonate*, $C_{18}H_{16}O_7N_4S$, which crystallises in large, orange-yellow needles, m. p. 252° (decomp.).

Potassium 5-nitrophenoxazine-3-sulphonate, $C_{12}H_7O_6N_2SK$, crystallises in brownish-red needles with a bronzy lustre; it is converted by aniline into the *aniline salt*, $C_{18}H_{15}O_6N_3S$, red needles with a metallic lustre, m. p. 285° (decomp.).

Potassium 5-nitrophenothiazine-3-sulphonate, $C_{12}H_7O_5N_2S_2K$, forms coppery-red crystals.

2:6-Dinitro-2-hydroxydiphenylamine, $C_{12}H_9O_5N_3$, crystallises in fan-shaped groups of long, reddish-violet needles, m. p. 191° ; it is converted by a 1% aqueous solution of sodium hydroxide into *5-nitrophenoxazine*, $C_{12}H_8O_3N_2$, crystallising in violet needles, m. p. 166° .

[With ERICH HERRE.]—IV. *2-Chloro-3:5-dinitrobenzenesulphonic Acid*.—*2-Chloro-5-nitrobenzenesulphonic acid* is converted by a mixture of concentrated nitric acid and fuming sulphuric acid (23% SO_3) into *2-chloro-3:5-dinitrobenzenesulphonic acid*; the *potassium salt*,



crystallises in glistening, white leaflets or needles. The latter substance is converted (1) by ammonia into *potassium 2:4-dinitroaniline-6-sulphonate*, $C_6H_4O_7N_3SK$, crystallising in yellow prisms, which explode slightly when heated; (2) by potassium hydroxide into *potassium 2:4-dinitrophenol-6-sulphonate*, $C_6H_3O_8N_2SK$, pale yellow needles, which explode slightly when heated; the *dipotassium salt*, $C_6H_2O_8N_2SK_2$, forms intensely yellow needles; the *barium salt*,



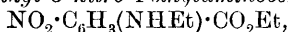
is a yellow, crystalline powder; (3) by aniline into *aniline 2:4-dinitrodiphenylamine-6-sulphonate*, $C_{18}H_{16}O_7N_4S$, glistening, yellow needles.

Sodium 3-nitrophenoxazine-5-sulphonate, $C_{12}H_7O_6N_2SNa$, crystallises in reddish-brown, glistening needles, and is reduced by zinc dust and ammonium chloride, yielding *3-aminophenoxazine-5-sulphonic acid*, $C_{12}H_{10}O_4N_2S$, which crystallises in almost colourless, long, slender needles.

Sodium 3-nitrophenothiazine-5-sulphonate, $C_{12}H_7O_5N_2S_2Na$, crystallises in glistening, brownish-violet needles. W. H. G.

Nitration of *p*-Diethylaminobenzoic Acid. FRÉDÉRIC REVERDIN and A. DE LUC (*Ber.*, 1909, 42, 1725—1730. Compare *Abstr.*, 1906, i, 273; 1907, i, 620; 1908, i, 167).—*3-Nitro-4-ethylaminobenzoic acid* (Baudisch, *Abstr.*, 1907, i, 132) is the chief product obtained by adding *p*-diethylaminobenzoic acid to nitric acid (30%) at 10° , and then allowing the temperature to rise to 25 — 30° . The same product is formed at different temperatures, and also when working in acetic acid solution. Other products formed at the same time are 1:3-dinitro-diethylaniline (van Romburgh, *Rec. trav. chim.*, 1883, 2, 40, 104, 107), 1:3-dinitroethylaniline, and 1:3:5-trinitroethylaniline. In only one experiment was mononitroethylaniline isolated.

Ethyl *p*-diethylaminobenzoate (Folin, *Amer. Chem. J.*, 1887, 9, 331) when nitrated yields *ethyl 3-nitro-4-ethylaminobenzoate*,



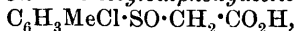
which crystallises in lemon-yellow needles, m. p. 92° . When the nitra-

tion is carried out in acetic acid solution, *ethyl 3:5-dinitro-4-ethylnitrosoaminobenzoate*, $\text{NO} \cdot \text{NEt} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{CO}_2\text{Et}$, lemon-yellow plates, m. p. 72° , and trinitroethylaniline are also formed. When oxidised with nitric acid (D 152) the nitrosoamine yields the corresponding *nitroamine*, $\text{NO}_2 \cdot \text{NEt} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{CO}_2\text{Et}$, which crystallises in colourless, pearly plates, m. p. 96° . With alcoholic potassium hydroxide, it gives a reddish-violet coloration. When boiled with dilute nitric acid, the nitrosoamine yields *3:5-dinitro-4-ethylaminobenzoic acid*.

The ester of the nitroamino-acid when boiled with sodium carbonate solution yields *3:5-dinitro-4-ethylnitroaminobenzoic acid*, which crystallises in pale yellow plates, m. p. 181° .

When the 3-nitro-4-ethylaminobenzoic acid is nitrated in acetic acid solution at 45° with fuming nitric acid, the products are *3:5-dinitro-4-ethylnitrosoaminobenzoic acid*, $\text{NO} \cdot \text{NEt} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{CO}_2\text{H}$, yellow plates, m. p. 152° , *3:5-dinitro-4-ethylaminobenzoic acid*, and *2:4-dinitroethylaniline*.
J. J. S.

[Preparation of Arylsulphoxyacetic Acids.] KALLE & Co. (D.R.-P. 208343).—*p*-Chloro-*o*-tolylsulphoxyacetic acid,

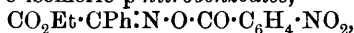


white needles, is obtained by oxidising *p*-chloro-*o*-tolylthiolacetic acid, $\text{C}_6\text{H}_3\text{MeCl} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, with alkaline hypochlorite. The homologues are similarly prepared. When any of these arylsulphoxyacetic acids containing a free ortho-position are treated with chlorosulphonic acid they give rise to vat dyes.
F. M. G. M.

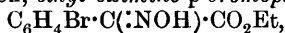
Condensation of Alkyl Nitrates or Nitrites with Ethyl Phenylacetate. WILHELM WISLICENUS and RUDOLF GRÜTZNER (*Ber.*, 1909, 42, 1930—1940. Compare *Abstr.*, 1902, i, 541).—Ethyl nitrate or nitrite does not condense with ethyl acetate, laevulate, or succinate, but successful results have been obtained with a few compounds containing the groups $\cdot\text{CH}_2\text{Ph}$ or $\cdot\text{CH}_2\text{CN}$.

When equal molecular quantities of ethyl nitrate and ethyl phenylacetate, or *ethyl p*-bromophenylacetate, m. p. 30° , b. p. $142\text{—}144^\circ/12\text{—}14\text{ mm.}$, are introduced into a cold alcoholic-etheral solution of potassium ethoxide (1 mol.), the potassium salt of phenylnitromethane or *p*-bromo-*o*-nitrotoluene and ethyl carbonate are formed.

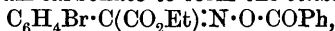
The interaction of equal molecular quantities of ethyl nitrite, ethyl phenylacetate, and potassium ethoxide in cold ethereal solutions yields the yellow, crystalline potassium salt of ethyl oximinophenylacetate, $\text{CO}_2\text{Et} \cdot \text{CPh} \cdot \text{N} \cdot \text{O} \cdot \text{K}$, the cold aqueous solution of which, by acidification, yields Gabriel's ethyl oximinophenylacetate, which is freed from the simultaneously-formed oximinophenylacetic acid (detected by the red coloration with ferric chloride) by removing the latter as the copper salt by distillation in a vacuum or by crystallisation from benzene and light petroleum. The potassium salt reacts with *p*-nitrobenzoyl chloride to form two isomeric *p*-nitrobenzoates,



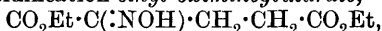
m. p. $112\text{—}113^\circ$ and $137\text{—}138^\circ$ respectively. By the interaction of ethyl nitrite, ethyl *p*-bromophenylacetate, and potassium ethoxide and subsequent acidification, *ethyl oximino-p-bromophenylacetate*,



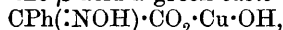
m. p. 159°, is obtained in colourless needles, which reacts with benzoyl chloride and potassium carbonate to form the *benzoate*,



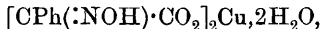
m. p. 90—91°. A benzene solution of succinonitrile and amyl nitrite (2 mols.) reacts with cold alcoholic-etheral potassium ethoxide to form a brown *potassium* salt, from which by acidification $\alpha\beta$ -*dioximino-succinonitrile*, $\text{CN}\cdot\text{C}(\text{:NOH})\cdot\text{C}(\text{:NOH})\cdot\text{CN}$, m. p. 137—138° (decomp.), is obtained, which separates from water in colourless leaflets containing $3\text{H}_2\text{O}$ and melting at 86° to a green liquid. Ethyl nitrite, potassium ethoxide, and ethyl α -acetoglutarate react in cold alcoholic-etheral solution to form, by elimination of ethyl acetate, a *potassium* salt, which yields by acidification *ethyl oximinoglutarate*,



m. p. 62—63°, which is also obtained from nitrosylsulphuric acid and ethyl α -acetoglutarate in concentrated sulphuric acid, and on hydrolysis yields Wolff's α -oximinoglutaric acid. The copper salts of the α - and the β -forms of oximinophenylacetic acid, described by Hantzsch, are basic salts; a solution of copper acetate or sulphate precipitates from an ethereal solution of the β -acid a green *basic copper* salt,



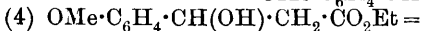
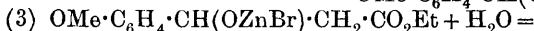
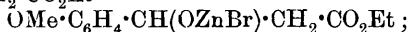
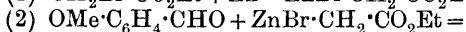
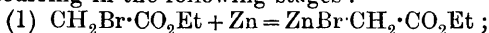
which reacts with the free acid to form the blue *normal* salt,



which is violet when anhydrous.

C. S.

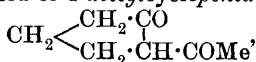
Synthesis of Methoxycinnamic Acid. NIKOLAI N. BUNGE (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 460—463).—The action of zinc on a mixture of ethyl bromoacetate and anisaldehyde (compare Andriewsky, *Abstr.*, 1908, i, 799) gives rise to ethyl methoxycinnamate (compare Vorländer, *Abstr.*, 1897, i, 272), the reaction occurring in the following stages:



T. H. P.

Ring Formation in Ketonic Acids. EDMOND É. BLAISE and A. KOEHLER (*Compt. rend.*, 1909, 148, 1401—1404. Compare this vol., i, 204).—The authors give an account of the conversion of the esters of ϵ - and δ -ketonic acids into cyclic compounds.

On treating the ethyl ester of heptan- ϵ -onoic acid with sodium ethoxide an excellent yield of 1-acetylcyclopentan-2-one,



is obtained. This has b. p. 75°/8 mm. and shows the reactions of a β -diketone. On ethylation it yields 1-acetyl-1-ethylcyclopentan-2-one, $\text{C}_9\text{H}_{15}\text{O}_2$, b. p. 97—99°/15 mm.; sodium ethoxide converts this into the *ethyl* ester of δ -ethylheptan- ϵ -onoic acid, $\text{COMe}\cdot\text{CHEt}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{Et}$,

b. p. 134—136°/14 mm. 1-Propionylcyclopentan-2-one, $C_8H_{12}O_2$, prepared from the ethyl ester of octan-ε-onoic acid, has b. p. 90°/13 mm. The *methyl* and *ethyl* derivatives of this diketone have also been prepared.

Propionylcyclohexanone, $CH_2 < \begin{smallmatrix} CH_2-CO \\ CH_2-CH_2 \end{smallmatrix} > CH \cdot COEt$, b. p. 122—123°/21 mm., is prepared from the ethyl ester of octan-ζ-onoic acid. Owing to the ease with which the ring is opened, alkylation of the acidylcyclohexanones leads to the formation of a mixture of the alkylacidylcyclohexanone with the original ketonic ester.

The authors have not succeeded in preparing cyclic compounds from η-ketonic esters. W. O. W.

Reduction of αβ-Unsaturated Ketones and Aldehydes. ALADAR SKITA (*Ber.*, 1909, 42, 1627—1636).—Usually αβ-unsaturated alicyclic ketones when treated with mild reducing agents give bimolecular ketones; with stronger agents the ketonic group is reduced as well as the ethenoid linking, and in a number of instances further complications ensue. It has been found that reduction of the ethenoid linking takes place readily without these complications when the substance in alcoholic solution is mixed with an aqueous solution of palladium chloride and gum arabic and the resultant solution exposed to hydrogen gas. *iso*Phorone is transformed into dihydroisophorone in 82% yield in two hours; ethyl 1-methyl-Δ¹-cyclohexene-3-one-6-carboxylate gives a 94% yield of the ethyl 1-methylcyclohexane-3-one-6-carboxylate, the oxime hydrochloride of which was analysed. Ethyl 1:3-dimethyl-Δ³-cyclohexenone-5-carboxylate gave ethyl 1:3-dimethylcyclohexanone-5-carboxylate, $C_{11}H_{18}O_3$, b. p. 133—135°/12 mm.; the oxime, $C_{11}H_{19}O_3N$, is an oil. Ethyl isophorone-carboxylate on reduction gave both modifications of ethyl dihydroisophoronecarboxylate (*Abstr.*, 1907, i, 1041), and phorone itself gave diisobutylcarbinol (*Grignard, Abstr.*, 1901, i, 679).

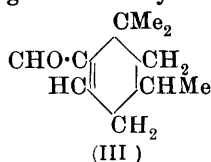
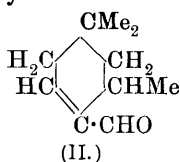
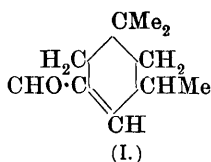
The aliphatic αβ-unsaturated aldehyde citral gave by Sabatier's method a series of cyclic compounds (*Enklaar, Abstr.*, 1908, i, 664), but palladium gives quite different results; 2 atoms of hydrogen are absorbed, and citronellal and citronellol are obtained together with an oil, b. p. 139—140°/15 mm., m. p. 57°. It is a bimolecular aldehyde,

probably $CMe_2 \cdot CH \cdot [CH_2]_2 \cdot CHMe \cdot CH \cdot CHO$
 $CMe_2 \cdot CH \cdot [CH_2]_2 \cdot CHMe \cdot CH \cdot CHO$ β-cycloCitral gave
 2:2:6-trimethylhexahydrobenzaldehyde on reduction. W. R.

Synthesis of Violet Perfumes. I. GEORG MERLING and ROBERT WELDE [in part, HEINRICH EICHWEDE and ALADAR SKITA] (*Annalen*, 1909, 366, 119—216).—An account of the authors' work on the synthesis of violet perfumes, the experimental part of which treats, however, only of the preparation and properties of some of the intermediate compounds obtained in the synthesis of α- and β-irone (compare Tiemann, *Abstr.*, 1894, i, 80; 1898, i, 376).

With the object of obtaining information on the relationship existing between the constitution of a substance and its odour, the following aldehydes were prepared (compare *Abstr.*, 1903, i, 502, 764; 1905, i, 653)

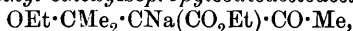
and their condensation products with acetone examined. As a result, it is found that the aldehydes derived from *cyclogeraniolenes* yield



products with acetone having an odour of violets when the aldehyde group is situated next to a methyl group or dimethyl group or between these groups; in the latter case the odour is exceedingly intense. The character of the acetone condensation product as a perfume disappears when the aldehyde group does not adjoin a methyl group.

The grouping $-\text{CMe}_2 \cdot \text{C}(\text{CHO}) \cdot \text{CMe}_2 <$ does not lead to the production of violet perfumes unless present in the *cyclogeraniolene* ring; for example, the condensation product of β -isopropylbutaldehyde with acetone does not smell like violets.

I. *Ethyl isoPropylideneacetoacetate*.—This ester combines with sodium ethoxide, yielding *ethyl ethoxyisopropylsodioacetoacetate*,



obtained as colourless, felted needles. It is a very unstable substance, being converted by carbon dioxide in aqueous solution into *ethyl ethoxyisopropylacetoacetate*, part ($\frac{1}{5}$) of which decomposes, yielding ethyl dimethylacrylate and ethyl acetate, whilst the remainder yields ethyl *isopropylideneacetoacetate* and alcohol. The sodium compound, when treated with methyl iodide in the absence of alcohol, yields ethyl trimethylacrylate, and, when acted on by an alcoholic solution of ethyl iodide, yields ethyl ether, ethyl acetate, ethyl dimethylacrylate (90%), ethyl *isopropylideneacetoacetate*, and an oil, b. p. above $93^\circ/7$ mm.

II. *Ethyl isoPhoronecarboxylate*.—An account of the preparation and properties of this compound has appeared previously (Abstr., 1905, i, 349). Contrary to the view advanced by Rabe (Abstr., 1906, i, 89), it is shown that this ester exists in a ketonic and enolic form. The pure *keto*-modification is a colourless oil, b. p. $135\text{--}142^\circ/10\cdot5\text{--}12$ mm.; the *enol*-form could not be isolated in a pure state. Ethyl *isophoronecarboxylate* is converted by sodium ethoxide and ethyl iodide into *ethyl isophoronecarboxylate ethyl ether*, $\begin{array}{c} \text{CH} \cdot \text{CMe}_2 \cdot \text{CH} \cdot \text{CO}_2\text{Et} \\ | \quad \quad | \\ \text{C}(\text{OEt}) \cdot \text{CH} \cdot \text{CMe} \end{array}$, a colourless oil, b. p. $136\text{--}137^\circ/8$ mm. An ethyl group is undoubtedly attached to oxygen in this compound, since it is hydrolysed by barium hydroxide solution, yielding *isophorone*.

III. *Reduction of Ethyl isoPhoronecarboxylate*.—The reduction of ethyl *isophoronecarboxylate* with sodium and alcohol leads to the production of a mixture of four stereoisomeric ethyl 4-hydroxycyclogeraniolanecarboxylates and the corresponding hydroxy-carbinols, the esters of two stereoisomeric hydroxy-acids, isomeric with 4-hydroxycyclogeraniolanecarboxylic acid, but probably containing a five-membered ring system, and small quantities of other substances.

A *hydroxycarbinol*, $\begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \\ | \quad \quad | \\ \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CHMe} \end{array}$, was isolated in a state of purity from the mixture obtained in the manner just described;

it crystallises in glistening prisms, m. p. 92—93°, b. p. 152°/8 mm.; the *diacetyl* derivative, $C_{14}H_{24}O_4$, is a colourless, odourless, viscid oil, b. p. 148—153°/10 mm.; the *oxalyl* derivative, $C_{12}H_{18}O_4$, is a colourless, crystalline powder, m. p. 248°.

IV. *Stereoisomeric 4-Hydroxycyclogeraniolane-carboxylic Acids* (2 : 6 : 6-Trimethyl-4-cyclohexanocarboxylic Acids).—*cis*-4-Hydroxy- α -cyclogeraniolane-carboxylic acid, $C_{10}H_{18}O_3$, crystallises in large, thin, iridescent scales, m. p. 145°; it changes into the *trans*-modification when kept, and, when distilled in a vacuum, is largely converted into the *trans*-form, yielding at the same time a small quantity of the lactone. The *ethyl* ester cannot be obtained in a pure state, since it partly breaks down into lactone and alcohol when distilled in a vacuum; the ester obtained after distillation is a colourless, viscid oil, b. p. 140—147°/11 mm. The *acetyl* derivative, $C_{12}H_{20}O_4$, crystallises in glistening prisms, m. p. 121—122°, and is converted by thionyl chloride into the *chloride*, $C_{12}H_{19}O_3Cl$, a colourless, limpid oil, b. p. 129—131°/8 mm. The *lactone*, $C_{10}H_{16}O_2$, crystallises in glistening, thick plates, m. p. 57·5—58°, b. p. 114·5°/6 mm., 119·5°/7 mm.

trans-4-Hydroxy- α -cyclogeraniolane-carboxylic acid crystallises in glistening prisms, m. p. 154—155°, b. p. 189—190°/7·5 mm.; it is converted into the *cis*-isomeride, and subsequently into the lactone, when distilled with potassium hydrogen sulphate at 116—134°/8·5 mm. and when boiled with 30—40% sulphuric acid. It yields the *acetyl* derivative just described when treated with acetic anhydride and a drop of concentrated sulphuric acid. The *ethyl* ester, $C_{12}H_{22}O_3$, is obtained as a silky, crystalline mass, b. p. 136·5°/7 mm., 134°/6 mm., 139°/8 mm.

Ethyl 4-chloro-2 : 6 : 6-trimethylcyclohexane-1-carboxylate, $C_{12}H_{21}O_2Cl$, obtained by the action of phosphorus pentachloride on the ester just described, is a colourless, odourless, limpid oil, b. p. 111—112°/6·5 mm.; the corresponding *bromo*-derivative, $C_{12}H_{21}O_2Br$, has b. p. 125—128°/6 mm.

cis-4-Hydroxy- β -cyclogeraniolane-carboxylic acid forms small, glistening crystals, m. p. 157—158°, b. p. 179·5°/7 mm. It decomposes at 240° into water and *lactone*, $C_{10}H_{16}O_2$, obtained as small, glistening crystals, m. p. 37—39°, b. p. 121·5°/5 mm., 127°/7 mm., 129°/8 mm., 134°/9·5 mm. The *acetyl* derivative, $C_{12}H_{20}O_4$, crystallises in glistening prisms, m. p. 143—144°. The *ethyl* ester, $C_{12}H_{22}O_3$, is a colourless, odourless, viscid oil, b. p. 136·5°/5 mm.

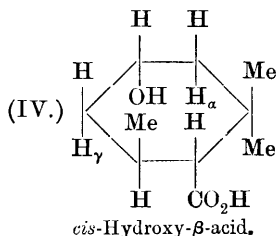
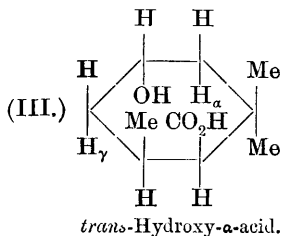
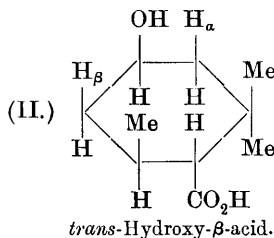
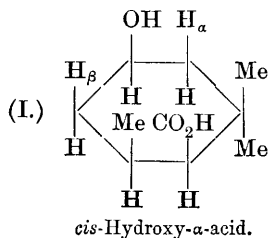
trans-4-Hydroxy- β -cyclogeraniolane-carboxylic acid forms small, colourless crystals, m. p. 151—152°, b. p. 176—177°/5 mm. It decomposes slowly at 300°, yielding the lactone, m. p. 37—39°, and is partly converted by heating for four hours with 40% sulphuric acid into the *cis*-form, which passes into Δ^3 -cyclogeranic acid. The *acetyl* derivative, $C_{12}H_{20}O_4$, crystallises in rosettes of colourless prisms, m. p. 110—111°. The *ethyl* ester is a colourless, viscid oil, b. p. 124°/5 mm. It is possible to convert *cis*-4-hydroxy- α -cyclogeraniolane-carboxylic acid into *trans*-4-hydroxy- β -cyclogeraniolane-carboxylic acid by the following series of changes. The *acetyl* derivative of the former compound is acted on by phosphorus pentachloride, and the *chloride* so formed decomposed by water. The *acetylated* acid thus obtained, when hydrolysed with alcoholic potassium hydroxide, yields the *trans*- β -compound.

Ethyl 4-keto- α -cyclogeraniolancarboxylate, $C_{12}H_{20}O_3$, obtained by oxidising the corresponding *cis*- or *trans*-hydroxy- α -compound, is a colourless, crystalline mass, and has b. p. $124^\circ/7$ mm., $119^\circ/6$ mm.; the *oxime*, $C_{12}H_{21}O_3N$, crystallises in glistening prisms, b. p. 148 — $156^\circ/6$ mm.; it does not melt at a constant temperature (99 — 117°); when reduced with sodium and alcohol it yields ethyl 4-amino-2:6:6-trimethylcyclohexancarboxylate (compare Skita, Abstr., 1907, i, 1040), b. p. 114 — $115^\circ/6$ mm. The latter substance when treated successively with methyl iodide and methyl-alcoholic potassium hydroxide yields the *iodide*, $C_{15}H_{30}O_2NI$; the corresponding *hydroxide* decomposes to a slight extent at 235° into trimethylamine and ethyl Δ^3 -cyclogeranate, but chiefly into methyl alcohol and *ethyl 4-dimethylamino-2:6:6-trimethylcyclohexane-1-carboxylate*, $C_{14}H_{27}O_2N$, a colourless oil b. p. 115 — $116^\circ/6$ mm. *Ethyl 4-keto- β -cyclogeraniolancarboxylate* is a colourless, viscid oil, b. p. $130^\circ/7$ mm. The *oxime*, obtained in the same manner as the α -compound, crystallises in glistening prisms and needles, m. p. 89 — 90° .

4-Keto- α -cyclogeraniolancarboxylic acid, $C_{10}H_{16}O_3$, cannot be prepared by hydrolysing the ester. It is obtained by oxidising the 4-hydroxy- α -acid, and crystallises in glistening prisms, m. p. 127 — 128° , b. p. 174 — $175^\circ/7$ mm. *4-Keto- β -cyclogeraniolancarboxylic acid*, prepared in a similar manner, forms glistening prisms, m. p. 118 — 120° , b. p. 174 — $175^\circ/7$ mm.

The esters of the above keto-acids condense with benzaldehyde in the presence of sodium ethoxide, yielding chiefly the *monobenzylidene* derivative, $C_{12}H_{18}O_2 \cdot CHPh$, a pale yellow oil, b. p. 200 — $202^\circ/5$ mm., whilst a mixture of mono- and di-benzylidene derivatives is obtained when hydrogen chloride is the condensing agent. The *dibenzylidene* compound could not be obtained in a pure condition.

V. *Configuraton of the Stereoisomeric 4-Hydroxycyclogeraniolancarboxylic Acids*.—This part of the paper is devoted to the deduction of the space formulæ of the 4-hydroxy-2:6:6-trimethylcyclohexane-1-carboxylic acids.—The following formulæ are assigned to the four acids:



In agreement with these formulæ are the following facts: (1) The acids (I) and (III) yield the same keto-acid when oxidised; the same also applies to the acids (II) and (IV). (2) The esters of the β -acids (II) and (IV) are hydrolysed with greater ease than the corresponding α -compounds, probably because of the steric hindrance produced by the two adjacent methyl groups in the latter case. (3) Water is eliminated from the acids (I) and (II) with exceedingly great difficulty, and only then after rearrangement into the other forms. On the contrary, water is eliminated from the acids (III) and (IV) with great readiness. In these two acids, the hydrogen atom (H_γ), which is in the same plane as the hydroxyl group with which it combines, is not influenced by a neighbouring methyl group as in the acids (I) and (II) (H_β). (4) Elimination of water from all four acids leads to the formation of the two stereoisomeric modifications of Δ^3 -cyclogeranic acid. A Δ^4 -cyclogeranic acid is not produced, owing to the hindering influence of the adjacent methyl group on the hydrogen atom H_α .

VI. *Stereoisomeric Methylisopropyl-3-cyclopentanolcarboxylic Acids* (?).—It is probable that the esters of these two acids present to the extent of 10% in the product obtained by reducing ethyl isophoronecarboxylate are stereoisomeric ethyl 5-methyl-1-isopropyl-3-cyclopentanol-1-carboxylates, $\text{CH}_2 \begin{matrix} \text{CH(OH) \cdot CH}_2 \\ \text{CHMe} - \text{CPr}_\beta \cdot \text{CO}_2\text{Et} \end{matrix}$, but confirmation of this is lacking. They are therefore designated provisionally *cis*-hydroxy-acid C and *trans*-hydroxy-acid C.

cis-Hydroxy-acid C, $\text{C}_{10}\text{H}_{18}\text{O}_3$, crystallises in glistening prisms or slender needles, m. p. $137-138^\circ$; it dissociates into water and lactone at $1-2^\circ$ above its m. p., also when boiled for a short time with 10% sulphuric acid. The ethyl ester is a colourless, viscid oil, which at $103.5-114^\circ/6$ mm. breaks down completely into alcohol and lactone. The lactone, $\text{C}_{10}\text{H}_{16}\text{O}_2$, forms large, glistening, brittle crystals, m. p. $43-44^\circ$, b. p. $112-113^\circ/7$ mm., $246^\circ/760$ mm.

trans-Hydroxy-acid C, $\text{C}_{10}\text{H}_{18}\text{O}_3$, crystallises in large, glistening prisms, m. p. $185-186^\circ$, b. p. $192^\circ/8$ mm. It passes at $270-280^\circ$ into the *cis*-form, which at once breaks down into water and lactone; the ethyl ester, $\text{C}_{12}\text{H}_{22}\text{O}_3$, is a colourless, viscid oil, b. p. $129.5^\circ/6$ mm.

Either of the esters just described when oxidised yields the ethyl ester of the keto-acid, $\text{C}_{12}\text{H}_{20}\text{O}_3$, a colourless, odourless, viscid oil, b. p. $123^\circ/7$ mm.; the oxime crystallises in colourless, crystalline nodules, m. p. $118-120^\circ$. The acid, $\text{C}_{10}\text{H}_{16}\text{O}_3$, crystallises in rosettes of needles, m. p. $123-124^\circ$; the barium salt forms flat, spear-shaped crystals; the dibenzylidene derivative, $\text{C}_{26}\text{H}_{28}\text{O}_3$, crystallises in slender, yellow needles, m. p. $112-114^\circ$. W. H. G.

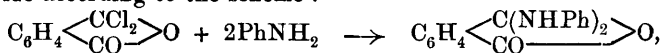
Amine Salts of Phthalamic, Phenylphthalamic, and Phenylsuccinamic Acids. SHIGERU KOMATSU' (*Mem. Coll. Sci. Eng. Kyōto*, 1908, 1, 431-436).—Aniline *o*-sulphanilinobenzoate has been obtained by Remsen and Kohler (*Abstr.*, 1895, i, 473), and aniline benzanilinosulphonate and toluidine benztoluidinosulphonate by Sohn (*Abstr.*, 1898, i, 428); but hitherto the amine salts of phenylphthalamic acid have not been obtained. The author has succeeded in preparing these by mixing absolute alcoholic solutions of amine and acid, and leaving the mixture for some days. *Aniline phenylphthamate*,

$\text{NHPH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{NH}_3\text{Ph}$, forms white, hexagonal crystals, m. p. $124-125^\circ$, which are decomposed by alkali or acid, or on heating in alcoholic or aqueous solution, into aniline and phenylphthalimide; the *methylamine* salt, colourless needles, m. p. 115° ; the *β -naphthylamine* salt, a white, crystalline precipitate, m. p. $170-173^\circ$, and the *benzylamine* salt, colourless needles, m. p. $138-139^\circ$, behave similarly. *Methylamine phthalamate* consists of colourless needles, m. p. $146-148^\circ$; *aniline phthalamate*, $\text{CONH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{NH}_3\text{Ph}$, has m. p. $185-187^\circ$.

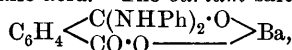
Methylamine phenylsuccinamate, $\text{CONHPh}\cdot\text{C}_2\text{H}_4\cdot\text{CO}_2\text{NH}_3\text{Me}$, forms colourless needles, m. p. $115-120^\circ$. E. H.

Isomeric Phenylphthalimides and Some Allied Compounds.

MITSURU KUHARA and SHIGERU KOMATSU (*Mem. Coll. Sci. Eng. Kyōto*, 1908, 1, 391—405).—By the action of aniline on phthalyl chloride, Fukui and Kuhara (*Abstr.*, 1902, i, 34) obtained an *as*-phenylphthalimide. Hoogewerff and van Dorp (*Abstr.*, 1903, i, 174), and also Dunlap and Cummer (*Abstr.*, 1903, i, 699), failed, however, to obtain the latter compound, and the former authors claim that the product of the reaction is a mixture of phthalanilide and *N*-phenylphthalimide, and that van der Meulen's phthalophenylisoimide (*Abstr.*, 1897, i, 281) is really *as*-phenylphthalimide. The present authors, repeating Kuhara and Fukui's experiments, have failed to isolate the substance described by them. When solutions of phthalyl chloride (1 mol.) and aniline (4 mols.) in 95% alcohol, each cooled at -10° , are mixed, phthalanilide is precipitated. The filtrate, after a time, deposits *N*-phenylphthalimide and a white, crystalline precipitate of *as*-dianilinophthalic acid, $\text{C}_{20}\text{H}_{18}\text{O}_3\text{N}_2$, m. p. $175-176^\circ$. Although the latter compound, which behaves as a dibasic acid, has the composition corresponding with hydrated phthalanilide, it is never formed from phthalanilide by the action of water. It seems probable that it is formed by the hydration of the lactonic *as*-phthalanilide, which could be formed from *as*-phthalyl chloride according to the scheme :

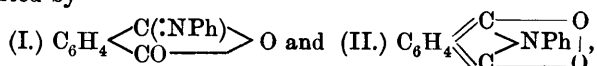


and hence would have the constitution $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NHPH})_2\cdot\text{OH}$. This view is supported by the fact that when heated in dry chloroform with phosphorus pentachloride, it gives a mixture of *N*-phenylphthalimide and von Gerichten's phthaldianil, $\text{C}_6\text{H}_4\left\langle\begin{array}{c}\text{C}(\text{NPh})_2 \\ \text{CO}\end{array}\right\rangle\text{NPh}$ (*Abstr.*, 1880, 473), which is also obtained when *N*-phthalanilide is treated with the same dehydrating agent (compare Remsen, *Abstr.*, 1897, i, 244; Henderson, *Abstr.*, 1901, i, 208). *as*-Dianilinophthalic acid is an unstable substance, decomposing into aniline and *N*-phenylphthalimide when treated with hot alcohol, acetic acid, or alkali, or on heating alone at 100° . It is split up by hot hydrochloric acid into aniline, *N*-phenylphthalimide, and phthalic acid. The *barium* salt,



forms a slightly yellow, crystalline precipitate; the *silver* salt, $\text{CO}_2\text{Ag}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NHPH})_2\cdot\text{OAg}$, a white, crystalline precipitate. The authors made repeated attempts to obtain van der Meulen's phthalophenylisoimide, but without success. When phenylphthalamic acid is

treated with acetyl chloride, a pale yellow substance is produced, having a variable m. p. (93—125°). From this, colourless needles, m. p. 83—84°, of a substance, $C_{14}H_9O_2N$, can be isolated, which is isomeric, but not identical, with either *n*-phenylphthalimide or Kuhara and Fukui's *as*-phenylphthalimide. To it the authors assign the name *β-as-phenylphthalimide*. The pale yellow substance on recrystallisation also gives amber-coloured, rhombic prisms, m. p. 125—126°, of a second *isomeride* of phenylphthalimide, also different from the *as*-phenylphthalimide and phthalophenylisomide. *β-as*-Phenylphthalimide in ethereal solution readily changes into *N*-phenylphthalimide. The latter is formed, together with aniline and phthalic acid, when the amber-coloured isomeride in acetic acid solution is heated at 120°. The possible formulæ of isomeric phenylphthalimides can be represented by



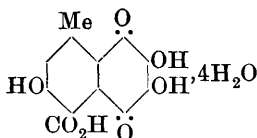
of which (I) can exist in two stereoisomeric forms. Owing to its colour and the fact that (like phthalylperoxide) crystals of it gently detonate on sudden heating, the second formula is suggested for the amber-coloured isomeride. The *β-as*-phenylphthalimide is supposed to have one of the two stereoisomeric forms, and either Kuhara and Fukui or van der Meulen's compound, the other. Possibly, however, van der Meulen's phthalophenylisomide is the pale yellow compound described above, that is, a mixture of two isomerides, particularly as this author gives the m. p. 115—116°, whilst Hoogewerff and van Dorp give 120—122°.

E. H.

Synthesis of Ethyl *p*-Orsellate. ANDREAS LIPP and E. SCHELLER (*Ber.*, 1909, 42, 1967—1972. Compare this vol., i, 451).—In the preparation of hexan-ε-one-β-ol, alcoholic ethyl sodioacetoacetate and propylene bromide are heated in a sealed vessel on the water-bath, the alcohol is removed by distillation, the residue is washed with water, and the insoluble oil is repeatedly shaken with dilute potassium hydroxide. The combined aqueous and alkaline washings when acidified with sulphuric acid deposit after some weeks a substance which is proved to be ethyl *p*-orsellate (Senhofer and Brunner, *Abstr.*, 1881, 265) by its conversion, by boiling 10% potassium hydroxide and subsequent acidification, into orcinol (*dibenzoate*, $C_6H_3Me(O \cdot COPh)_2$, m. p. 86—87°).

C. S.

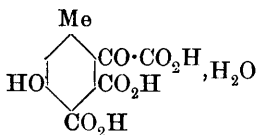
Carminic Acid. OTTO DIMROTH (*Ber.*, 1909, 42, 1611—1627, 1735).—This communication deals largely with a re-investigation of the oxidation products of carminic acid with a view to establish its constitution. When an aqueous solution of this acid at 0° is treated with sulphuric acid and potassium permanganate, 7—8 equivalents of oxygen are used up in oxidising it.



This solution on heating for three-quarters of an hour at 90° evolves carbon dioxide, and the ether extract gives *carminazarin*, annexed

formula, which crystallises from water in garnet-red needles, decomp.

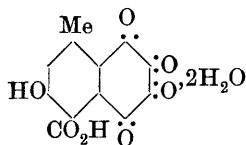
240—250°. The *potassium* salt, $C_{12}H_7O_7K$, is violet. It is very similar to *isonaphthazarin* in its behaviour; its alkaline solution turns quickly to 5:6-dicarboxy-4-hydroxy-o-tolyl glyoxylic acid, annexed formula, when a stream of oxygen is passed through the solution at 70°; it crystallises in colourless needles, m. p. 230° (decomp.); phenylhydrazine gives the phenylhydrazine salt of the *phenylhydrazone*, $C_{23}H_{22}O_7N_4$, which forms almost colourless leaflets. When heated with sulphuric acid, this dicarboxylic acid forms cochinelic acid and carbon dioxide.



5:6-dicarboxy-4-hydroxy-o-tolyl glyoxylic acid, annexed formula, when a stream of oxygen is passed through the solution at 70°; it crystallises in colourless needles, m. p. 230° (decomp.); phenylhydrazine gives the phenylhydrazine salt of the *phenylhydrazone*,

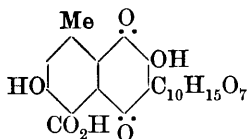
$C_{23}H_{22}O_7N_4$, which forms almost colourless leaflets. When heated with sulphuric acid, this dicarboxylic acid forms cochinelic acid and carbon dioxide.

Another similarity to *isonaphthazarin* is the behaviour of *carminazarin* towards nitric acid in glacial acetic acid, the tetraquinone, *carminazarinquinone*, annexed formula, being obtained; this forms almost colourless prisms, and when heated with water or acetic acid passes back into *carminazarin*. The aqueous solution is turned first yellowish-brown by alkalis, then green, and finally blue.



The intermediate compound formed in the oxidation of *carminic* acid by permanganate at 0° is best observed when the barium salt is used; an almost colourless barium salt is finally obtained, which yields an almost colourless acid, $C:O:H = 1:0.94:1.75$. It is believed to be of the nature of a α -hydroxy- α -carboxylic acid, which would therefore readily pass into the *carminazarin*.

Carminic acid when oxidised in acetic acid with manganese dioxide gives *carminoquinone*, which has not been isolated, but regenerates the parent acid on reduction with sulphur dioxide.



Carminic acid is considered not to be a symmetrical compound, but to have the annexed constitution, the nature of the $C_{10}H_{15}O_7$ group remaining to be determined. W. R.

Alkylated Carminic Acids. CARL LIEBERMANN and HANS LIEBERMANN (*Ber.*, 1909, 42, 1922—1930).—A paper published in consequence of Dimroth's recent reference to dimethylcarminic acid (preceding abstract).

Carminic acid, which is not esterified by alcoholic hydrogen chloride, yields with methyl sulphate and 10% potassium hydroxide only a red, crystalline *dimethoxy*-derivative, $C_{22}H_{20}O_{11}(OMe)_2$; the acid and silver oxide moistened with ether form with methyl iodide a mixture of the *pentamethoxy*- and the *hexamethoxy*-derivatives, $C_{22}H_{17}O_8(OMe)_5$ and $C_{22}H_{16}O_7(OMe)_6$, which have respectively an orange and a yellow colour, and are separated by the solubility of the former in 1% sodium hydroxide.

Dealkylation of the preceding ethers by concentrated hydrochloric acid at 70° yields the red *tetramethoxy*-compound, $C_{22}H_{18}O_9(OMe)_4$. The presence of the methoxyl in place of the hydroxyl groups has the usual effect of decreasing the solubility of the ethers in water, and

diminishes the colour intensity; the di- and tetra-methoxy-derivatives alone form lakes.

An almost complete dealkylation of the ethers is effected by hydrobromic acid, D 1.49, at 95—100°, the product being the anhydrocarminic acid, which is obtained by heating carminic acid alone at 150° (Abstr., 1898, i, 682), or with hydrobromic acid at 100°. By treatment with silver oxide and methyl iodide, anhydrocarminic acid yields a brownish-red *tetramethoxy*-derivative, $C_{22}H_{12}O_6(OMe)_4$, which is insoluble in alkalis.

One probable result of the oxidation of carminic acid to carminazarin (Dimroth, *loc. cit.*) will be the rejection of the bisindone formula of the former; this is not a necessary consequence, however, for even if carminazarin eventually proves to be a naphthalene derivative, its formation from an indone compound is not without analogy in the conversion of indones into naphthalene derivatives. The authors point out that the formula of carminic acid suggested by C. Liebermann and Voswinkel (Abstr., 1904, i, 903) receives support from the discovery of carminazarin; they are inclined to retain the indone formula for α - and β -bromocarmin (Abstr., 1897, i, 539). C. S.

Benzoylacrylic Acid. Condensation of Glyoxylic Acid with Certain Ketones. J. BOUGAULT (*Compt. rend.*, 1909, 148, 1270—1272. Compare Abstr., 1908, i, 796; this vol., i, 102).—The fixation of acetophenone by benzoylacrylic acid, whereby diphenacylacetic acid is produced, is not due to direct combination, as previously supposed, but arises from the decomposition of benzoylacrylic acid into acetophenone and glyoxylic acid, followed by condensation of 2 mols. of the former with 1 mol. of the latter. This is supported by the observation that α -hydroxy- β -benzoylpropionic acid gives diphenacylacetic acid under the same conditions. This acid, moreover, is obtained in excellent yield by allowing a mixture of glyoxylic acid and acetophenone to remain for twenty-four hours in contact with dilute aqueous alkali containing a little alcohol.

The following compounds have been prepared in the same way: *dianisacylacetic acid*, $CH(CH_2 \cdot CO \cdot C_6H_4 \cdot OMe)_2 \cdot CO_2H$, m. p. 112°; *dipiperacylacetic acid*, $CH(CH_2 \cdot CO \cdot C_6H_3 \cdot O_2 \cdot CH_2)_2 \cdot CO_2H$, m. p. 112°.

W. O. W.

Organic Syntheses by means of Sunlight. III. Phenyl *iso*Amyl Ketone and Physical Constants of Compounds of Amylene with Benzaldehyde and Ketones. EMANUALE PATERNÒ and F. TRAETTA-MOSCA (*Gazzetta*, 1909, 39, i, 449—454).—In order to throw light on the constitution of the compound yielded by benzaldehyde and amylenes (β -methyl- Δ^2 -butylene) (this vol., i, 393), the authors have prepared phenyl *iso*amyl ketone from *iso*amyl iodide and benzonitrile by means of the Grignard reaction (compare Blaise, Abstr., 1902, i, 164). The ketone is a transparent liquid, b. p. 255—256°, with a faint aromatic odour, and on cooling solidifies to a white, crystalline mass, m. p. -2° , and is probably identical with the ketone, b. p. 240—241°/720 mm., obtained by Perkin and Calman (Trans., 1886, 49, 166). Its *semicarbazone*, $C_5H_{11} \cdot CPh \cdot N \cdot NH \cdot CO \cdot NH_2$, m. p.

150—151°, and *oxime*, m. p. 71—72°, were prepared, but it was not found possible to obtain the phenylhydrazone. The results show, however, that the compound obtained by Paternò and Chieffi (this vol., i, 393) cannot be regarded as a phenyl amyl ketone, since it does not give the characteristic ketone reactions.

The densities of this compound, and also of phenyl *iso*amyl ketone, have been determined at various temperatures with the following results. (1) Phenyl *iso*amyl ketone: D_4^0 0.9744, D_4^{15} 0.9623, $D_4^{31.3}$ 0.9498, $D_4^{48.5}$ 0.9363, D_4^{100} 0.8925; the molecular volume is hence 180.74 at 0°, 183.0 at 15°, and 230.1 at 255°. (2) Compound obtained from benzaldehyde and amylene: D_4^0 0.9855, $D_4^{15.3}$ 0.9731, $D_4^{41.1}$ 0.9583, $D_4^{54.5}$ 0.9413, $D_4^{99.5}$ 0.9047; molecular volume, 178.7 at 0°, 181.0 at 15°, and 220.5 at 231°. These numbers are in agreement with the general rule, that molecular volumes of ketones are greater than those of non-ketonic compounds.

The non-existence of a carbonyl oxygen in the compound obtained from benzaldehyde and amylene is also supported by the value of the index of refraction.

T. H. P.

New Derivatives of Catechol. I. LAZENNEC (*Bull. Soc. chim.*, 1909, [iv], 5, 501—509).—A continuation of the work of Moureu on catechol derivatives (Abstr., 1899, i, 433, 494, 679, 700). Bromoacetophenone, $\text{COPh}\cdot\text{CH}_2\text{Br}$, condenses with the sodium derivative of catechol in presence of alcohol to form *o*-hydroxyphenoxyacetophenone, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{COPh}$, m. p. 111°, which crystallises from benzene in colourless needles, is readily soluble in alcohol, ether, or chloroform, less so in benzene, and insoluble in water or light petroleum. The *oxime*, m. p. 109°, forms colourless needles from benzene or methyl alcohol; the *hydrazone*, m. p. 91°, separates from a mixture of benzene and light petroleum in small, bright yellow crystals; the *semicarbazone*, m. p. 145.5°, is colourless, and crystallises from methyl alcohol. The *benzoate*, m. p. 136—137°, forms colourless, rectangular tablets from methyl alcohol; the *methyl ether*, m. p. 101°, crystallises from ether in long, colourless needles, and the *ethyl ether*, m. p. 81°, forms somewhat truncated, rectangular tablets from alcohol.

On treatment with nitric acid (D 1.42) in presence of acetic acid, *o*-hydroxyphenoxyacetophenone yields a *dinitro*-derivative, m. p. 168°, which crystallises from alcohol in golden-yellow needles. This is oxidised by permanganate to benzoic acid, and when boiled during four hours with hydrobromic acid furnishes Nietzki and Moll's 3:5-dinitrocatechol (Abstr., 1893, i, 699). From these results and analogy with the nitration of guaiacol (Grimaux and Lefèvre, Abstr., 1891, 1031), it is concluded that the dinitro-derivative has the nitro-groups in the catechol nucleus and occupying positions 3 and 5 with respect to the hydroxyl group.

T. A. H.

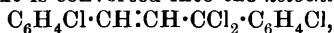
Fission of Phenyl Aryl Ketones and Phenyl Naphthyl Ketones by Sodamide. Mlle. PAULINE LUCAS (*Ann. Chim. Phys.*, 1909, [8], 17, 127—139. Compare Haller, Abstr., 1908, i, 987).—The constitution of the ketones obtained by treating *o*-, *m*-, and *p*-xylenes with benzoyl chloride in presence of aluminium chloride has been

determined by allowing the ketones to react with sodamide, and then examining the products of decomposition when the sodium derivative is treated with water. Thus the ketone obtained from *o*-xylene is shown to be phenyl *o*-xylyl ketone ($\text{Me}_2\text{:CO} = 1:2:4$), since the additive compound it forms with sodamide yields on hydrolysis a mixture of benzamide and the amide of 1:2:4-xylic acid. The action of benzoyl chloride on *m*-xylene leads to the formation of a non-homogeneous substance containing phenyl *m*-xylyl ketone ($\text{Me}_2\text{:CO} = 1:3:4$). The ketone obtained from *p*-xylene has been identified with phenyl *p*-xylyl ketone ($\text{Me}_2\text{:CO} = 1:4:5$).

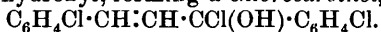
The reaction between phenyl β -naphthyl ketone and sodamide follows the usual course; in the case of phenyl α -naphthyl ketone, however, the *sodium* compound, $\text{C}_{10}\text{H}_7\cdot\text{CPh}(\text{ONa})\cdot\text{NH}_2$, regenerates the ketone when treated with water and yields only traces of benzamide.

W. O. W.

Dibenzylideneacetone and Triphenylmethane. III. Keto-chloride and Chlorocarinol of *p,p*-Dichlorobenzylideneacetophenone [*p*-Chlorophenyl *p*-Chlorostyryl Ketone]. FRITZ STRAUS and A. ACKERMANN (*Ber.*, 1909, 42, 1804—1823. Compare Straus and Caspari, *Abstr.*, 1907, i, 609; Straus and Ecker, *Abstr.*, 1906, i, 859).—*p*-Chlorophenyl *p*-chlorostyryl ketone is easily prepared by the condensation of *p*-chlorobenzaldehyde with *p*-chlorobenzophenone by Claisen's method. It is converted into the *keto*chloride,



on boiling with phosphorus pentachloride in benzene solution; this crystallises very well. It does not form an additive compound with bromine. In all instances the group CCl_2 reacts, so that only one chlorine atom is replaced; thus moist silver oxide replaces one of the chlorine atoms by hydroxyl, forming a *chlorocarinol*,



The behaviour is thus completely analogous to that of dibenzylideneacetone [*distyryl* ketone]. In presence of hydrogen chloride in neutral solvents or acetyl chloride it is re-converted into the *keto*-chloride.

When kept or even on boiling with methyl alcohol it could not be converted into the methyl ether, and to prepare this compound the presence of traces of mineral acids are necessary. The chlorocarinol can be heated for a short time above its melting point before a slow decomposition takes place. On prolonged heating, change takes place with the formation of ketone; the primary change consists in the elimination of water to form anhydrides, which could not be isolated. At higher temperatures, a second decomposition sets in, which gives rise to *keto*chloride, and by reactions brings about the decomposition of this; this phase is particularly marked if the heating is not carried out in a vacuum so as to remove the water formed in the primary change. The chlorocarinol is completely stable towards reagents which eliminate hydrogen chloride, for example, silver salts, alkalis, and tertiary bases.

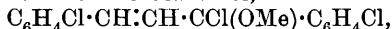
*Keto*chloride, carbinol, and methyl ether all dissolve in concentrated sulphuric acid with an intense, yellowish-red coloration, due to the

formation of the same sulphate in each case. The ketochloride and carbinol dissolve in liquid sulphur dioxide without colour, due to their dissociation being very small. The corresponding *chlorobromide*, $C_6H_4Cl \cdot CH : CH \cdot CClBr \cdot C_6H_4Cl$, also forms colourless, concentrated solutions in sulphur dioxide, but these gain rapidly in colour when diluted.

p-Chlorophenyl *p*-chlorostyryl ketone crystallises in well-formed, yellow plates, m. p. 156—157°, and dissolves in concentrated sulphuric acid with an intense yellow colour and a strong, green fluorescence. The introduction of the two para-chlorine atoms causes the colour as compared with phenyl styryl ketone to be distinctly more red. The *dibromide*, $C_6H_4Cl \cdot CHBr : CHBr \cdot CO \cdot C_6H_4Cl$, forms snow-white, soft needles, m. p. 160—161°. The *phenylhydrazone* separates in colourless, matted needles, m. p. 149°. Its solutions show an intense, bright blue fluorescence.

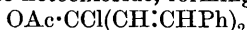
The *ketochloride*, that is, *p*-chlorophenyl-*p*-chlorostyryldichloromethane, $C_6H_4Cl \cdot CH : CH \cdot CCl_2 \cdot C_6H_4Cl$, crystallises in colourless, transparent prisms, m. p. 54—55°. It dissolves in concentrated sulphuric acid to a reddish-yellow liquid, and does not form an additive compound with bromine or a coloured complex with mercuric chloride; with tin tetrachloride a deep violet precipitate is obtained; this is strongly dissociated in solution.

The *methyl ether* of the chlorocarbinol,



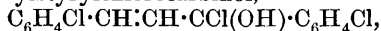
is obtained as a bright yellow oil.

Acetic acid acts on the ketochloride, forming the compound



and eliminating hydrogen chloride. A state of equilibrium is rapidly reached, and subsequently the amount of acid liberated slowly increases. The ketochloride of *pp*-dichlorostyryl ketone behaves similarly, but the hydrolysis of the ketone commences only after prolonged action.

p,p-Dichlorophenylstyrylchlorocarbinol,



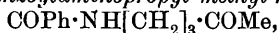
forms colourless, matted needles, m. p. 67—68°.

E. F. A.

Dibenzylideneacetone and Triphenylmethane. IV. Differences in the Reactivity of Halogens in the $-CCl_2$ -Group. FRITZ STRAUS and WERNER HÜSSY (*Ber.*, 1909, 42, 2168—2182).—The authors have studied the rate at which the halogen in the $-CCl_2$ -group is replaced by hydroxyl by shaking ethereal solutions of various compounds with water, and titrating the amount of free hydrochloric acid contained in 20 c.c. of the aqueous layer by means of *N*/10-alkali hydroxide; the results are illustrated by means of curves. A certain parallelism seems to exist between the reactivity of the halogens and their electrolytic dissociation; since the latter phenomenon is accompanied by the formation of coloured ions, the authors examined the absorption spectra of phenyl styryl ketone and distyryl ketone and several of their derivatives in sulphuric acid solution. The bearing of the experimental results on the transformation of the ordinary valency into Werner's carbonium valency is discussed. P. H

New Methods of Preparation of Aliphatic Amino-ketones. SIEGMUND GABRIEL (*Ber.*, 1909, 42, 1238—1243. Compare also following abstracts).—Phthalylglycyl chloride and its homologues easily exchange chlorine for phenyl, and yield phthalimino-derivatives of aliphatic aromatic ketones, $C_6H_4O_2 \cdot N \cdot [CH_2]_x \cdot C(=O)Ph$, and from these by hydrolysis the mixed amino-ketones are obtained (compare Abstr., 1908, i, 649). Two methods for preparing aliphatic amino-ketones have been devised: (1) Phthalylglycyl chloride by condensation, for example, with ethyl sodiomalonate gives either ethyl phthalylglycylmalonate or ethyl phenylglycylacetate by the loss of the carbethoxy-group. Hydrolysis of the acetate gives phthaliminoacetone, and afterwards α -aminoacetone. (2) The other method consists in condensing a bromoalkylphthalimide with ethyl sodioacetoacetate and hydrolysis of the resulting ethyl phthaliminoalkylacetoacetate, which yields finally an aminoalkyl ketone or its anhydride, carbon dioxide being liberated.

When bromoethylphthalimide is boiled with an alcoholic solution of ethyl sodioacetate for four to five hours and the oily product hydrolysed with 20% hydrochloric acid, 2-methylpyrrolidine (Hielscher, Abstr., 1898, i, 338) is obtained. The platinichloride has m. p. 200° (decomp.), and the aurichloride, m. p. 154—157° (decomp.). This on benzoylation gives γ -benzoylaminoethyl methyl ketone,



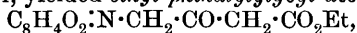
which crystallises from ether in needles, m. p. 66—67°.

In a similar manner γ -bromopropylphthalimide yields 2-methyltetrahydropyridine (compare Lipp, Abstr., 1896, i, 317) in addition to δ -phthaliminobutyl methyl ketone, which was only obtained in an impure condition. The intermediate product, ethyl phthaliminopropylacetoacetate, $C_6H_4 \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} N \cdot [CH_2]_3 \cdot CH(C(=O)Me) \cdot CO_2Et$, has also been isolated; it separates from ether in snow-white crystals, m. p. 65°.

W. R.

Phthaliminoacyl Chlorides and Ethyl Sodiomalonate. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1909, 42, 1243—1249. Compare preceding abstract).—Condensation of ethyl sodiomalonate with phthaliminoacyl chlorides is not possible in alcoholic solution, as the acyl chloride forms an ester. The general method employed was to prepare the ethyl sodiomalonate by dissolving the finely divided metal in a benzene solution of ethyl malonate. To the gelatinous mass so obtained the phthaliminoacyl chloride in benzene was added, and after twelve hours the liquid was heated at 100°. The excess of sodium was then removed by hydrochloric acid, the benzene and unchanged ester distilled in a current of steam, and from the oily residues left behind the various derivatives were prepared.

The oil from the interaction of phthalylglycyl chloride and ethyl sodiomalonate gave, on treatment with hydrogen iodide (b. p. 127°), phthaliminoacetone, $C_6H_4O_2 \cdot N \cdot CH_2 \cdot C(=O)Me$, m. p. 124°. The oil, when rubbed with alcohol, yielded ethyl phthalylglycyl acetate,



which crystallises from alcohol in needles, m. p. 110°.

The oil from β -phthalylalanyl chloride and ethyl sodiomalonate

crystallises slowly, and on recrystallisation from methyl alcohol *ethyl β-phthalylalanylacetate*, $C_8H_4O_2 \cdot N \cdot [CH_2]_2 \cdot CO \cdot CH_2 \cdot CO_2Et$, is obtained in slender prisms, m. p. 121—122°. When the crude substance is boiled for four hours with 20% hydrochloric acid, *methyl β-amino-propyl ketone* was obtained. It was characterised by its *platinichloride*, $C_8H_{20}O_2N_2Cl_6Pt$, which forms yellow plates, 195—205° (decomp.)—the *picrate* is yellow, m. p. 129—130°—and *aurichloride*, m. p. 152° (decomp.).

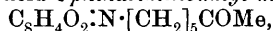
On the other hand, the oil from γ -phthaliminobutyryl chloride yields, on hydrolysis with 20% hydrochloric acid, 2-methylpyrroline. δ -Phthaliminovaleryl chloride on similar treatment gives 2-methyltetrahydropyridine in 35% yield. These two ring compounds are best prepared from the bromoalkylphthalimides (compare preceding abstract).

W. R.

ϵ -Amino-ketones. SIEGMUND GABRIEL (*Ber.*, 1909, 42, 1249—1259. Compare Abstr., 1908, i, 648).— ϵ -Aminohexophenone is stable and does not form an anhydro-derivative, unlike the γ - and δ -aminoketones. It has been considered desirable to study a purely aliphatic ϵ -aminoketone from this point of view.

A new and more convenient method for the preparation of ϵ -aminohexophenone is through ϵ -benzoyl leucine (ϵ -benzoylaminohexoic acid). This acid (compare Braun, this vol., i, 230) is obtained from ϵ -chloro-amybenzamide by converting into nitrile and hydrolysis of the nitrile. The acid has been characterised by its *silver* salt, $C_{13}H_{16}O_3NaAg$. The ϵ -benzoylaminohexoyl chloride was next prepared, and this on heating with aluminium chloride in benzene forms ϵ -benzoylaminohexophenone, $COPh \cdot NH \cdot [CH_2]_5COPh$, which separates from alcohol in crystals, m. p. 95°. When this ketone is heated with glacial acetic and hydrochloric acids at 170° for three hours, ϵ -aminohexophenone hydrochloride is formed. The *picrate*, $C_{18}H_{20}O_8N_4$, crystallises from water with 1 mol. H_2O , m. p. 95°, and from alcohol in anhydrous condition, m. p. 128—129°.

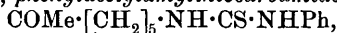
A better method of preparing δ -bromobutylphthalimide (Abstr., 1899, i, 595) from γ -chlorobutyronitrile is described. This imide, on boiling for five hours with sodium ethoxide and ethyl acetoacetate, yields the corresponding phthalimino-ester, which gives on hydrolysis with 20% hydrochloric acid ϵ -phthaliminoamyl methyl ketone,



in largest amount; it crystallises in snow-white leaflets, m. p. 71—72°; a quantity of methyl ϵ -aminoamyl ketone is formed at the same time. For this preparation it is much better to use δ -iodobutylphthalimide, $C_{12}H_{12}O_2NI$, and potassium ethoxide. The iodo-derivative is obtained by heating δ -phenoxybutylphthalimide and hydriodic acid for one and a-quarter hours, and forms needles, m. p. 88—89.5°; some δ -iodobutylamine hydriodide is formed simultaneously. When ϵ -phthaliminoamyl methyl ketone is heated with a mixture of hydrochloric and glacial acetic acids for three hours in a sealed tube at 170°, *methyl ϵ -aminoamyl ketone*, $NH_2 \cdot [CH_2]_5 \cdot COMe$, is formed; the *platinichloride*, $C_{14}H_{32}O_2N_2Cl_6Pt$, forms orange leaflets, m. p. 180—181° (decomp.); the *picrate*, $C_{13}H_{20}O_9N_4 \cdot H_2O$, needles, m. p. 79—80°. It

has been found better, however, when preparing larger quantities of the compound to condense ϵ -benzoylaminoheptoxyl chloride and ethyl sodiomalonate in benzene solution and hydrolyse the resulting ester with hydrochloric acid.

When methyl ϵ -aminoamyl ketone picrate is heated at 100° it loses 2 mols. of water and forms the *picrate* of cyclo-2-methyldehydro-hexamethyleneimine, $\text{MeC} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$, $\text{C}_6\text{H}_5\text{O}_7\text{N}_3$, which crystallises from alcohol in needles, m. p. $188-189^\circ$. The anhydro-heptacyclic base has not been obtained from the ϵ -amino-ketone hydrochloride and 33% potassium hydroxide; the oily base so obtained gives with phenylthiocarbimide, *phenylacetylamylthiocarbamide*,



which crystallises from alcohol in prisms, m. p. 99.5° . That the hydrochloric acid solution contains the ϵ -amino-ketone is shown by its yielding the *phenylhydrazone*, $\text{N}_2\text{HPh} \cdot \text{COMe} \cdot [\text{CH}_2]_5 \cdot \text{NH}_2$, HCl , H_2O , which crystallises from acetone in leaflets, m. p. $98-99^\circ$ (decomp.), and gradually decomposes in the air. The oily base when treated with solid potassium hydroxide gave an oil, b. p. $60-160^\circ/19$ mm. The fraction b. p. $100-160^\circ/19$ mm. gave, on analysis, numbers intermediate between those of the amino-ketone and anhydro-base, both fractions gave the same picrate as previously obtained.

The ease with which the anhydro-base picrate passes back into the amino-ketone picrate is noteworthy; a solution of the anhydro-base picrate in 50% alcohol on evaporation in the air deposits the picrate of the ketone. This formation of an unstable heptacyclic base distinguishes methyl ϵ -aminoamyl ketone from the phenyl ϵ -aminoamyl ketone.

W. R.

Reduction of ϵ -Amino-ketones. SIEGMUND GABRIEL (*Ber.*, 1909, 42, 1259-1268).—The easy formation of an unsaturated seven-membered ring compound, 2-methylcyclodehydrohexamethyleneimine (preceding abstract), suggested experiments being carried out to reduce this to 2-methylhexamethyleneimine, a reaction which proceeds easily with five- and six-membered *cycloimines* (*Abstr.*, 1908, i, 275, 649). As the *cycloimine* had not been obtained pure, methyl ϵ -aminoamyl ketone hydrochloride was reduced with sodium and alcohol and the product distilled in a current of steam; 2-methylcyclohexamethyleneimine, $\text{NH} \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \end{smallmatrix}$, is an oil, b. p. $148-150^\circ/760$ mm., D_{20}^{20} 0.8590, n_D^{20} 1.45862, having a powerful coniine-like odour and a strong alkaline reaction; the *hydrochloride*, $\text{C}_7\text{H}_{16}\text{NCl}$, forms silken needles, m. p. 196° ; the *aurichloride*, $\text{C}_7\text{H}_{16}\text{NCl}_4\text{Au}$, golden-yellow needles, m. p. 95° ; the *platinichloride*, needles, m. p. 196° ; the *picrate*, m. p. 131° ; the *nitrosoamine*, $\text{C}_7\text{H}_{14}\text{ON}_2$, is a yellow oil, b. p. $240-242^\circ/746$ mm.; the *benzenesulphonyl* derivative forms crystals, m. p. 78° .

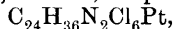
This easy formation of a seven-membered ring is somewhat surprising, although the lactam of ϵ -aminohexanoic acid is formed to a slight extent from the acid (*Abstr.*, 1899, i, 595). Blaise and

Houillon (Abstr., 1906, i, 692, 704) have shown that *cyclooctamethyleneimine* is not obtained from octamethylenediamine hydrochloride by heat, but 2-butylpyrrolidine, and that instead of *cyclodecamethyleneimine*, 2-hexylpyrrolidine is the product when a similar experiment is carried out. As the tendency in these imines, as in other cases, is to form five- or six-membered rings, it was necessary to ascertain if, in the compound under consideration, 2-propylpyrrolidine was not the substance really obtained: 2-ethylpiperidine is already known and differs from it.

2-Propylpyrrolidine, $\text{NH} \begin{matrix} \text{CHPr} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{matrix}$, was therefore synthesised

by two different methods, and shown to be different from the imine prepared by the reduction of the ϵ -amino-ketone. The first method used was to condense ethyl sodioethylmalonate with γ -phthalimino-butyryl chloride in dry benzene, hydrolyse the ethyl phthalimino-butyrylethylmalonate with hydrochloric acid to 2-propylpyrroline, reduce this with tin and hydrochloric acid to 2-propylpyrrolidine, isolate the benzenesulphonyl derivative, and hydrolyse this with a mixture of glacial acetic and hydrochloric acids in a sealed tube at 170° for one and a-half hours. The yield by this method was very meagre, and the second method was accordingly devised, namely, to condense bromoethylphthalimide and ethyl potassiobutyrylacetate in benzene; subsequent hydrolysis of the ester gives 2-propylpyrroline, which was worked up as in the first method. The *hydrochloride* is deliquescent; the *platinichloride* has m. p. 92° when it contains water of crystallisation, and 135° when anhydrous; *aurichloride*, m. p. 120° , and the *picrate*, m. p. $104-104.5^\circ$; 1-benzenesulphonyl-2-propylpyrrolidine, $\text{C}_{13}\text{H}_{19}\text{O}_2\text{NS}$, crystallises from alcohol in needles, m. p. $66-67.5^\circ$.

ϵ -Aminohexophenone on reduction with sodium and alcohol gives 2-phenylcyclohexamethyleneimine, $\text{C}_{12}\text{H}_{17}\text{N}$; a basic, colourless oil, b. p. $276-278/753$ mm.; its *hydrochloride*, $\text{C}_{12}\text{H}_{18}\text{NCl}$, m. p. $205-206^\circ$; *aurichloride*, $\text{C}_{12}\text{H}_{18}\text{NCl}_4\text{Au}$, needles, m. p. 166° ; *platinichloride*,



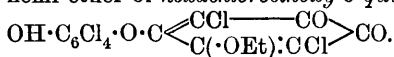
orange, hexagonal plates, m. p. 197° (decomp.); *picrate*, yellow prisms, m. p. 154° . It also yields an oily *nitrosoamine*, and 1-benzenesulphonyl-2-phenylhexamethyleneimine, $\text{C}_{18}\text{H}_{21}\text{O}_2\text{NS}$, plates, m. p. $81-82^\circ$.

W. R.

Benzoquinone from the Standpoint of the Law of Entropy and the Partial Valency Hypothesis. ARTHUR MICHAEL (*J. pr. Chem.*, 1909, [ii], 79, 418-440).—A theoretical paper in which the characteristic chemical behaviour of benzoquinone is explained by reference to the chemical potential and the entropy relationships of its various transformations. It is likewise shown that the arguments based on the partial valency hypothesis employed by Thiele (Abstr., 1899, i, 554) and Posner (Abstr., 1904, i, 1029) to account for the chemical changes of benzoquinone are quite untenable.

W. H. G.

Hemi-Ether of Hexachloroethoxy-*o*-quinocatechol. C. LORING JACKSON and G. L. KELLEY (*Ber.*, 1909, 42, 1865—1867).—The product obtained by the action of ethyl alcohol on tetrachloro-*o*-benzoquinone, and melting at 210° (decomp.) (Abstr., 1907, i, 856), appears to be the hemi-ether of *hexachloroethoxy-*o*-quinocatechol*,



The same product is formed by the action of ethyl alcohol on hexachloro-*o*-quinocatechol ether or on the half ether of heptachloro-*o*-quinocatechol. When reduced with an alcoholic solution of sulphur dioxide, it yields a *compound*, $\text{C}_{14}\text{H}_8\text{O}_5\text{Cl}_6$, m. p. 173°, from which a *tetra-acetyl* derivative, $\text{C}_{14}\text{H}_3\text{Ac}_4\text{O}_5\text{Cl}_6$, m. p. 165°, is obtained.

Methyl alcohol reacts with tetrachloro-*o*-benzoquinone, yielding a product, m. p. 198°, which cannot be reduced by sulphur dioxide, and hence is probably the methyl-monohemiacetal of hexachloro-*o*-quinocatechol ether.

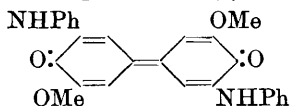
J. J. S.

Disodiophenolphthaloquinone or Disodioaciphenolphthalein.

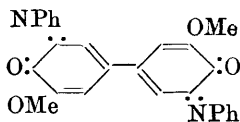
C. FLEIG (*J. Pharm. Chm.*, 1909, [vi], 29, 465—471).—When phenolphthalein is added in excess to a solution of sodium hydroxide, the sodium derivative formed has the composition $\text{C}_{20}\text{H}_{12}\text{O}_4\text{Na}_2$ (compare Meyer and Spengler, Abstr., 1905, i, 440). It was obtained as a reddish-violet mass by evaporating the solution, and could not be prepared in a crystalline condition. Its behaviour with various solvents is described in the original. Its solution in water furnishes precipitates with many metallic salts, and these are usually unstable and are decomposed on boiling, yielding phenolphthalein and the corresponding metallic oxide. The possible systematic names for this substance are discussed, and the two given in the title are selected as most appropriate.

T. A. H.

Nomenclature of the Lignones. CARL LIEBERMANN (*Ber.*, 1909, 42, 1851—1852).—Bezdik and Friedländer (this vol., i, 415) have applied the term “lignone” to certain binuclear quinones. The term “lignone blues” has been applied previously to the compounds obtained by the action of primary aromatic bases on coerulignone (Liebermann and Flatau, Abstr., 1897, i, 224; Liebermann and Cybulski, Abstr., 1898, i, 378), considered as derivatives of the aniline compound, lignone-blue (I).



(I.)



(II.)

The formula (II), containing two atoms of hydrogen less, is not definitely excluded.

In Friedländer's nomenclature, lignone-blue becomes bis-3-anilino-5-methoxybenzolignone, etc. This nomenclature is cumbersome, but may become necessary as the number of lignones increases.

C. H. D.

Preparation of Leuco-derivatives of Hydroxyanthraquinones. FARBERWERKE VORM. MEISTER, LUCIUS and BRÜNING (D.R.-P. 207668).—The sodium salt of leuco-1-amino-4-hydroxyanthraquinone-8-sulphonic acid, yellow needles, is produced on adding sodium hyposulphite to an alkaline solution of the anthraquinone derivative. The product is then transformed into the leuco-derivative of quinizarin-5-sulphonic acid by boiling with 10% hydrochloric acid. This reduction can be effected on the unsubstituted, or the hetero-nuclearly substituted, *p*-aminohydroxy- and *p*-diamino-anthraquinones.

F. M. G. M.

Preparation of Mercaptans of the Anthracene Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 206536).—Thiol and disulphide derivatives of anthraquinone are obtained by heating together the halogenated anthraquinones and the alkali sulphides or hydrosulphides. *α*-Thiolanthraquinone, $C_{14}H_8O_2S$, prisms, m. p. 187°, prepared from *α*-chloroanthraquinone and sodium sulphide in boiling alcohol, is accompanied by its oxidation product, the corresponding disulphide, $(C_{14}H_7O_2)_2$. The latter is reduced to the former by alkaline hyposulphite in alcoholic solution. *β*-Thiolanthraquinone, brown needles, is similarly obtained from *β*-chloroanthraquinone and sodium hydrosulphide.

4-Thiol-1-*p*-tolylaminoanthraquinone, $C_7H_7 \cdot NH \cdot C_{14}H_6O_2 \cdot SH$, dark blue needles, prepared from 1-chloro-4-*p*-tolylaminoanthraquinone and sodium hydrosulphide, yields on sulphonation a violet wool dye.

F. M. G. M.

Preparation of Mercaptans of the Anthraquinone Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 208640).—The thiocyanogen derivatives of the aromatic series are gradually converted into thiols either by heating with hydrochloric acid or by treatment with alkali hydrosulphides. These processes fail in the anthraquinone series, for hydrochloric acid does not hydrolyse the thiocyanogen group, whilst hydrosulphides reduce the carbonyl group. It has now been found that alkali hydroxides effect this transformation.

α-Thiocyanoanthraquinone (obtained from *α*-diazoanthraquinone and potassium thiocyanate), when boiled with alcoholic sodium hydroxide, gives rise to the *α*-thiolanthraquinone, $C_{14}H_7O_2 \cdot SH$, which crystallises in yellow needles, m. p. 187°.

β-Thiolanthraquinone, pale yellow flakes, is similarly obtained from *β*-diazoanthraquinone.

F. M. G. M.

[The Sulphonation of Alizarin and Anthraflavic Acid.] R. WEDEKIND & Co. (D.R.-P. 205965).—When alizarin and anthraflavic acid are sulphonated with fuming acid (20–4% SO_3) in the presence of mercury, the operation takes place more readily than in the absence of the metal, and new sulphonic acids are produced.

F. M. G. M.

[Preparation of Bornyl and Menthyl Sulphuric Acids.] CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 208790).—It has been found that pure bornylsulphuric acid can be obtained (as its sodium salt) by the action of methylene sulphate on borneol in benzene solution, with subsequent treatment successively with barium and sodium carbonates.

Sodium bornyl sulphate is a colourless, very easily soluble salt, and resembles sodium menthyl sulphate, which is similarly prepared.

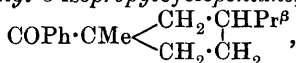
F. M. G. M.

Preparation of Menthyl α -Bromoisovalerate. LÜDXY & Co. (D.R.-P. 208789).—The introduction of bromine into menthyl *isovalerate* enhances the specific action of the drug in hysteria and neurasthenia.

Menthyl α -bromoisovalerate, colourless, syrupy liquid, b. p. 150—160°/50 mm. and 205—208°/760 mm., is prepared by mixing, even in the cold, or more rapidly on warming, menthol and α -bromoisovaleryl chloride (obtained by direct bromination of *isovaleryl* chloride).

F. M. G. M.

Synthesis of Derivatives of Racemic Fenchone. LOUIS BOUVEAULT and LEVALLOIS (*Compt. rend.*, 1909, 148, 1399—1401. Compare Abstr., 1908, i, 134, 193; 1909, i, 108).—The *chloride* of dihydrocampholenic acid has been obtained as a colourless liquid, b. p. 98°/16 mm. When treated with benzene in presence of aluminium chloride, it yields 3-benzoyl-1-isopropylcyclopentane, $C_{15}H_{20}O$, a pale yellow liquid, b. p. 166°/12 mm., the *oxime* of which has m. p. 128°. When treated with sodamide and methyl iodide the benzoyl derivative yields 1-benzoyl-1-methyl-3-isopropylcyclopentane,



b. p. 172°/15 mm. The *oxime* occurs in needles, m. p. 96·5°. Treatment of the methylketone with sodamide leads to the formation of benzene and 1-methyl-3-isopropylcyclopentane-1-carboxylamide, which should be identical with *r*-dihydrofencholenamide if the constitution previously ascribed to this compound is correct. The natural product has m. p. 116°, whilst the synthetic amide has m. p. 109°; it is probable, however, that the low m. p. is due to the presence of an isomeric compound.

W. O. W.

Preparation of Mixed Santalyl Esters of Dibasic Acids. J. D. RIEDEL (D.R.-P. 208637).—Methyl *santalylsuccinate*, an oil, D_{25}^{20} 1·058, is prepared by treating santalol or sandal wood oil with succinic anhydride at 100—120°, and then alkylating the resulting santalylsuccinic acid with methyl sulphate and aqueous potassium hydroxide.

Methyl *santalylphthalate*, pale yellow oil, D_{25}^{20} 1·085, is similarly obtained from santalylphthalic acid, methyl *p*-toluenesulphonate, and aqueous potassium hydroxide.

Methyl *santalylcamphorate*, pale yellow oil, D_{25}^{20} 1·04, is produced by condensing santalol with camphoric anhydride and alkylating the intermediate santalylcamphoric acid.

F. M. G. M.

Constitution of Camphor and Its Derivatives. X. Electrolytic Reduction of Camphorcarboxylic Acid to *cis*- and *cis-trans*-Borneolcarboxylic Acids. Bornylenecarboxylic Acid (Preparation of Pure Bornylene). XI. Relationship of the Camphylglycols to the Borneolcarboxylic Acids. JULIUS BREDT (*Annalen*, 1909, 366, 1—70).—An investigation of the isomeric borneolcarboxylic acids obtained by the electrolytic reduction of camphorcarboxylic acid (compare Abstr., 1906, i, 680). It is shown that the two acids are *cis*- and *cis-trans*-isomerides, but although they have the same chemical constitution, nevertheless they behave differently towards an alkaline solution of potassium permanganate; the *cis*-acid, m. p. 102—103°, is readily and completely oxidised to camphoric acid, whilst the *cis-trans*-isomeride, m. p. 171°, remains unaltered when treated similarly. On the other hand, both acids yield camphoric acid when oxidised with nitric acid, and yield the same bornylenecarboxylic acid when subjected to dry distillation. The *cis*-acid is converted into the *cis-trans*-acid by acetyl chloride.

The acid described in the previous communication (*loc. cit.*) as dehydroborneolcarboxylic acid (camphenecarboxylic acid) is shown to be bornylenecarboxylic acid, since it yields camphoric acid when oxidised, and by suitable treatment gives rise to bornylene. The addition of hydrogen chloride or hydrogen bromide to bornylenecarboxylic acid takes place in the usual manner, that is, the halogen enters the β -position to the carboxyl group when the solvent employed is glacial acetic acid. When aqueous acids are employed, however, a chloro- or bromo-camphanecarboxylic acid is obtained. The latter have the same composition as those obtained by using glacial acetic acid, but have different properties; when heated with alkalis they yield a hydroxy-acid isomeric, but not identical, with either of the borneolcarboxylic acids obtained by the reduction of camphorcarboxylic acid. The nature of the isomerism is not yet clear.

The β -halogencamphanecarboxylic acids, prepared in glacial acetic acid, when treated with alkali yield bornylenecarboxylic acid, and also bornylene, which has been obtained in a state of purity for the first time. A lactone is also formed simultaneously as the result of intramolecular rearrangement.

The view previously advanced (*loc. cit.*), that the borneolcarboxylic acid, m. p. 170—171°, is probably related to *trans*-camphylglycol, m. p. 117—118°, as a hydroxy-acid to its glycol, is shown to be correct, since the *trans*-glycol is converted by oxidation with potassium permanganate into borneolcarboxylic acid, m. p. 170—171°. It has also been found possible to isolate an isomeric camphylglycol, m. p. 87°, corresponding with the borneolcarboxylic acid, m. p. 102—103°.

[With HERMANN SANDKUHL.]—*cis*-Borneolcarboxylic acid, $C_{11}H_{18}O_3$, is far more soluble in toluene at the ordinary temperature than at 0°, and may be separated from the isomeride, m. p. 171°, by making use of this property. It crystallises in large, transparent, colourless prisms, m. p. 101°; the crystalline calcium salt, $(C_{11}H_{17}O_3)_2Ca \cdot 2H_2O$, is more soluble in cold than in hot water; the affinity constant $K = 0.0105$.

cis-trans-Borneolcarboxylic acid, m. p. 171°, has an affinity constant

$K = 0.00255$. The *acetate*, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H} \\ | \\ \text{CH} \cdot \text{OAc} \end{smallmatrix}$, obtained by the action of acetyl chloride (two parts) on either *cis*- or *cis-trans*-borneolcarboxylic acid (1 part), forms colourless crystals, m. p. 122—123°. When four parts of acetyl chloride are employed, an amorphous, indifferent substance is obtained, which is probably a mixture of *acetylborneolcarboxylic acid anhydride*, $(C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CO}^- \\ | \\ \text{CH} \cdot \text{OAc} \end{smallmatrix})_2\text{O}$, and an *anhydride* of *cis-trans*-borneolcarboxylic acid, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CO} \cdot \text{O} \cdot \text{CH} \\ | \qquad \qquad | \\ \text{CH} \cdot \text{O} \cdot \text{CO} \cdot \text{CH} \end{smallmatrix} > C_8H_{14}$.

An *acid*, $C_{11}H_{18}O_3$, m. p. 126°, was isolated from the product obtained by the electrolytic reduction of camphorcarboxylic acid; the *calcium* salt, $(C_{11}H_{17}O_3)_2Ca$, was analysed. It is possible that this acid is another of the four possible stereoisomeric borneolcarboxylic acids.

Bornylenecarboxylic acid, $C_{11}H_{16}O_2$, m. p. 112—113°, b. p. 158°/13 mm., is most readily prepared by the distillation of acetylborneolcarboxylic acid at 157°/14 mm.; the *anhydride*, $C_{22}H_{30}O_3$, is a white, crystalline substance, m. p. 97°, b. p. 220—225°/15 mm. The acid, when oxidised with an aqueous 2½% solution of potassium permanganate, yields camphoric acid, hydroxyoxidocamphanecarboxylic acid, and other acids which have not yet been investigated. *Hydroxyoxidocamphanecarboxylic acid* (annexed formula) crystallises in white leaflets, m. p. 208—209°; the *calcium* salt, $(C_{11}H_{15}O_4)_2Ca \cdot 4H_2O$, crystallises in needles.

β-Bromocamphanecarboxylic acid, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H} \\ | \\ \text{CHBr} \end{smallmatrix}$, is obtained by the action of hydrogen bromide in glacial acetic acid on bornylene-carboxylic acid; it crystallises in large needles, m. p. 90—91°; the *sodium* salt forms large leaflets. Small quantities of a *hydroxy-acid*, $C_{11}H_{18}O_3$, are obtained in the preparation of the preceding acid; it crystallises in slender, felted needles, m. p. 169°, and yields a *dehydro-acid*, $C_{11}H_{16}O_2$, when its aqueous solution is boiled for some time; the latter substance crystallises in needles, m. p. 55°.

β-Chlorocamphanecarboxylic acid, $C_{11}H_{17}O_2Cl$, prepared in a similar manner, has m. p. 84—85°.

α-Bromocamphanecarboxylic acid, $C_{11}H_{17}O_2Br$, forming granular crystals, m. p. 157°, is obtained, together with the *β*-bromo-acid just described, by the action of concentrated hydrobromic acid on bornylene-carboxylic acid; it is converted by a hot solution of sodium carbonate into a *hydroxy-acid*, $C_{11}H_{18}O_3$, which forms granular crystals, m. p. 176°, and does not yield camphoric acid when hydrolysed.

The *β*-halogenated camphanecarboxylic acids when heated with aqueous alkalis yield a mixture of bornylene, bornylenecarboxylic acid, and *γ*-hydroxycarbohydrocamphenolactone, the proportions of which vary with the conditions employed. The production of bornylene is favoured by using excess of alkali and heating rapidly to a high temperature under pressure.

Bornylene obtained by this method is a crystalline substance, m. p.

113°, b. p. 146°/740 mm., $[\alpha]_D^{18} - 21.69^\circ$ ($c = 10.45$ in toluene), $[\alpha]_D^{18} - 26.96^\circ$ ($c = 4.42$ in methyl alcohol) (compare Wagner, Abstr., 1900, i, 554; Tschugaeff, Abstr., 1905, i, 71).

γ -Hydroxycarbohydrocamphenolactone, having the annexed formula, forms colourless crystals, m. p. 183°, b. p. 145—147°/12 mm.; the calcium salt,

$(C_{11}H_{17}O_3)_2Ca$, crystallises with H_2O , which is liberated when the salt is exposed to the air. The lactone is oxidised by hot nitric acid (D 1.27), yielding

camphenilol- γ -dicarboxylic acid, the lactone (annexed formula) of which forms long, feathery crystals, m. p. 230°; the barium salts, $(C_{11}H_{13}O_4)_2Ba$ and

$(C_{11}H_{14}O_5)_2Ba$, were prepared and analysed; the latter is very unstable, being decomposed by carbon dioxide.

ortho-Camphanecarboxylic acid, $C_8H_{14} \begin{smallmatrix} < CH \cdot CO_2H \\ & CH_2 \end{smallmatrix}$, is prepared by reducing β -bromocamphanecarboxylic acid with potassium amalgam; it is a crystalline substance, m. p. 90—91°, b. p. 153°/13 mm.

The reduction of hydroxymethylenecamphor with sodium and alcohol leads to the production of a mixture of *cis*-camphylglycol and *cis-trans*-camphylglycol (compare Farbwerke vorm. Meister, Lucius and Brüning, Abstr., 1902, i, 299). The separation is effected by crystallisation from ethyl acetate. The *cis*-camphylglycol, $C_{11}H_{20}O_2$, separates out first as transparent, colourless needles, m. p. 87°. It is oxidised by potassium permanganate to camphoric acid, and when distilled yields bornylenecarbinol (dehydrocamphylglycol), crystallising in long needles, m. p. 67—68°, b. p. 119—121°/13 mm. The *cis-trans*-glycol does not lose water when treated in the same way as the *cis*-isomeride, and when oxidised with potassium permanganate yields *cis-trans*-borneolcarboxylic acid.

W. H. G.

The Camphenilone Group. I. Camphenilol. GUSTAV KOMPPA (*Annalen*, 1909, 366, 71—78).—An account of the preparation and properties of several compounds derived from camphenilone.

Camphenilyl acetate, $C_9H_{15}OAc$, prepared by the action of acetic anhydride on camphenilol, is a colourless liquid having an intense ethereal odour, b. p. 95—97°/17 mm., $D_4^{20} 0.9974$, $n_D^{20} 1.4628$. Camphenilylphenylurethane, $C_9H_{15}O \cdot CO \cdot NHPh$, prepared from camphenilol and phenylcarbimide, crystallises in slender needles, m. p. 99.5°. Camphenilyl hydrogen phthalate, $CO_2H \cdot C_6H_4 \cdot CO_2 \cdot C_9H_{15}$, obtained by heating camphenilol with phthalic anhydride at 150—180°, forms short, broad crystals, m. p. 148.5—149°.

Camphenilylamine, $C_5H_8 \begin{smallmatrix} < CMe_2 \\ & CH \cdot NH_2 \end{smallmatrix}$, prepared by reducing campheniloneoxime with sodium and alcohol, is obtained as a crystalline mass, m. p. 90—92° (in a sealed tube), b. p. 180—185.5°, having an odour reminiscent of bornylamine and putrid fish offal; the hydro-

chloride, $C_9H_{15}\cdot NH_2\cdot HCl$, forms long, stout needles, which do not melt at 200° ; the *platinichloride*, $C_{18}H_{34}N_2\cdot H_2PtCl_6$, crystallises in pale yellow, thin tetrahedra, which become black, but do not melt, at $230-235^\circ$; the *picrate*, $C_{15}H_{20}O_7N_4$, crystallises in yellow needles, m. p. $205-207^\circ$.

Camphenilylcarbamide, $NH_2\cdot CO\cdot NH\cdot C_9H_{15}$ obtained by the action of potassium cyanate on camphenylamine hydrochloride in aqueous solution, forms small, slender, glistening needles, m. p. $167.5-168^\circ$. *Camphenilylphenylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot C_9H_{15}$, prepared by the action of phenylthiocarbimide on an ethereal solution of camphenylamine, crystallises in square prisms, m. p. 154° .

W. H. G.

New Method for the Hydration of Pinene. II. Partial Proximate Analysis and Purification of Crude Pinene. III. Examination of the Alcohols Formed and Origin of Fenchyl Alcohol. PHILIPPE BARBIER and VICTOR GRIGNARD (*Bull. Soc. chim.*, 1909, [iv], 5, 512-519, 519-526).—The method already described (Abstr., 1908, i, 94), depending on the action of an aqueous solution of benzenesulphonic acid on pinene in presence of acetic acid, has been improved by the addition of acetic anhydride to the reaction mixture, whereby the time necessary for completion has been reduced from twelve to from one and a-half to two hours.

The hydrocarbons recovered unchanged from the first hydration consist mainly of pinene, which is purer than the initial product, since on oxidation it yields only traces of nopinic acid. It contains in addition a hydrocarbon of low b. p., which is unsaturated, but is not bornylene. In order to eliminate pinene from the recovered unchanged products, these were subjected to the hydration process three times in succession. At this stage the recovered hydrocarbons still contained the hydrocarbons of low b. p., some terpadienes, camphene, and some pinene, the last-mentioned being now partly racemised. After two further hydrations the pinene and terpadienes were completely removed. The residual hydrocarbons from 4 kilos. of crude pinene after these six hydrations consisted of the following fractions: b. p. $148-152^\circ$ (6 grams), b. p. $152-154^\circ$ (12 grams), b. p. $154-158^\circ$ (25 grams), and b. p. $158-161^\circ$ (12 grams). The last three deposited partly racemic camphene on cooling. This had m. p. 42° , and optical rotation $-0.40'$ in a 100 mm. tube. The mother liquor from the camphene and the first fraction (b. p. $148-152^\circ$) on treatment with sulphuric acid were largely polymerised, and left a saturated product, $C_{10}H_{18}$, b. p. $157-160^\circ$.

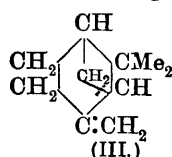
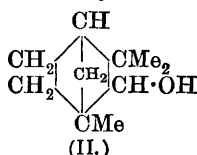
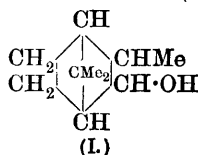
The terpadienes in the hydrocarbons recovered from the fourth hydration appeared to consist of *l*-limonene, dipentene, and possibly terpinolene, all probably produced by the dehydration of α -terpineol.

From a consignment of *l*-rotatory turpentine oil of unknown origin, a low boiling fraction consisting of methylcyclohexane and dimethylcyclohexane was isolated by a combination of fractional distillation and the hydration process. No opinion is offered as to whether or not these are normal constituents of turpentine oil.

The products of hydration are a series of alcohols, which occur in the

reaction mixture as acetates, and are isolated by distilling off the unchanged hydrocarbons under reduced pressure and saponifying the residue boiling above 170° . This method answers for the first three hydrations, but after that stage the quantity available is small, and separation is effected by converting the alcohols into their acid phthalates. The products of the first hydration are *l*- α -terpineol mixed with a little of the racemic form, *d*-fenchyl alcohol with a little of the racemic form, and a crystalline product, m. p. 195 — 200° , which is laevorotatory and gives a phenylurethane, m. p. 139 — 142° . This may be a mixture of borneol and isoborneol, or possibly a new alcohol. No new products are then obtained until the fourth hydration, when a mixture of borneol and isoborneol (m. p. 195 — 196° ; phenylurethane, m. p. 130°) is produced. In the latter hydrations a small quantity of a liquid alcohol is also formed.

It is suggested that the fenchyl alcohol and the alcohol melting at 195 — 200° result from the hydration of nopinene, since they are no longer formed when this has disappeared. Wallach's formula for fenchyl alcohol (I) does not account for such a formation, but Semmler's (II) does if the formula generally accepted for nopinene be written as follows (III), since it may be assumed that the "bridge" is



broken, the double linking hydrated, and the "bridge" re-formed.

T. A. H.

Elimination of Hydrogen Chloride from *d*-Limonene Nitrosochloride. A New Carvoxime. ERNST DEUSSEN and ALFRED HAHN (*Chem. Zentr.*, 1909, i, 1237; from *Zeitsch. Riech.-Geschmackstoffe*, 1909, 1, 25—26).—When *d*-limonene nitrosochloride is treated with 1 mol. of sodium methoxide, the *l*-carvoxime formed is accompanied by a considerable quantity of an oil, which has approximately the same composition. This oil is slightly dextrorotatory, or optically inactive, or slightly laevorotatory, owing to varying quantities of a *d*-carvoxime being present in admixture with *l*-carvoxime. By means of a difference in solubility of the benzoyl compound, a separation of the two oximes was effected; the *d*-benzoylcarvoxime purified from alcohol has m. p. 77° and $[\alpha]_D + 75.3^{\circ}$, and is unimolecular in benzene solution.

d-Carvoxime, $\text{C}_{10}\text{H}_{14} \cdot \text{N} \cdot \text{OH}$, crystallises from aqueous alcohol in glistening needles, m. p. 57 — 58° ; $[\alpha]_D + 68.3^{\circ}$ in benzene solution. It may be obtained from *d*-limonene α - or *d*-limonene β -nitrosochloride, and is called β -carvoxime to distinguish it from the well known *l*-carvoxime or α -compound, m. p. 72° . When heated with dilute sulphuric acid it yields an oil smelling strongly of carvone.

J. V. E.

Terpinenes. IWAN KONDAKOFF (*J. pr. Chem.*, 1909, 79, 497—505).—A review of recent work on terpinene. The conclusion is drawn

that the terpinene prepared by the methods hitherto described is always a mixture of isomerides.
W. H. G.

Cubebin. II and III. EFISIO MAMELI (*Gazzetta*, 1909, 39, i, 477—493, 494—508. Compare Abstr., 1908, i, 20).—The action of a large number of substances, especially of halogen hydracids in acetic acid solution, on cubebin yield cubebin ether, m. p. 78° (compare Pomeranz, Abstr., 1888, 162, 1100), which is formed by dehydration of cubebin, $2C_{10}H_{10}O_3 = H_2O + C_{20}H_{18}O_5$. Cubebin and its derivatives undergo a series of reactions similar to those of the pinacones and their derivatives; just as the pinacone yields by dehydration a pinacolin which gives a pinacolic alcohol on reduction, so also cubebin yields cubebin ether, and this, on reduction, a monohydric alcohol (*vide infra*).

Cubebin ether, $[\alpha]_D + 23.03^\circ$, does not contain carbonyl or hydroxyl oxygen, and has the probable formula: $C_6H_8O(C_6H_3O_2 \cdot CH_2)_2$.

Cubebinol, $OH \cdot C_6H_9(C_6H_3O_2 \cdot CH_2)_2$, prepared by reducing cubebic acid by means of sodium and alcohol, crystallises from a mixture of light petroleum and benzene in spherical tufts of silky, white needles, m. p. 92°, $[\alpha]_D + 34.81^\circ$. Addition of 4Br yields a bromide, m. p. 70—85°, which could not be purified. Cubebinol rapidly decolorises permanganate, the only products observed being carbon dioxide, an acid obtained only as a syrup, and piperonylic acid (?). It reduces Nessler's reagent and ammoniacal silver solution, but not Fehling's solution. Its *acetyl* derivative, $C_{22}H_{22}O_6$, crystallises from alcohol in tufts of silky needles, m. p. 71°, $\alpha_D + 23.12^\circ$; its *benzoyl* derivative, $C_{27}H_{24}O_6$, m. p. 154—155°, $\alpha_D - 21.68^\circ$, and its *phenylurethane*, $C_{27}H_{25}O_6N$, m. p. 154—155°, were also prepared.

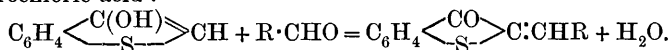
Measurements of the velocity of acetylation of cubebinol indicate that it is a primary alcohol.
T. H. P.

Composition of Tannin. LEO F. ILJIN (*Ber.*, 1909, 42, 1731—1735).—The following methods have been used for the purification of commercial tannin. (1) Dialysis in a parchment thimble, conversion of the dialysed product into the lead derivative, and decomposition of this with hydrogen sulphide. The product was finally precipitated by the addition of chloroform to the solution of the tannin in alcohol and ethyl acetate. (2) Modification of Walden's method (Abstr., 1899, i, 212). (3) Rosenheim and Schidrowitz's method (Trans., 1898, 73, 882). (4) Fractional precipitation of the aqueous solution with sodium chloride. (5) Fractional precipitation of the solution in alcohol and ethyl acetate with chloroform.

All the products had relatively high rotations, $[\alpha]_D^{20.5} + 65$ —75°, and the percentage composition did not agree with that of a digallic acid (Nierenstein, Abstr., 1908, i, 90, 897).
J. J. S.

Dyes of the Thionaphthen Series. PAUL FRIEDLÄNDER (*Monatsh.*, 1909, 30, 347—354).—The analogy of 2-hydroxythionaphthen to α -naphthol on the one hand and to indoxyl on the other (Abstr., 1906, i, 378; 1907, i, 334) is further illustrated by the formation of thioindogenides and hydroxyazo-compounds.

Like indoxyl, it condenses with aromatic aldehydes to form thioindogenides of almost the same colour as the corresponding indogenide. The yellow colour is intensified, but not changed essentially, by the presence of auxochromic groups in the aldehyde molecule. The condensation is effected by warming equal molecular quantities of 2-hydroxythionaphthen and an aldehyde in light petroleum or solvent naphtha, or in alcohol or glacial acetic acid with a few drops of hydrochloric acid :

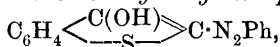


In practice it is convenient to use sodium 2-hydroxythionaphthen-1-carboxylate, which loses carbon dioxide when heated in glacial acetic acid, yielding 2-hydroxythionaphthen.

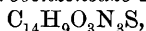
Thioindogenides have been prepared from the following aldehydes and ketones :

Thioindogenide from	M. p.	Colour.	Coloration with conc. H_2SO_4 .	Colour of Na salt in solution.
Benzaldehyde	127°	Yellow	Cherry-red	—
<i>o</i> -Nitrobenzaldehyde ...	171	Orange-red	Bluish-violet	—
<i>m</i> -Nitrobenzaldehyde ...	223—224	Yellow	Bluish-violet	—
<i>p</i> -Nitrobenzaldehyde ...	231	Orange-red	—	—
Salicylaldehyde	209	Orange-yellow	—	Carmine-red
<i>m</i> -Hydroxybenzaldehyde	212	Citron-yellow	—	Pale yellow
<i>p</i> -Hydroxybenzaldehyde	262	Orange-yellow	—	Orange-red
Protocatechualdehyde ..	above 280	Brownish-Orange-yellow	Cherry-red	Reddish-violet
2 : 4-Dihydroxybenz-aldehyde	—	Orange-brown	—	Bluish-red
Piperonal	207	Yellow	Bluish-violet	—
Fluorenone	200—202	Brick-red	Olive-green	—

2-Hydroxythionaphthen couples readily in alkaline solution with diazonium salts. 1-Benzeneazo-2-hydroxythionaphthen,



m. p. 191—192°, forms orange-yellow needles, and is soluble in sodium hydroxide solution. 1-*p*-Nitrobenzeneazo-2-hydroxythionaphthen,



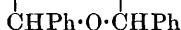
forms sparingly soluble, orange-red needles, gives a bluish-violet solution in sodium hydroxide or hot sodium carbonate, and develops a cherry-red coloration with concentrated sulphuric acid. C. S.

Bromination of Certain Tetrahydropyrone Compounds.

W. SCHTVAN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 477—482).—By the formation of two double linkings in the nucleus of tetrahydropyrone compounds, the author shows that the latter contain the pyrone ring.

Attempts to oxidise ethyl diphenyltetrahydropyronedicarboxylate, $\text{C}_{23}\text{H}_{24}\text{O}_6$, m. p. 114—126°, were unsuccessful.

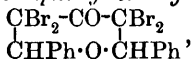
Ethyl 3 : 5-dibromo-2 : 6-diphenyltetrahydropyrone-3 : 5-dicarboxylate, $\text{CO}_2\text{Et} \cdot \text{CBr} \cdot \text{CO} \cdot \text{CBr} \cdot \text{CO}_2\text{Et}$



, prepared by brominating ethyl diphenyltetrahydropyronedicarboxylate, separates from acetic acid in crystals,

m. p. 171° (decomp.), and has the normal molecular weight in freezing nitrobenzene. Removal of 2HBr from this compound by means of pyridine in presence of silver nitrate yields ethyl 2:6-diphenylpyrone-3:5-dicarboxylate (compare Dünschmann and Pechmann, Abstr., 1891, 673), m. p. $140.5\text{--}141^{\circ}$, which, with ammonia, gives the ester, m. p. 195° , obtained by Petrenko-Kritschenko and Petroff (Abstr., 1908, i, 564); hydrolysis of the ester yields the acid, m. p. $250\text{--}258^{\circ}$.

3:3:5:5-Tetrabromo-2:6-diphenyltetrahydropyrone,



obtained by the action of bromine on sodium diphenyltetrahydropyrone-3:5-dicarboxylate, crystallises from alcohol in monoclinic plates, m. p. $165\text{--}171^{\circ}$.

Bromination of diphenyltetrahydropyrone, m. p. 130° , in acetic acid yields a tetrabromo-derivative, which separates from alcohol in small, radiating, monoclinic crystals, m. p. $197\text{--}200^{\circ}$, and is apparently isomeric with the preceding compound, m. p. $165\text{--}171^{\circ}$.

T. H. P.

Cinchona Alkaloids. GEORG ROHDE (*Ber.*, 1909, 42, 2182).—Polemical in regard to the paper by Rabe (this vol., i, 408).

P. H.

Preparation of Easily Soluble Double Salts of Sodium Theobromine. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 208188).—Therapeutically important theobromine compounds are obtained by combining sodium theobromine with the alkali halides.

Sodium theobromine-sodium chloride results from the mixing of concentrated solutions of its generators. This and other double salts of sodium theobromine with alkali halide are white, easily soluble powders, with a bitter taste and an alkaline reaction. They dissolve in dilute alcohol and glycerol, but are insoluble in absolute alcohol and other anhydrous solvents.

F. M. G. M.

Fission of Disulphides with Neighbouring Double Linkings. EMIL FROMM (*Ber.*, 1909, 42, 1945—1959).—The ready formation of thiocarbamides from carbon disulphide and aromatic amines in the presence of hydrogen peroxide is explained by Braun by the intermediate production of a thiuram disulphide, which breaks down into sulphur, carbon disulphide, and the thiocarbamide (Abstr., 1900, i, 644). Since disulphides with neighbouring double linkings are decomposed by water, alkalis, or amines with elimination of sulphur, the author has suggested that thiuram disulphides, which are disulphides of this type, are hydrolysed by water: $\text{S}_2(\text{CS}\cdot\text{NHPh})_2 + \text{H}_2\text{O} = \text{S} + \text{NHPh}\cdot\text{CS}\cdot\text{SH} + \text{NHPh}\cdot\text{CS}\cdot\text{OH}$; by the decomposition of these products, aniline and phenylthiocarbimide are formed, from which the thiocarbamide is produced (Abstr., 1906, i, 656). Braun (Abstr., 1907, i, 123) objects to this explanation on the ground that hydrogen sulphide, but not carbon disulphide, is formed in the preparation of the thiocarbamide. In the present paper the author, whilst pointing out that Braun's objection does not harmonise with his own explanation of the

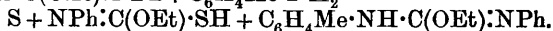
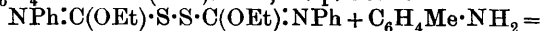
formation of the thiocarbamide (see above), withdraws his previous explanation, since he has obtained evidence that the fission of the thiuram disulphide is effected, not by water, but by the excess of the aromatic amine in accordance with the scheme: $S_2(CS \cdot NHR)_2 + 2R' \cdot NH_2 = S + NHR \cdot CS \cdot NHR' + NHR \cdot CS \cdot SH, NH_2R'$. This simple reaction occurs only rarely, for example, piperidylthiuram disulphide and piperidine at 120° yield *dipiperidylthiocarbamide*, $(C_5NH_{19})_2CS$, m. p. 58° , and piperidine piperidylthiocarbamate (Ehrenberg, Abstr., 1887, 1026). A disturbing influence is sometimes introduced by the decomposition of the arylthiocarbamate into hydrogen sulphide and a thiocarbamide; thus piperidylthiuram disulphide and aniline in boiling alcohol yield sulphur, hydrogen sulphide, and phenylpiperidylthiocarbamide. Another complication is caused by one amine ousting another from the disulphide. Such an instance is found in Braun's diphenyldimethylthiuram disulphide (Abstr., 1902, i, 271), which, reacting with piperidine at 110° or with aniline or phenylhydrazine in boiling alcohol, has the two $-NMePh$ groups replaced by the amine, so that with piperidine, dipiperidylthiocarbamide, piperidine piperidylthiocarbamate and sulphur are formed, with aniline, hydrogen sulphide, sulphur and diphenylthiocarbamide, and with phenylhydrazine, hydrogen sulphide, sulphur and diphenylthiocarbamide. The action of phenylhydrazine on piperidylthiuram disulphide is still more complex, the products being hydrogen sulphide, ammonia, and phenylthiosemicarbazide. The initial decomposition of the disulphide follows the rule, sulphur, piperidylphenylhydrazinothiocarbamide and phenylhydrazine piperidylthiocarbamate being formed; the last breaks down into hydrogen sulphide and another molecule of piperidylphenylhydrazinothiocarbamide, whilst the sulphur, acting on the excess of phenylhydrazine, generates ammonia, which displaces the piperidyl group from the thiocarbamide, forming phenylthiosemicarbazide.

Thiuram disulphides are attacked most easily by phenylhydrazine or aniline, less readily by piperidine, and with the greatest difficulty by methylaniline. This behaviour explains why piperidylthiuram disulphide (Ehrenberg, *loc. cit.*) and diphenyldimethylthiuram disulphide (Braun, *loc. cit.*) are readily prepared, whilst phenylthiuram disulphide cannot be obtained, being attacked by the excess of aniline and forming diphenylthiocarbamide.

The decomposition of thiuram disulphide (thiocarbamic disulphide) by aniline has been investigated by Klason (Abstr., 1887, 1025), and his results are confirmed by the author. The decomposition of the disulphide by phenylhydrazine in the cold yields sulphur, ammonia, hydrogen sulphide, phenylthiosemicarbazide, and diphenylthiocarbamide. The formation of the products obtained by these two decompositions is in perfect harmony with the author's scheme of the fission of a thiuram disulphide by an amine.

[With ADOLF ROESICKE and MAX TAUSENT.]—Jacobson's phenylthiourethane sulphide (Abstr., 1886, 376), which is more readily obtained by oxidising phenylthiourethane, dissolved in sodium hydroxide, D 1.3, and a little alcohol, by iodine in potassium iodide, is a disulphide with neighbouring double linkings, and its fission by *p*-toluidine at 125° results in the formation of sulphur, phenylthiourethane, *phenyl-*

p-tolylcarbamide, m. p. 231°, and *phenyl-p*-tolylethyl- ψ -carbamide, $C_6H_4Me \cdot NH \cdot C(OEt) : NPh$, m. p. 265° :



The phenyl-*p*-tolylcarbamide is formed by the action of phenylthio-urethane on the ψ -carbamide, whereby phenyl-*p*-tolylcarbamide and ethyl phenyliminothiocarbonate are produced, the presence of the latter being detected by warming the mixture with hydrochloric acid at 150°, whereby ethyl mercaptan is liberated (compare Liebermann, *Annalen*, 1881, 207, 149). C. S.

The Fission of Cyclic Bases by Cyanogen Bromide. II. JULIUS VON BRAUN (*Ber.*, 1909, 42, 2035—2057. Compare Abstr., 1907, i, 960).—The breaking of the ring in cyclic bases by cyanogen bromide extends to all those compounds, $X \triangleleft N \cdot R$, in which R is a homologue of methyl. Methyl, allyl, and benzyl compounds are not broken down. A number of piperidine derivatives have now been examined. In each case, the initial compound, $C_5NH_{10} \cdot X$, is treated with cyanogen bromide, and the relative quantities of the three products, $C_5NH_{10} \cdot CN$, XBr , and $Br \cdot [CH_2]_5 \cdot NX \cdot CN$, estimated. The brominated compounds are isolated by replacing the bromine by the groups NHR or NR_2 . The cyanamides are best converted into guanidines.

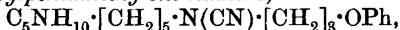
Piperidinocyanamide only reacts with difficulty with ammonium salts, but readily with the salts of primary amines. The *guanidine* derivative from *p*-tolylamine, $C_5NH_{10} \cdot C(NH) \cdot NH \cdot C_6H_4Me$, has m. p. 115°; the *picrate*, m. p. 132°, and *platinicyanide*, m. p. 205° (decomp.), are described. The compound from aniline does not crystallise well; its *picrate* has m. p. 107°, and *platinicyanide*, m. p. 195°.

Diperidinoguanidine, $NH : C(C_5NH_{10})_2$, is a colourless liquid, b. p. 175—177°/12 mm.; the *picrate*, m. p. 148°, and *platinicyanide*, m. p. 192° if slowly heated.

γ -Phenoxypropylpiperidine, $C_5NH_{10} \cdot [CH_2]_3 \cdot OPh$ (Gabriel and Stelzner, Abstr., 1896, i, 703), is best prepared from piperidine and phenyl iodopropyl ether. It forms an oil, b. p. 172°/13 mm.; the *hydriodide* has m. p. 183°, and the *methiodide*, m. p. 159—160°. It gives a mixed oily product with cyanogen bromide, which on hydrolysis with hydrobromic acid yields γ -bromopropyl- ϵ -bromoamylcyanamide, $Br[CH_2]_3 \cdot N(CN) \cdot [CH_2]_5Br$, an oil. At higher temperatures the hydrolysis gives rise to an impure *hydrobromide* of γ -bromopropyl- ϵ -bromoamylimine, $Br[CH_2]_3 \cdot NH \cdot [CH_2]_5Br$, HBr , m. p. 202—210°.

Sodium phenoxide converts the oily product into $\alpha\gamma$ -propyleneglycol diphenyl ether, $CH_2(CH_2 \cdot OPh)_2$, and *diphenoxypropylecyanamide*, $OPh \cdot [CH_2]_3 \cdot N(CN) \cdot [CH_2]_5 \cdot OPh$, m. p. 36°. The cyano-group is attacked by acids with great difficulty.

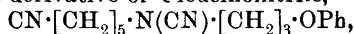
The oily product condenses with bases. Piperidine forms *piperidyl-cyanophenoxypropylpentamethylenediamine*,



a yellow, basic liquid. The salts are oily. The product from methyl-aniline contains *phenoxypropylmethylaniline*, $OPh \cdot [CH_2]_3 \cdot NMePh$, b. p.

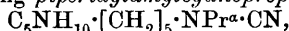
217°/10 mm., *picrate*, m. p. 111°, and ϵ -cyano- ϵ -phenoxy- α -phenyl- α -methylpropylpentamethylenediamine. Aniline forms the corresponding *phenyl* derivative, $\text{NHPh} \cdot [\text{CH}_2]_5 \cdot \text{N}(\text{CN}) \cdot [\text{CH}_2]_3 \cdot \text{OPh}$, a yellowish-red, viscous liquid, yielding oily salts and derivatives.

Potassium cyanide also condenses with the oil, yielding γ -phenoxy-butyronitrile and a derivative of ϵ -leucinonitrile,



which on hydrolysis forms the corresponding *derivative* of leucine, m. p. 131°.

1-Propylpiperidine, best prepared from dibromopentane and propylamine, reacts violently with cyanogen bromide. The product reacts with piperidine, forming *piperidylamylcyanopropylamine*,



an oil, from which the cyano-group may be removed, yielding *piperidylamylpropylamine*, b. p. 146—150°/12 mm.; *picrate*, m. p. 175°; *platinichloride*, m. p. 228° (decomp.).

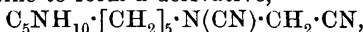
Ethyl β -piperidylpropionate (Wedekind, *Ber.*, 1899, 32, 727) has b. p. 230°; the *picrate*, m. p. 127°; *hydrobromide*, m. p. 154°. The product of the action of cyanogen bromide condenses with piperidine, forming dipiperidylguanidine and other products.

γ -Phthaliminopropylpiperidins, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{N} \cdot [\text{CH}_2]_3 \cdot \text{C}_5\text{NH}_{10}$, from bromopropylphthalimide and piperidine in the cold, forms white crystals, m. p. 50°; *picrate*, m. p. 190°. Cyanogen bromide forms γ -bromopropylphthalimide.

1-Ethylpiperidine and cyanogen bromide yield *piperidylamylcyanoethylamine*, $\text{C}_5\text{NH}_{10} \cdot [\text{CH}_2]_5 \cdot \text{NEt} \cdot \text{CN}$, b. p. 191—192°/11 mm.; the *amine* obtained on hydrolysis has b. p. 132°/10 mm.; *picrate*, m. p. 151°; *platinichloride*, m. p. 220°.

ζ -Ethylaminoheptoic acid, $\text{NHEt} \cdot [\text{CH}_2]_6 \cdot \text{CO}_2\text{H}$, has m. p. 129—130°, and partly forms an internal anhydride on heating. The *platinichloride* has m. p. 117°.

Piperidylacetonitrile and cyanogen bromide form a product which reacts with piperidine to form a derivative,

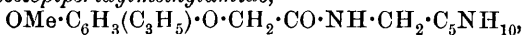


a heavy oil (compare *Abstr.*, 1908, i, 675). *Piperidylacetonitrile picrate* has m. p. 157°.

C. H. D.

Preparation of *N*-Substituted Aminomethyl Derivatives of Eugenol- and *iso*Eugenol-acetamides. ALFRED EINHORN (D.R.-P. 208255).—The condensation products of the acetamides of eugenol and *isoeugenol* with formaldehyde and secondary aliphatic amines are basic substances possessing the property of producing local anaesthesia. This condensation may be effected either in one stage, or the methylol and dimethylol compounds may first be produced, and then condensed with the aliphatic bases.

Eugenolacetopiperidylmethylanilide,



crystals, m. p. 48—52° (*hydrochloride*, white needles, m. p. 142—144°), is prepared by boiling in alcoholic solution either (1) eugenol-acetamide, formaldehyde, and piperidine; (2) *N*-methyloleugenol-

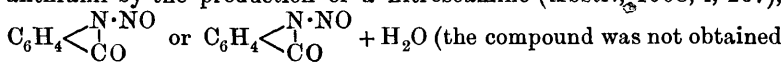
acetamide, $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{C}_3\text{H}_5) \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{OH}$, and piperidine, or (3) eugenolacetamide and piperidomethanol, $\text{C}_5\text{H}_{10}\text{N} \cdot \text{CH}_2 \cdot \text{OH}$, or methylenedipiperidine, $\text{CH}_2(\text{C}_5\text{H}_{10}\text{N})_2$. Analogously constituted compounds are obtained by substituting diethylamine and other secondary bases for piperidine in the above condensation, and also from *isoeugenolacetamide*.
F. M. G. M.

Course of the Friedel-Craft Reaction with Unsymmetrical Polycarboxylic Acids. ALFRED KIRPAL (*Monatsh.*, 1909, 30, 355—361).—The divergent results of the condensation of cinchomeric anhydride and benzene by aluminium chloride obtained by Philips (Abstr., 1894, i, 554), Freund (Abstr., 1898, i, 43), and Fulda (Abstr., 1900, i, 53) has induced the author to repeat the condensation. He obtains the two isomeric substances *4-benzoylnicotinic acid* and *3-benzoylisonicotinic acid*, of which the former is soluble in boiling water. The two acids are obtained separately by condensing 3-methyl cinchomeronate 4-chloride and 4-methyl cinchomeronate 3-chloride respectively with benzene and aluminium chloride. 4-Benzoylnicotinic acid has m. p. 226° , forms a *hydrochloride*, $\text{C}_{13}\text{H}_9\text{O}_3\text{N} \cdot \text{HCl}$, m. p. 240° (decomp.), and yields above its m. p. 4-benzoylpyridine, m. p. 72° . 3-Benzoylisonicotinic acid at its m. p., 270° , is changed to 3-benzoylpyridine, b. p. 307° .

C. S.

Anthranil. XI. EUGEN BAMBERGER (*Ber.*, 1909, 42, 1647—1676).—Polemical. A reply to Heller (Abstr., 1908, i, 267).
C. S.

Anthranil. XII. Anthranil and Methylantranil. EUGEN BAMBERGER and JARL LUBLIN (*Ber.*, 1909, 42, 1676—1707. Compare preceding abstract).—Heller claims to support his imide formula for anthranil by the production of a nitrosoamine (Abstr., 1908, i, 267),



sufficiently pure to decide between the two formulæ). The authors show that the nitrosoamine is in reality *o-aldehydophenylnitrosohydroxylamine*, $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{NO}) \cdot \text{OH}$, m. p. 52.5° (decomp.), the chief points in the proof being (1) the acid character of the substance; (2) the striking resemblance between the iron salt, which is soluble in ether, and the iron salt of nitrosophenylhydroxylamine; (3) its decomposition by cold mineral acids, forming a solution of diazo-salts, among which the presence of diazotised *o*-aminobenzaldehyde is detected by the formation of salicylaldehyde by warming, and (4) its conversion into *o*-azoxybenzaldehyde.

o-Aldehydophenylnitrosohydroxylamine is obtained by slowly adding very finely powdered and sifted sodium nitrite to a continuously-stirred solution of anthranil in 23% hydrochloric acid at -17° , washing the resulting crystals with 23% hydrochloric acid at -17° and with water at 0° (the filtrate contains *o*-aldehydodiazobenzene chloride), drying them on porous tile at 0° , and converting them by alcoholic potassium hydroxide at -15° into the white, crystalline *potassium salt*, the aqueous solution of which, when decomposed by metaphosphoric acid, yields pure aldehydophenylnitrosohydroxylamine.

From the potassium salt the *silver, lead, nickel, cobalt, copper, mercury, and barium* salts have been obtained. The *p*-nitrophenylhydrazone, $C_{13}H_{11}O_4N_5$, has m. p. 171° (decomp.; corr.). An alcoholic solution of *o*-aldehydophenylnitrosohydroxylamine, containing a little water, deposits *o*-azoxybenzaldehyde (Abstr., 1907, i, 163) when kept overnight at -10° .

With regard to the homology of anthranil and methylantranil, Heller states (*loc. cit.*) that these compounds do not behave alike to hydrochloric acid and sodium nitrite under the same conditions, since anthranil yields the (so-called) nitrosoamine, whereas methylantranil forms methylantranil dichloride (Bamberger and Elger, Abstr., 1903, i, 561). The author points out that the conditions are not the same; he and Elger used 39% hydrochloric acid, whilst Heller used 23% acid. With 39% hydrochloric acid and sodium nitrite at -16° to -18° , anthranil behaves like methylantranil, forming a *dichloride*, $C_7H_5ONCl_2$, m. p. 77° . Moreover, methylantranil behaves with 23% hydrochloric acid and sodium nitrite at -17° like anthranil, forming *o*-acetylphenylnitrosohydroxylamine, $COMe \cdot C_6H_4 \cdot N(NO) \cdot OH$, and *o*-acetyldiazobenzene chloride. Anthranil and methylantranil are therefore analogously constituted. C. S.

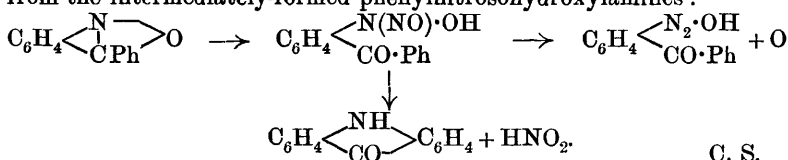
Anthranil. XIII. Diazotisation of Anthranils and Conversion of Arylanthranils into Acridones. EUGEN BAMBERGER (*Ber.*, 1909, 42, 1707—1723).—Methylantranil (2-methylbenz- ψ -oxazole), $C_6H_4 \begin{smallmatrix} \diagup CMe \\ N \diagdown \end{smallmatrix} O$, is converted by nitrous acid into a

diazonium salt of *o*-aminoacetophenone (Abstr., 1903, i, 561). Other ψ -benzoxazoles, such as anthranil and its *Bz*-chlorinated or brominated derivatives (preceding abstract), phenylantranil, *p*-tolylantranil, anthroxanic acid, and its aldehyde behave in a similar manner, as also do thioanthranil and benzoxazole; substituted phenylnitrosohydroxylamines are probably formed as intermediate products (preceding abstract). The process of diazotisation differs somewhat for each substance, but as a rule the substance is dissolved in 62 or 75% sulphuric acid and treated with 10% nitrite at 0° to -10° , and the resulting solution is added to alkaline α -naphthol; the red colour usually develops at once, but only after forty-eight hours in the case of benzoxazole, and after ten days in the case of benzthiazole.

The compounds obtained by Zincke by the condensation of *o*-nitrobenzaldehyde and aromatic amines or phenols in the presence of hydrochloric acid may be formulated as ψ -benzoxazoles (Abstr., 1906, i, 110, 515) or as acridones (Abstr., 1904, i, 530). Since the compounds react with 62% sulphuric acid or 23% hydrochloric acid and 10% sodium nitrite at 0° to form diazonium salts, they are probably ψ -benzoxazoles; 3-methylacridone is stable to 62% sulphuric acid and sodium nitrite at 0° .

The action of sulphuric acid and sodium nitrite on phenyl- and *p*-tolyl-anthranil yields only a small quantity of the diazonium salt, the chief product being acridone and 3-methylacridone respectively. Since 62% sulphuric acid alone at -10° does not cause the formation

of the acridone, the latter and the diazonium salt are probably obtained from the intermediately-formed phenylnitrosohydroxylamines:



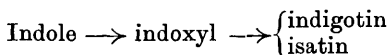
C. S.

Phenylanthranil (2-Phenyl- ψ -benzoxazole). EUGEN BAMBERGER and SVEN LINDBERG (*Ber.*, 1909, 42, 1723—1725).—Phenylanthranil is obtained by the oxidation of *o*-aminobenzophenone by Caro's acid, or, better, by the reduction of *o*-nitrobenzophenone by tin and hot glacial acetic acid. It has m. p. 52—53°, is volatile with steam, and yields acridone when strongly heated (compare Kliegl, this vol., i, 255).

C. S.

Researches on Indole. I. Action of Oxidising Agents. CH. PORCHER (*Bull. Soc. chim.*, 1909, [iv], 5, 526—540).—It is shown that whereas indole is oxidised by hydrogen peroxide, yielding indoxyl and oxidation products of this, the action of ammonium persulphate and of quinone is quite different. The action of hydrogen peroxide is probably akin to that which goes on in the organism.

When indole is added to an aqueous solution of hydrogen peroxide, the latter quickly becomes yellowish-green, and indigotin begins to separate after some hours. On shaking the filtrate with amyl alcohol, indoxyl is dissolved out, and is recognised by its oxidation to indigotin on shaking with alkali, or its conversion into indirubin in presence of isatin and hydrochloric acid. This latter test is delicate, and can be used for the detection of indoxyl free, or in the form of its derivatives. It is always necessary in applying the test to mixtures to separate the indoxyl first by extraction with chloroform or ether. The oxidation of indole by hydrogen peroxide goes on more rapidly at 100°, and under these conditions the reaction appears to take place according to the scheme:



There is also formed some indirubin, which, however, disappears if the oxidation is prolonged. Isatin was detected by the indophenine reaction, and indigo-red was separated from indigotin by extraction with ether. The oxidation of indole to indoxyl, and eventually indigotin, can be used for the detection of this substance in presence of its homologues, such as scatole.

The chief product of the action of ammonium persulphate on indole in water at 100° is a black, flocculent precipitate, and neither indoxyl nor indigotin could be detected, although under certain conditions isatin was formed and possibly indirubin. With quinone in solution, in ether, and in presence of light, indole gives some indirubin, but not indigotin. Details of the methods of applying the various tests used for the detection of the oxidation products are given in the original.

T. A. H.

Iodo-2-methylindole. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1909, **60**, 289—291. Compare Rhode, *ibid.*, 1905, **44**, 161; Neuberg, *Abstr.*, 1907, i, 995).—A crystalline *iodo-2-methylindole*, C_9H_8NI , can be prepared by adding finely divided iodine to a mixture of sodium hydrogen carbonate and an alcoholic solution of 2-methylindole.

It forms pale brownish-violet plates, m. p. 82° , decomposes when exposed to light, and the addition of nitrous acid liberates iodine.

J. J. S.

Perhydrogenated Quinolines. HERMANN FINGER and W. BREITWIESER (*J. pr. Chem.*, 1909, [ii], **79**, 454—456).—3-Cyano-6-methylquinoline when reduced with sodium and alcohol yields 6-methyldecahydroquinoline, although 6-methylquinoline when similarly treated does not yield the decahydro-derivative.

3-Cyano-6-methylquinoline, $C_{11}H_8N_2$, prepared by diazotising 3-amino-6-methylquinoline (compare Noelting and Trautmann, *Abstr.*, 1891, 325) and treating the diazo-compound with potassium cuprous cyanide, forms small, colourless crystals, m. p. $104-105^\circ$; all attempts to hydrolyse it to the corresponding acid have been unsuccessful.

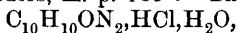
6-Methyldecahydroquinoline, prepared in the manner described or by reducing 6-methyltetrahydroquinoline with hydriodic acid and phosphorus, is a colourless, crystalline substance, m. p. 44° , b. p. $222-225^\circ/750$ mm.; the *hydrochloride*, $C_{10}H_{19}N, HCl$, was analysed. The base interacts with phenylcarbimide, yielding the corresponding *thiocarbamide* derivative, $C_{17}H_{24}N_2S$, a crystalline substance, m. p. 138° .

W. H. G.

Amino- and Hydroxy-quinolones. HERMAN DECKER and HARRY ENGLER (*Ber.*, 1909, **42**, 1736—1742. Compare *Abstr.*, 1903, i, 719).—5-Amino-1-methyl-2-quinolone, $C_9NH_5OMe \cdot NH_2$, obtained by reducing the corresponding nitro-compound (*Abstr.*, 1901, i, 654) with an aqueous solution of ammonium sulphide, separates from benzene in pale yellow crystals, m. p. 213° . The *hydrochloride*, $C_{10}H_{10}ON_2, HCl$, crystallises in clear yellow needles, m. p. 221° , and the *acetyl* derivative, $C_{12}H_{12}O_2N_2, H_2O$, crystallises from water in yellow needles, m. p. 237° . 5-Amino-1-ethyl-2-quinolone, $C_{11}H_{12}ON_2$, obtained in a similar manner from 5-nitro-1-ethylquinolone, crystallises in small, glistening plates, m. p. $177-178^\circ$. The crystals obtained from its aqueous solutions contain $1H_2O$. The *hydrochloride* crystallises from water in glistening, pale yellow needles containing $2H_2O$. It loses the water of hydration at 120° , and then melts and decomposes at 235° .

8-Amino-1-methylquinolone is somewhat less soluble in water or alcohol than the isomeric-6-amino-compound, and separates from benzene in small, glistening, yellow crystals, m. p. 180° . The *formyl* derivative crystallises from dilute alcohol in colourless needles, m. p. 88° , containing water of crystallisation. The *acetyl* derivative has m. p. 174° .

7-Amino-1-methyl-2-quinolone is less soluble than its isomerides, crystallises with H_2O , which it loses in a desiccator, and sublimes in colourless, glistening needles, m. p. 185° . The *hydrochloride*,

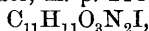


forms golden-yellow needles, which lose their H_2O at $110\text{--}120^\circ$ and then melt and decompose at 244° . The *acetyl* derivative, $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_2$, crystallises from benzene in glistening prisms, m. p. 211° .

[With WLADIMIR RUMINE.]—5-Nitro-6-methoxyquinoline,



obtained by nitrating *p*-methoxyquinoline, crystallises from alcohol in orange-yellow needles, m. p. $104\text{--}105^\circ$. The *nitrate* forms colourless crystals, m. p. 195° ; the *hydrochloride* has m. p. 219° ; the *sulphate*, m. p. 205° ; the *chromate* forms a brown precipitate, m. p. 162° , and the *picrate*, a yellow precipitate, m. p. 211° . The *methiodide*,



has m. p. 275° , and yields a *picrate*, which crystallises in yellow needles, m. p. 168° , and a *chromate*, as orange-coloured plates, which decompose at 160° . The methyl sulphate derivative is readily soluble, and when oxidised with potassium ferricyanide yields 5-nitro-6-methoxy-1-methyl-2-quinolone, $\text{OMe}\cdot\text{C}_9\text{NH}_4\text{MeO}\cdot\text{NO}_2$, which has m. p. 194° and sublimes at 198° .

J. J. S.

A New Synthesis of Dihydroisoquinoline Derivatives.

HERMAN DECKER and WALTER KROPP (*Ber.*, 1909, 42, 2075—2078).—The formation of 3:4-dihydroisoquinoline derivatives from β -phenylethylamine by loss of water (Bischler and Napieralski, *Abstr.*, 1893, i, 608) is of importance as leading to compounds closely related to the opium and other alkaloids. The reaction only takes place at a high temperature, and fails in certain cases. It is now found that the condensation proceeds regularly below 100° in presence of aluminium chloride.

1-Phenyl-3:4-dihydroisoquinoline, $\text{C}_{15}\text{H}_{13}\text{N}$, prepared by warming benzoylphenylethylamine with phosphorus pentachloride, removing the phosphoryl chloride by distillation, warming the residue with light petroleum and aluminium chloride, and purifying by extracting the alkaline solution with ether, forms an oil, b. p. $194\text{--}196^\circ/23\text{ mm.}$ (corr.). The platinichloride, $(\text{C}_{15}\text{H}_{13}\text{N})_2\text{H}_2\text{PtCl}_6$, has m. p. $230\text{--}233^\circ$ when quickly heated (compare Bischler and Napieralski, *loc. cit.*); the *picrate* forms flat, yellow, rhombic needles, m. p. 175° .

Phenylacetyl- β -phenylethylamine, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, prepared from β -phenylethylamine, crystallises from aqueous alcohol in plates, m. p. $94\text{--}95^\circ$.

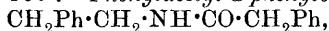
β -Phenylethylamine *picrate* has m. p. 171° (corr.) (compare Michaelis, Schroeter, and Linow, *Abstr.*, 1893, i, 703).

C. H. D.

Synthesis of isoQuinoline Bases. AMÉ PICTET and FRANCIS W. KAY (*Ber.*, 1909, 42, 1973—1979).—Since the majority of the opium alkaloids are derived from 1-benzylisoquinoline, a simple method for the synthesis of this and similar bases is desirable. Many investigators have achieved partial success; the authors find that a modification of Bischler and Napieralski's method (*Abstr.*, 1893, i, 608) gives the desired result. Acyl- ω -phenylethylamines, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{R}$, and phosphoric oxide are heated in boiling benzene, toluene, or xylene, the selection of the solvent being determined by the particular acyl compound under examination. The

constitution of the resulting dihydroisoquinoline base is determined by its oxidation to the corresponding isoquinoline by acidified potassium permanganate.

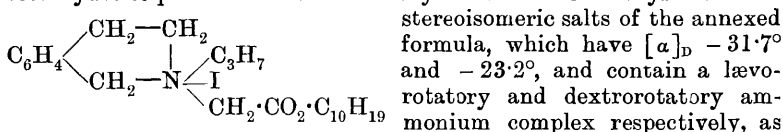
1-Phenyl-3:4-dihydroisoquinoline, $C_{15}H_{13}N$, m. p. 73—74°, b. p. 320°/718 mm., prepared from benzoyl- ω -phenylethylamine, forms a hydrochloride, m. p. 222—223°, platinichloride, m. p. 229—230° (decomp.), and a picrate, m. p. 163°. 1-Methyl-3:4-dihydroisoquinoline forms a hydrochloride, m. p. 160°, a nearly colourless platinichloride, m. p. 223°, picrate, m. p. 188—190°, and a dichromate, which decomposes at 150—160°. Phenylacetyl- ω -phenylethylamine,



m. p. 95°, is obtained by shaking equal molecular quantities of ω -phenylethylamine and phenylacetyl chloride with 20% sodium hydroxide below 0°. When heated with phosphoric oxide in boiling xylene, it yields 1-benzyl-3:4-dihydroisoquinoline, $C_{16}H_{15}N$, b. p. 300° (decomp.), or 196—197°/12 mm. (picrate, m. p. 174—175°; platinichloride, m. p. 197°, decomp.), which is oxidised to 1-benzylisoquinoline by potassium permanganate and glacial acetic acid. C. S.

Another Case of Stereoisomerism of Compounds containing Asymmetric Nitrogen and Active Asymmetric Carbon.

EDGAR WEDEKIND and F. NEY (*Ber.*, 1909, 42, 2138—2142).—The fractional crystallisation of the product of the interaction of 2-propyltetrahydroisoquinoline with *l*-menthyl iodoacetate has yielded two



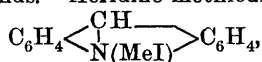
shown by the fact that, on treatment with silver oxide in methyl-alcoholic solution, they yield different betaines, one of which is dextro-, and the other lævo-rotatory.

isoQuinoline propioidide, obtained by mixing isoquinoline with propyl iodide, separates from alcohol in yellow crystals, m. p. 115—118°; on reduction with tin and hydrochloric acid it is converted into 2-propyltetrahydroisoquinoline, a light yellow oil, b. p. 259—260°/743 mm.

The latter substance, when gently warmed with *l*-menthyl iodoacetate, yields a glassy, viscous substance, which, on crystallisation from acetone, gives glistening needles of menthyl 2-propyltetrahydroisoquinolinium-iodide-1-acetate, $C_{24}H_{38}O_2NI$, m. p. 189° (decomp.); the mother liquors contain a more soluble isomeric variety, m. p. 169° (decomp.); the less fusible substance has $[\alpha]_D - 23.2^\circ$, and the more fusible one, $[\alpha]_D - 31.7^\circ$. The betaines obtained from these two substances very rapidly became inactive, and were too unstable to be examined more closely. P. H.

Action of Grignard's Solutions on Halogen Ammonium Compounds. MARTIN FREUND and GEORG BODE (*Ber.*, 1909, 42, 1746—1766. Compare *Abstr.*, 1906, i, 600; this vol., i, 417).—Organic ammonium compounds which yield pseudo-bases under the

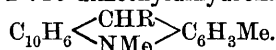
influence of alkalis react with Grignard's compounds in such a manner that the hydroxyl of the ψ -base is replaced by an alkyl group. This generalisation is illustrated in the case of various acridinium and isoquinolinium compounds. Acridine methiodide,



yields a ψ -base, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}(\text{OH}) \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \text{C}_6\text{H}_4$, and with organo-magnesium compounds yields alkyl derivatives of 10-methyldihydroacridine, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CHR} \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \text{C}_6\text{H}_4$. The following compounds have been prepared from acridine methiodide by this method: 9-Phenyl-10-methyldihydroacridine (Berthsen and Bender, Abstr., 1883, 1134); 9-benzyl-10-methyldihydroacridine, $\text{C}_{21}\text{H}_{19}\text{N}$, colourless needles, m. p. 108° , which reacts with an alcoholic solution of iodine, yielding a black periodide, and from this sulphurous acid liberates benzylacridine methiodide (Decker and Hock, Abstr., 1904, i, 620); 10-methyl-9-ethyldihydroacridine, $\text{C}_{16}\text{H}_{17}\text{N}$, colourless needles, which turn yellowish-brown on exposure to the air, m. p. $70-73^\circ$; 9:10-dimethyldihydroacridine, $\text{C}_{15}\text{H}_{15}\text{N}$, colourless, pearly plates, m. p. $135-140^\circ$; 10-methyl-9-isopropyldihydroacridine, $\text{C}_{17}\text{H}_{19}\text{N}$, colourless needles, m. p. $99-102^\circ$.

10-Methyl-9-diethyldihydroacridine, $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}_2\text{Et}_2 \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \text{C}_6\text{H}_4$, is formed by the action of ethyl magnesium bromide on ethylacridine methiodide. It crystallises from alcohol in colourless prisms, m. p. $80-85^\circ$.

Grignard compounds also react with the methiodide of 2'-methyl-1:2-naphthacridine (Ullmann and Naef, Abstr., 1900, i, 360), yielding derivatives of 2':10-dimethyldihydronaphthacridine,



2':9:10-Trimethyldihydronaphthacridine, $\text{C}_{20}\text{H}_{19}\text{N}$, crystallises from alcohol in colourless plates, m. p. $150-160^\circ$; 2':10-dimethyl-9-ethyldihydronaphthacridine, $\text{C}_{21}\text{H}_{21}\text{N}$, forms colourless needles, m. p. 132° , after sintering at 125° ; 9-phenyl-2':10-dimethyldihydronaphthacridine, $\text{C}_{25}\text{H}_{21}\text{N}$, crystallises from ethyl acetate in colourless needles, m. p. $187-191^\circ$, and the corresponding 9-benzyl derivative, $\text{C}_{26}\text{H}_{23}\text{N}$, crystallises from alcohol in colourless needles, m. p. 145° . The substituted dihydroacridines do not possess basic properties. The product obtained by the action of magnesium on an ethereal solution of ethylene bromide does not react with acridine methiodide (compare Abstr., 1906, i, 602). The methiodide of diacetylbenzoflavin (Hewitt and Fox, Trans., 1905, 87, 1058) does not react with Grignard reagents.

isoQuinoline methiodide, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH:CH} \\ \diagup \quad \diagdown \\ \text{CH:NMeI} \end{array}$, reacts with Grignard compounds, yielding 1-alkyl derivatives of 2-methyl-1:2-dihydroisoquinoline, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH=CH} \\ \diagup \quad \diagdown \\ \text{CHR}\cdot\text{NMe} \end{array}$. 1:2-Dimethyl-1:2-dihydroisoquinoline, $\text{C}_{11}\text{H}_{13}\text{N}$, has b. p. $150^\circ/20\text{ mm.}$; the *platinichloride*, $(\text{C}_{11}\text{H}_{13}\text{N})_2\cdot\text{H}_2\text{PtCl}_6$,

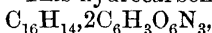
sinters at 160° and decomposes at 167° . When the base is reduced with sodium and alcohol it yields 1:2-dimethyltetrahydroisoquinoline, $C_{11}H_{15}N$, as a colourless liquid, b. p. $121-125^{\circ}/20$ mm.; the corresponding methiodide, $C_{12}H_{18}NI$, crystallises from alcohol in plates.

2-Methyl-1-ethyl-1:2-dihydroisoquinoline, $C_{12}H_{15}N$, has b. p. $165^{\circ}/45$ mm., and when reduced with tin and hydrochloric acid yields the tetrahydro-base, $C_{12}H_{17}N$, as an oil, b. p. $135^{\circ}/30$ mm.; the methiodide, $C_{13}H_{20}NI$, of the latter crystallises in prisms, sinters at 158° , and decomposes at $159-160^{\circ}$.

1-Phenyl-2-methyl-1:2-dihydroisoquinoline, $C_{16}H_{15}N$, has b. p. $220^{\circ}/30$ mm., and crystallises from alcohol in colourless needles, m. p. $55-60^{\circ}$. The platinichloride has m. p. 158° (decomp.).

1-Phenyl-2-methyltetrahydroisoquinoline, $C_{16}H_{17}N \cdot H_2O$, crystallises from dilute alcohol in colourless needles, m. p. $120-130^{\circ}$, after sintering at $65-70^{\circ}$. The methiodide, $C_{17}H_{20}NI$, forms colourless prisms, m. p. $240-243^{\circ}$. 1-Benzyl-2-methyl-1:2-dihydroisoquinoline, $C_{17}H_{17}N$, has b. p. $170-180^{\circ}/9$ mm., and the platinichloride has m. p. $150-155^{\circ}$. The corresponding tetrahydro-base, $C_{17}H_{19}N$, has b. p. $177-180^{\circ}/12$ mm., and yields a platinichloride, which crystallises in orange-red plates, m. p. 200° . The picrate forms rhombic plates, m. p. $165-166^{\circ}$; the hydriodide, prisms, m. p. $175-180^{\circ}$, and the methiodide, $C_{18}H_{22}NI$, prisms, m. p. $239-242^{\circ}$.

When the methiodide of 1-benzyl-2-methyltetrahydroisoquinoline is treated with silver oxide in the presence of dilute alcohol and then with concentrated sodium hydroxide solution, it yields *o*-dimethylaminoethylstilbene, $CHPh \cdot CH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NMe_2$. The hydrochloride, $C_{18}H_{21}N \cdot HCl$, crystallises from dilute alcohol in colourless prisms, m. p. $105-110^{\circ}$, containing $1H_2O$. When dried at 110° it has m. p. $160-165^{\circ}$. The hydriodide has m. p. $160-167^{\circ}$, and the methiodide, $C_{19}H_{24}NI$, m. p. $175-185^{\circ}$. When the methiodide is heated with aqueous-alcoholic sodium hydroxide, it yields *o*-vinylstilbene, $C_{16}H_{14}$, as an oil. This hydrocarbon forms a picrate,



which crystallises from dilute alcohol in orange-red needles, m. p. $95-100^{\circ}$, and a tetrabromide, $CH_2Br \cdot CHBr \cdot C_6H_4 \cdot CHBr \cdot CHBrPh$, which crystallises from glacial acetic acid in colourless plates, m. p. $165-168^{\circ}$.

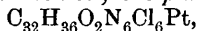
The derivatives of 1:2-dihydroisoquinoline are much less stable than derivatives of 3:4-dihydroisoquinoline (cotarnine derivatives).

Definite products have not been obtained by the action of Grignard compounds on dinaphthazine methiodide, *m*-tolyliminazole methiodide, or pyridine methiodide.

J. J. S.

Behaviour of Hydroxy-*p*-phenylenediamine and its Unsymmetrical Dialkyl Derivatives in Acetic Acid Solution on Oxidation with Air. FRIEDRICH KEHRMANN and W. POPLAWSKI (*Ber.*, 1909, 42, 1275-1278).—A warm aqueous solution of *o*-hydroxy-*p*-phenylenediamine hydrochloride and sodium acetate gives, on passing air through it, a small quantity of 3:9-diaminophenoxazonium chloride (*Abstr.*, 1903, i, 280). This result confirms the constitution previously assigned to the substance. A 50% yield of 3:9-tetramethyldiamino-

phenoxazonium nitrate, $C_{16}H_{18}O_4N_4 \cdot H_2O$, is obtained by the oxidation of a similar solution of *o*-hydroxy-*as*-dimethyl-*p*-phenylenediamine; it forms long, green, metallic needles; the *platinichloride*,

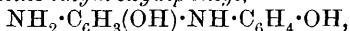


is a dark blue, microcrystalline powder. The unsymmetrical hydroxy-dimethyl-*p*-tolylene-diamine also gives a dye of the Capri-series under like conditions. W. R.

Quinonoid Compounds. XVIII. *meri*-Quinoneimines. III.

RICHARD WILLSTÄTTER and JEAN PICCARD (*Ber.*, 1909, 42, 1902—1907. Compare Abstr., 1908, i, 475, 915).—It has been found possible to isolate the violet dye obtained by the oxidation of *p*-aminophenol with cold ferric chloride solution. It has the composition $C_{12}H_{10}O_2N_2 \cdot HCl$, and may be crystallised from dilute acid provided precautions are taken. It forms brilliant, opaque prisms with a coppery lustre, and may also be obtained in a pure state by oxidising its leuco-compound with ferric chloride in 2*N*-hydrogen chloride solution. Its solutions have a violet colour, and are not decolorised by the addition of much water or of acid. The dye does not yield quinone with acids, and when oxidised with dichromate only one-half of the molecule is converted into benzoquinone. The dye thus appears to be a condensation product of anilinoquinone constitution.

The *leuco-base*, *aminodihydroxydiphenyl*,



obtained by reducing the dye with stannous chloride, yields a *hydrochloride*, $C_{12}H_{12}O_2N_2 \cdot 2HCl$, in the form of prisms sparingly soluble in alcohol. The *basic chloride*, $C_{12}H_{12}O_2N_2 \cdot HCl$, is readily soluble in alcohol. The base forms crystalline aggregates, m. p. 202—203°, and its alkaline solutions readily turn red. J. J. S.

Compounds of Benzidine with Sugars, and a Method for Removing Dextrose from Mixtures of Dextrose and Lævulose. OSCAR ADLER (*Ber.*, 1909, 42, 1742—1746).—Alcoholic solutions of benzidine react with sugars, yielding crystalline compounds analogous to compounds of sugars with aniline and toluidine (Sorokin, Abstr., 1887, 526, 683). They form light crystalline powders, insoluble in ether, but soluble in hot alcohol or water. Their solutions react in much the same manner as their components.

A crystalline compound with lævulose could not be isolated, even when the solutions were evaporated to syrupy consistency. When an alcoholic solution containing both dextrose and lævulose is mixed with benzidine and concentrated by evaporation, the greater part of the dextrose can be removed in the form of the crystalline benzidine derivative, and the mother liquors are then much richer in lævulose.

Didextrose benzidide, $C_{24}H_{34}O_{10}N_2$, crystallises from 96% alcohol in colourless, microscopic needles, m. p. 127° (decomp.). Its alcoholic solution is strongly lævorotatory, and it can be fermented by yeast. *Diarabinose benzidide*, $C_{22}H_{28}O_8N_2$, forms a pale yellow, microcrystalline powder, m. p. 86° (decomp.), and its solution in 50% alcohol is inactive. *Dimaltose benzidide*, $C_{36}H_{52}O_{20}N_2$, is a colourless, microcrystalline

powder, m. p. 175°, after previous sintering. Its aqueous solution is dextrorotatory, and exhibits mutarotation. J. J. S.

Nucleus-substituted Triphenylmethane Dyes. HERMANN FINGER (*J. pr. Chem.*, 1909, [ii], 79, 492—497).—An account of the preparation and properties of trichloro- and trimethoxy-magenta. The introduction of the chlorine into the magenta benzene nuclei results in the production of lighter shades of colour in dyeing, whilst the methoxy-groups produce a deepening effect towards violet.

3 : 3'-Dichloro-4 : 4'-diaminodiphenylmethane, $C_{13}H_{12}N_2Cl_2$, prepared by boiling methylenedi-*o*-chloroaniline, m. p. 74° (Bischoff and Reinfeld, *Abstr.*, 1903, i, 247, give m. p. 84°), with *o*-chloroaniline and *o*-chloroaniline hydrochloride in alcohol, is a crystalline substance, m. p. 105°; the *dihydrochloride*, m. p. 201°, is very unstable.

The colour base obtained by heating 3 : 3'-dichloro-4 : 4'-diaminodiphenylmethane with *o*-chloroaniline, *o*-chloroaniline hydrochloride, and arsenic acid, could not be obtained in a colourless or crystalline condition; the *hydrochloride* is a dark red powder with a metallic green reflex; the *picrate* was prepared and analysed.

4 : 4'-Diamino-3 : 3'-dimethoxydiphenylmethane, $C_{15}H_{18}O_2N_2$, prepared from methylenedi-*o*-anisidine, is a crystalline substance, m. p. 100°; the *diacetyl* derivative, $C_{19}H_{22}O_4N_2$, crystallises in nodules, m. p. 180·5°, and when oxidised with chromic acid yields *diacetyldiamino-dimethoxybenzophenone*, $C_{19}H_{20}O_5N_2$, crystallising in pale yellow leaflets, m. p. 208—209°.

4 : 4'-Diamino-3 : 3'-dimethoxybenzophenone, $C_{15}H_{18}O_3N_2$, forms small, pale yellow crystals, m. p. 227°, and when reduced yields 4 : 4'-diamino-3 : 3'-dimethoxybenzhydrol, obtained as a fine yellow powder, m. p. 160°. *Trimethoxymagenta*, $C_{22}H_{24}O_3N_3Cl$, prepared from 4 : 4-diamino-3 : 3'-dimethoxydiphenylmethane by heating with *o*-anisidine hydrochloride, *o*-nitroanisole, and a small quantity of ferric chloride at 180°, is obtained as coppery-red granules with a green reflex; the colour base is almost black. W. H. G.

New Kind of Isomerism in the Hydroxy- and Alkoxy-Malachite-Green Series. EMIL VOTOČEK and CYRILL KRAUZ (*Ber.*, 1909, 42, 1602—1611. Compare *Abstr.*, 1907, i, 245).—In a few cases the condensation previously investigated of hydroxy- and alkoxy-aldehydes with dimethylaniline proceeded abnormally, and a more accurate study of these interactions has now been made. The condensation of β -naphthaldehyde and dimethylaniline in alcoholic hydrogen chloride at 120° for twenty hours gave the leuco-base of methyl-violet (hexamethyltriaminotriphenylmethane). This abnormal result is shown to be due to the aldehyde on heating liberating formic acid, which then condenses with the dimethylaniline to form tetramethyldiaminobenzhydrol, and this in its turn yields the leuco-base with more of the aniline. The leuco-base from protocatechualdehyde is dihydroxytetramethyldiaminotriphenylmethane (compare *Abstr.*, 1897, i, 157), identical with that obtained from the hydrol and catechol. Resorcin aldehyde in a similar manner gives a *dihydroxytetramethyldiaminotriphenylmethane*, $C_{23}H_{26}O_2N_2$, m. p. 204—205°, and when

oxidised gives a dirty blue dye; pyrogallaldehyde, a *trihydroxytetramethyldiaminotriphenylmethane*, $C_{23}H_{26}O_3N_2$, of m. p. 170—172°, which oxidises to a dirty blue dye.

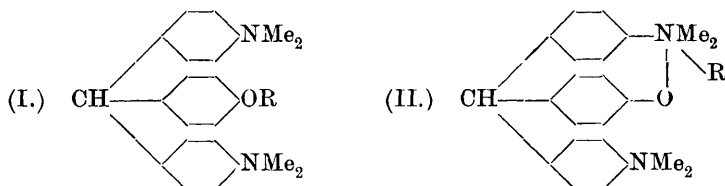
The leuco-base obtained from gentisinaldehyde and dimethylaniline is not identical with that from the hydrol-quinol condensation, although this would be expected to give the same compound if, as is usual, the para-positions to the amino-groups were those affected in the change. The base is a *dihydroxytetramethyldiaminotriphenylmethane*, $C_{23}H_{26}O_2N_2$, of m. p. 165°; the corresponding dye is blue.

In order further to elucidate the differences existing in these compounds, the methoxymalachite-greens have been studied. *o*-Methoxybenzaldehyde gives with dimethylaniline a *methoxyleucomalachite-green*, $C_{24}H_{28}ON_2$, of m. p. 155°, which, although identical in m. p. and composition with that formerly obtained from anisole and tetramethyldiaminobenzhydrol (1907, *loc. cit.*), is yet a different substance, giving a mixed m. p. of 118° and a dye stable towards alkalis. Likewise, the leuco-bases from *m*- and *p*-methoxybenzaldehydes are different from the hydrol compound. The leuco-base from the hydrol-phenol condensation on methylation by means of methyl sulphate in a closed tube at 100° for four hours gives the same leuco-base as is obtained from anisole. There are therefore four methoxyleuco-bases obtained, and only three theoretically possible.

The *ethoxyleucomalachite-greens*, $C_{25}H_{30}ON_2$, from *o*-, *m*-, and *p*-ethoxybenzaldehyde have m. p.'s 119°, 120°, and 125° respectively, whereas that formerly obtained from phenetole, as well as the methylation of the phenol leuco-base, has m. p. 165°.

The dye from the anisaldehyde-dimethylaniline condensation on hydrolysis with hydrochloric acid in a closed tube at 140° gave methyl chloride, phenol, and 4 : 4'-tetramethyldiaminobenzophenone (Michler's ketone), and similar results were obtained with the dyes from *o*- and *m*-hydroxybenzaldehydes. The conclusion is drawn that in these condensations both the amino-groups are in the para-positions.

The suggestion is made that one series of the leuco-bases is normal, and in the other they have a betaine-like structure, thus :



that from the hydrol having the structure (II). It is further shown that the leuco-base from anisaldehyde is transformed into the leuco-base from the hydrol by heating with hydrochloric acid in a sealed tube at 120° for one hour, but the reverse change with sodium hydroxide did not take place.

W. R.

Hydrazones of Sugars and their Acetates. ADOLF HOFMANN (*Annalen*, 1909, 366, 277—323).—With the object of gaining some knowledge as to the nature of the isomerism of the dextrophenyl-

hydrazones described by Behrend and Lohr (Abstr., 1908, i, 765), attempts have been made to prepare isomeric phenylhydrazones of various sugars. Although mixtures of isomerides were obtained, it was not found possible in any case to isolate both forms. Noteworthy is the fact that *p*-bromophenylhydrazine reacts with lævulose in alcoholic solution only in the presence of acetic acid, whilst it does not appear to condense with lactose under any conditions; further, α -phenylbenzylhydrazine interacts with lactose only in the presence of acetic acid, whilst maltose does not yield an α -phenylbenzylhydrazone.

Attempts were also made to isolate the second isomeride of the phenylhydrazones exhibiting mutarotation, by conversion into acetates. The solution of the hydrazone in pyridine, after attaining a state of equilibrium, was treated with acetic anhydride, but in no case was even a mixture of isomerides obtained. The acetates prepared in this manner are probably penta-acetates; the imino-hydrogen atom of the hydrazone is apparently not replaced by acetyl, since benzaldehydephenylhydrazone is not acetylated in pyridine solution.

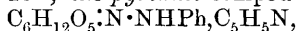
Dextrose- α -phenylhydrazone and β -phenylhydrazone yield isomeric acetates, neither of which exhibits mutarotation, from which observation the conclusion is drawn that one of the dextrosephenylhydrazones is a true hydrazone, whilst the other is a hydrazide (compare Behrend and Lohr, *loc. cit.*).

Dextrose- α -phenylhydrazone acetate, $C_{22}H_{28}H_{10}N_2$ or $C_{24}H_{30}O_{11}N_2$, crystallises in long, white needles, sinters at 150° , m. p. $152-153^\circ$, $[\alpha]_D + 11.97^\circ$ (in pyridine); the corresponding *β -phenylhydrazone acetate* is an amorphous substance, sinters at 40° , m. p. $50-70^\circ$ (decomp.), $[\alpha]_D + 100.15^\circ$ to $+101.34^\circ$.

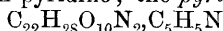
Dextrose-p-bromophenylhydrazone, $C_{12}H_{17}O_5N_2Br$, crystallises in long, thin prisms, sinters at 146° , m. p. $164-166^\circ$ (decomp.); the solution in pyridine has an initial value, $[\alpha]_D - 43.67^\circ$, and final value, $[\alpha]_D + 18.94^\circ$. Dextrose- α -phenylbenzylhydrazone in pyridine has an initial value, $[\alpha]_D - 46.33^\circ$, and final value, $[\alpha]_D - 48.16^\circ$; the *penta-acetate*, $C_{29}H_{34}O_{10}N_2$, is an amorphous, pale yellow mass, sinters at 40° , m. p. $60-80^\circ$, $[\alpha]_D + 112.48^\circ$ (in pyridine).

Mannosephenylhydrazone does not exhibit mutarotation; the *acetate*, $C_{22}H_{28}O_{10}N_2$ or $C_{24}H_{30}O_{11}N_2$, is an amorphous, reddish-brown mass, sinters at 40° , m. p. $60-70^\circ$.

Galactosephenylhydrazone in pyridine, ten minutes after dissolution, has the value $[\alpha]_D + 20.54^\circ$ to $+20.70^\circ$; the final value is $[\alpha]_D + 9.34^\circ$ to $+9.23^\circ$; the *pyridine* compound,



crystallises in snow-white leaflets, sinters at 153° , m. p. $156-158^\circ$ (decomp.), $[\alpha]_D + 17.39^\circ$ (initial value), $+7.99^\circ$ (final value), in pyridine; the *acetate*, $C_{22}H_{28}O_{10}N_2$ or $C_{24}H_{30}O_{11}N_2$, crystallises in colourless leaflets, m. p. $131-133^\circ$, $[\alpha]_D$ about $+44^\circ$ (initial value), about 42° (final value), in pyridine; the *pyridine* compound,



or $C_{24}H_{30}O_{11}N_2, C_5H_5N$, forms white leaflets, sinters at 103° , m. p. $108-110^\circ$, $[\alpha]_D$ about $+38^\circ$ (initial value), about 37° (final value).

Galactose-p-bromophenylhydrazone, $C_{12}H_{17}O_5N_2Br$, crystallises in long,

thin needles, sinters at 164° , m. p. $166-167^{\circ}$ (decomp.). The corresponding α -phenylbenzylhydrazone has the value $[\alpha]_D -14.26^{\circ}$ in pyridine, and does not exhibit mutarotation; the *pyridine* compound, $C_6H_{12}O_5 \cdot N \cdot NPh \cdot CH_2Ph, C_5H_5N$, forms crystals, which sinter at 106° , m. p. $110-112^{\circ}$, $[\alpha]_D -11.35^{\circ}$ (in pyridine); the *penta-acetate*, $C_{29}H_{34}O_{10}N_2$, crystallises in short, colourless prisms, sinters at 125° , m. p. $128-130^{\circ}$, $[\alpha]_D +93.21^{\circ}$ (in pyridine); the *pyridine* derivative, $C_{29}H_{34}O_{10}N_3 \cdot C_5H_5N$, forms snow-white leaflets, m. p. $105-110^{\circ}$, $[\alpha]_D +81.85^{\circ}$.

Attempts to prepare a phenylhydrazone of lævulose were unsuccessful; the *phenylhydrazone* compound, $C_6H_{12}O_5 \cdot N \cdot NPh, NPh \cdot NH_2$, crystallises in long, pale yellow needles and prisms, sinters at $50-60^{\circ}$, m. p. $140-150^{\circ}$ (decomp.); the initial values of $[\alpha]_D$ in alcohol and pyridine are $+6.37^{\circ}$ and $+8.30^{\circ}$ respectively, whilst the final values are -3.27° and $+3.44^{\circ}$ respectively; the *pyridine* compound, $C_6H_{12}O_5 \cdot N \cdot NPh, C_5H_5N$, forms small, white plates, sinters at 96° , m. p. $98-100^{\circ}$ (decomp.), $[\alpha]_D +8.61^{\circ}$ (initial value), $+3.36^{\circ}$ (final value), in pyridine; the *acetate*, $C_{22}H_{28}O_{10}N_2$ or $C_{24}H_{30}O_{11}N_2$, is a coloured, amorphous mass. Lævulose yields with *p*-bromophenylhydrazine in alcohol containing acetic acid a thick jelly, from which a simple substance could not be isolated.

Maltose-phenylhydrazone and *p*-*bromophenylhydrazone* could be obtained only as syrups.

Lactose- α -phenylbenzylhydrazone sinters at 162° , and decomposes at $164-166^{\circ}$ (compare Lobry de Bruyn and van Eckenstein, Abstr., 1907, i, 41); the solution in pyridine, $[\alpha]_D -34.7^{\circ}$ to -36.1° , does not exhibit mutarotation; the *octa-acetate*, $C_{41}H_{50}O_{18}N_2$, is an amorphous substance, sinters at 50° , m. p. $60-80^{\circ}$ (decomp.), $[\alpha]_D +62.22^{\circ}$.

W. H. G.

Action of Sulphites on Aromatic Amino- and Hydroxy-compounds. VI. Action of Sulphites on Hydrazines, particularly the Naphthylhydrazines. HANS TH. BUCHERER and MAXIMILIAN SCHMIDT (*J. pr. Chem.*, 1909, [ii], 79, 369-417. Compare Bucherer and Seyde, Abstr., 1908, i, 455).—By means of the sulphite method it is possible to pass from an amine to a phenol, thus: $R \cdot NH_2 + 3NaHSO_3 = RO \cdot SO_2Na + Na_2SO_3 + NH_4HSO_3$; $RO \cdot SO_2Na + 2NaOH = R \cdot ONa + Na_2SO_3 + H_2O$. An analogous reaction should take place with an arylhydrazine, the only difference being the elimination of hydrazine instead of ammonia. The action of sodium hydrogen sulphite on α -naphthylhydrazine and the 4-sulphonic acid has been studied, and found to follow the course indicated. The yield of hydrazine is, however, very small, owing to the occurrence of other reactions; for example, the sulphite ester formed by the action of sodium hydrogen sulphite on α -naphthylhydrazine interacts with the latter substance, forming hydrazonaphthalene, thus: $C_{10}H_7 \cdot NH \cdot NH_2 + C_{10}H_7 \cdot O \cdot SO_2Na = C_{10}H_7 \cdot NH \cdot NH \cdot C_{10}H_7 + NaHSO_3$. The hydrazo-compound is, however, unstable, and is oxidised to the corresponding azo-compound, which combines with the hydrogen sulphite in the nascent state, forming the salt, $C_{10}H_7 \cdot NH \cdot N(SO_3Na) \cdot C_{10}H_7$. A small part of the hydrazonaphthalene undergoes transformation into naphthidine,

whilst another portion changes into 2 : 2'-dinaphtha-1 : 1'-carbazole with elimination of ammonia.

β -Naphthylhydrazine does not behave exactly like the α -compound. In this case the yield of hydrazine is very small, and naphthol is not produced, since the sulphite ester formed immediately reacts at once with the naphthylhydrazine still present.

The yield of hydrazine is shown to be diminished by the destructive action of the hydrogen sulphite. It is also found that phenylhydrazine is decomposed by sodium hydrogen sulphite in a similar manner : $2\text{NHPh}\cdot\text{NH}_2 + 4\text{NaHSO}_3 = 2\text{NHPh}\cdot\text{NH}\cdot\text{SO}_3\text{Na} + \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$. With the object of increasing the yield of hydrazine, therefore, an attempt was made to remove it from the destructive influence of the hydrogen sulphite by the addition of benzaldehyde. The desired result was, however, not obtained ; for example, sodium β -naphthylhydrazine-6-sulphonate reacts with benzaldehyde, yielding the corresponding benzylidene derivative, but the latter does not react with sodium hydrogen sulphite.

The action of sodium hydrogen sulphite on 1 : 1'-dinaphthylcarbamide-4 : 4'-disulphonic acid was also investigated. It is found that the carbamide derivative is hydrolysed with the formation of naphthionic acid, which reacts with sodium hydrogen sulphite, yielding ammonia and sodium 1-naphthylsulphite-4-sulphonate. Dinaphthylcarbohydrazidedisulphonic acid, when similarly treated, remains practically unchanged, and does not react in the manner expected, namely : $(\text{R}\cdot\text{NH}\cdot\text{NH})_2\text{CO} + 2\text{NaHSO}_3 = 2\text{RO}\cdot\text{SO}_2\text{Na} + (\text{NH}_2\cdot\text{NH})_2\text{CO}$.

2-Naphthylhydrazine-6-sulphonic acid, $\text{C}_{10}\text{H}_{10}\text{O}_2\text{N}_2\text{S}$, is prepared by reducing the corresponding diazo-compound ; it crystallises in microscopic prisms ; the sodium salt ($1\text{H}_2\text{O}$) crystallises in hexagonal leaflets.

The action of sodium hydrogen sulphite on β -naphthylhydrazine results in the formation of sodium 1 : 1'-dinaphtha-2 : 2'-carbazole-N-sulphonate, $\text{C}_{20}\text{H}_{12}\text{O}_3\text{NSNa}$, crystallising in tufts of small, slender needles, 1 : 1'-dinaphtha-2 : 2'-carbazole, 2 : 2'-diamino-1 : 1'-dinaphthyl, and hydrazine.

1-Naphthylhydrazine-4-sulphonic acid, when treated with benzaldehyde and sodium hydrogen sulphite, yields sodium 1-benzylidenenaphthylhydrazone-4-sulphonate, $\text{C}_{17}\text{H}_{13}\text{O}_3\text{N}_2\text{SNa}$, crystallising in yellowish-white, glistening leaflets. 2-Naphthylhydrazine-6-sulphonic acid, when similarly treated, yields the corresponding benzylidene derivative, crystallising in white leaflets. Naphthionic acid, when treated with aqueous sodium hydroxide and carbonyl chloride, yields 1 : 1'-dinaphthylcarbamide-4 : 4'-disulphonic acid ; the crystalline sodium salt, $\text{C}_{21}\text{H}_{14}\text{O}_7\text{N}_2\text{S}_2\text{Na}_2$, was analysed.

Sodium 1 : 1'-dinaphthylcarbohydrazide-4 : 4'-disulphonate,



obtained by acting on sodium 1-naphthylhydrazine-4-sulphonate with carbonyl chloride, crystallises in pink, microscopic leaflets. β -Azonaphthalene is not attacked when boiled with sodium hydrogen sulphite ; in the presence of phenylhydrazine, however, it yields 2 : 2'-diamino-1 : 1'-dinaphthyl. Azobenzene is reduced to hydrazobenzene when treated in a similar manner.

β -Hydroxynaphthoic acid interacts with sodium hydrogen sulphite and β -naphthylhydrazine, yielding sodium 1 : 1'-dinaphtha-2 : 2'-carb-

azole-N-sulphonate, $C_{20}H_{12}O_3NSNa$, crystallising in long needles, 2:2'-diamino-1:1'-dinaphthyl, and 1:1'-dinaphthyl-2:2'-carbazole.

Similarly, α -naphthylhydrazine leads to the formation of *sodium 1:2'-dinaphthyl-2:1'-carbazolesulphonate*, $C_{20}H_{12}O_3NSNa$, crystallising in white needles, α -naphthylamine, and α -dinaphthylamine.

Unsuccessful attempts were made to prepare 2:2'-diamino-1:1'-dinaphthyl by the action of ammonium sulphite and ammonia on β -dinaphthol.

W. H. G.

Preparation of 1-Aryl-5-halogenmethyl-2:4-dialkyl-3-pyrazolones. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 208593).—1-Aryl-5-methyl-2:4-dialkyl-5-pyrazolone, like the isomeric 1-aryl-3-methyl-2:4-dialkyl-5-pyrazolones, unites with bromine or chlorine, forming a dihalide, from which hydrogen halide can be eliminated with the formation of 1-aryl-5-bromomethyl-2:4-dialkyl-3-pyrazolones. $CH_2X \cdot C \begin{smallmatrix} \swarrow \\ \text{NAr} \cdot \text{NR} \end{smallmatrix} \begin{smallmatrix} \searrow \\ \text{CR} - \text{CO} \end{smallmatrix}$, where X is a halogen atom and R and Ar are alkyl and aryl groups respectively.

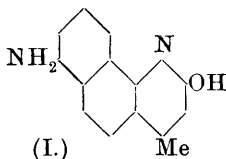
1-Phenyl-2:4-dimethyl-5-bromomethyl-3-pyrazolone, m. p. 127—130°, is thus obtained from 1-phenyl-2:4:5-trimethyl-3-pyrazolone and bromine in chloroform solution, and subsequently eliminating hydrogen bromide by the action of sodium hydroxide. By boiling this compound with water, 1-phenyl-2:4-dimethyl-5-hydroxymethyl-3-pyrazolone is produced, and by the action of diethylamine, 1-phenyl-2:4-dimethyl-5-diethylaminomethyl-3-pyrazolone (leaflets, m. p. 123°) is obtained.

F. M. G. M.

Quinoline Derivatives of 1:5-Naphthylenediamine. A Case of Hydrolysis in Glacial Acetic Acid. HERMANN FINGER and C. SPITZ (*J. pr. Chem.*, 1909, [ii], 79, 445—449).—Whilst investigating the quinoline derivatives of 1:5-naphthylenediamine, the remarkable observation was made that the diacetyl derivative of 4:10-dihydroxy-2:8-dimethyl(1:5)-naphthadiquinoline when dissolved in glacial acetic acid is hydrolysed, yielding the diacetate of the base.

1:5-Naphthylenediamine and ethyl acetoacetate interact at the ordinary temperature, yielding *ethyl 1:5-naphthylenediaminediacetonate*, $C_{10}H_6(NH \cdot CMe \cdot CH \cdot CO_2Et)_2$, which crystallises in glistening, silvery leaflets, m. p. 178—179°, and is converted at 220—240° into 4:10-dihydroxy-2:8-dimethyl-(1:5)-naphthadiquinoline; the diacetyl derivative of the latter substance forms small crystals, m. p. 258°.

When 1:5-naphthylenediamine and ethyl acetoacetate are heated together at 160°, they yield *bisacetoacetyl-1:5-naphthylenediamine*, $C_{18}H_{18}O_4N_2$, obtained as a red, crystalline substance decomposing when heated. The same reagents condense in the presence of concentrated sulphuric acid, yielding a substance which, when heated with the sulphuric acid at about 160°, is converted into 7-amino-2-hydroxy-4-methyl-1-naphthaquinoline (formula I), compact, yellow crystals, which do not melt at 300°; the diacetyl, benzoyl, and benzylidene derivatives have been prepared.



(1:5)-Naphthadiquinoline, formula II, is prepared by heating

1 : 5-naphthylenediamine, glycerol, sulphuric acid, and arsenious oxide together at 150°; it forms small, yellow crystals, m. p. 217—217·5°; the *dihydrochloride* and *dinitrate* were analysed.

2 : 8-Dimethylnaphthadiquinoline, obtained by heating 1 : 5-naphthylenediamine with para-aldehyde and concentrated hydrochloric acid at 100—110°, crystallises in glistening, silvery leaflets, m. p. 238—240°; the *picrate*, $C_{18}H_{14}N_2 \cdot C_6H_3O_7N_3$, forms yellow crystals.

1 : 5-Naphthylenediamine condenses with benzaldehyde and pyruvic acid in alcoholic solution, yielding 2 : 8-diphenyl-(1 : 5)-naphthadiquinoline-4 : 10-dicarboxylic acid, which crystallises in small, pale yellow needles.

W. H. G.

[Preparation of Anthrapyridones.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 209033).—The acylaminoanthraquinones can be condensed to anthrapyridones by acid as well as alkaline condensing agents. 4-Chloro-1-anthrapyridone is obtained by heating 4-chloro-1-acetylaminanthraquinone with anhydrous sodium acetate and nitrobenzene. Anthrapyridone may be prepared by heating α -acetylaminanthraquinone with anhydrous sodium acetate and acetic anhydride.

F. M. G. M.

New Synthesis of isoOxazoles. II. JULIUS SCHMIDT and KARL TH. WIDMANN (*Ber.*, 1909, 42, 1869—1886).—The product described as 5-methylisooxazole (Abstr., 1908, i, 457; compare Claisen, this vol., i, 185) is now shown to be a bimolecular cyanoacetone,



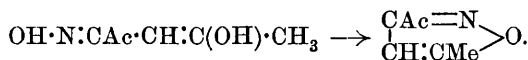
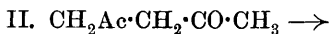
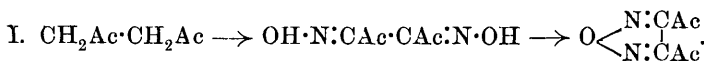
which in the course of several months sets to a hard, crystalline cake of the polymeride, $(\text{COMe} \cdot \text{CH}_2 \cdot \text{CN})_n$.

The yellow oil obtained in the preparation of ethyl 5-methylisooxazole-3 : 4-dicarboxylate (Abstr., 1908, i, 457) is probably β -oximino- $\alpha\beta$ -diacetylpropionic acid, $\text{OH} \cdot \text{N} : \text{C} \text{Ac} \cdot \text{CHAc} \cdot \text{CO}_2\text{H}$. A better yield is obtained when ethyl diacetylsuccinate is treated with fuming nitric acid at 25°. It has a penetrating odour, is distinctly acid to litmus, and decomposes when distilled under reduced pressure.

The following products have been obtained by the action of fuming nitric acid on ethyl acetylsuccinate at 15—20°: Ethyl oximinoacetylsuccinate, ethyl 5-methylisooxazole-3 : 4-dicarboxylate, oximino-succinic acid, (Ebert, Abstr., 1885, 1122), and ethyl α -oximino-propionate (Cramer, Abstr., 1891, 823),

Ethyl β -oximino- α -acetylsuccinate, $\text{CO}_2\text{Et} \cdot \text{CHAc} \cdot \text{C}(\text{CO}_2\text{Et}) : \text{N} \cdot \text{OH}$, is a colourless oil, b. p. 100—105°/35 mm., and is undoubtedly an intermediate product between the acetylsuccinate and the isooxazole derivative.

The main products obtained by the action of fuming nitric acid on acetonylacetone at 10° are diacetylfulazan and 4-acetyl-5-methylisooxazole, and the formation of these compounds can be represented by the following schemes :



Diacetylfurazan, $\begin{array}{c} \text{CAc} : \text{N} \\ \text{CAc} : \text{N} \end{array} \text{O}$, forms colourless crystals, m. p.

127—129° (decomp.). The *dioxime*, $\text{C}_6\text{H}_8\text{O}_3\text{N}_4$, separates from aqueous alcohol in pale yellow crystals, which decompose at 197°. The *phenylhydrazone*, $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_4$, forms brilliant yellow prisms, m. p. 170° (decomp.); the *p-nitrophenylhydrazone*, $\text{C}_{12}\text{H}_{11}\text{O}_4\text{N}_5$, brown prisms, m. p. 145—147° (decomp.), and the *semicarbazone*, $\text{C}_4\text{H}_9\text{O}_3\text{N}_5$, yellow plates, m. p. 185° (decomp.).

4-Acetyl-5-methylisooxazolone, $\text{C}_6\text{H}_7\text{O}_2\text{N}$, distils at 65—70° (20 mm.), and solidifies to a crystalline mass, which melts at about 30°. The *phenylhydrazone*, $\text{C}_{12}\text{H}_{13}\text{ON}_3$, forms colourless crystals, m. p. 166—168°, and the *p-nitrophenylhydrazone*, $\text{C}_{12}\text{H}_{12}\text{O}_3\text{N}_4$, decomposes at about 230°.

J. J. S.

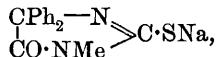
New Method for the Preparation of Thiohydantoin and the Elimination of Sulphur from them. HEINRICH BILTZ [with P. KREBS and K. SEYDEL] (*Ber.*, 1909, 42, 1792—1800. Compare *Abstr.*, 1908, i, 462).—Benzil unites with carbamide in alcoholic alkali hydroxide solutions to form 5:5-diphenylhydantoin; apparently, in the first place diphenylglyoxaloneglycol is formed by simple addition, and this undergoes pinacolin rearrangement into the hydantoin (*Abstr.*, 1908, i, 462). This view has been confirmed by the preparation of the glycol by another method: when heated with alcoholic alkali hydroxide, it is transformed into hydantoin.

It is now shown that thiocarbamide behaves similarly, 5:5-diphenylthiohydantoin being obtained from benzil and thiocarbamide.

In the thiohydantoin, the hydrogen in position 3 is labile and replaceable by an alkali metal, which becomes, however, attached to

the sulphur atom, $\begin{array}{c} \text{CPh}_2 \cdot \text{NH} \\ \text{CO} \text{---} \text{N} \end{array} \text{C} \cdot \text{SNa}$, and is easily replaced by methyl.

Thiohydantoin already substituted in position 3, likewise dissolve in alkali hydroxides; here the imide hydrogen (position 1) is replaced by metal, which again becomes attached to sulphur,



and is again easily replaced by methyl. Two isomeric monomethyl and two dimethyl derivatives of diphenylthiohydantoin are thus obtained.

Sulphur is easily removed from the thiohydantoin by the action of bromine water in alcoholic solution, or by boiling with dilute sulphuric acid, or by oxidation with permanganate in alkaline solution, the two last methods having the advantage that further substitution cannot occur. In the case of 5:5-diphenyl-1:3-dimethylthio-

hydantion, these methods fail, but sulphur is easily eliminated by heating in acetic acid solution with mercuric oxide.

5:5-*Diphenylthiohydantoin* forms short prisms, m. p. 235°. Small quantities of diphenylacetylenedithiodiurein (Anschütz and Geldermann, Abstr., 1891, 725) are formed at the same time. 5:5-*Diphenyl-2-methylthiohydantoin* crystallises in well-formed prisms, m. p. 207°. 5:5-*Diphenyl-3-methylthiohydantoin* forms colourless needles, m. p. 185°. 5:5-*Diphenyl-2:3-dimethylthiohydantoin* crystallises in monoclinic prisms, m. p. 168°. 4:5-*Dihydroxy-2-thiol-4:5-diphenyl-1:3-dimethyl-tetrahydroglyoxaline*, prepared by condensing benzil with dimethylthiocarbamide, forms crystals, m. p. 158—159°. When melted it loses a molecule of water and forms 5:5-*diphenyl-1:3-dimethylthiohydantoin*, which crystallises in lustrous, colourless plates, m. p. 141—142°.

5:5-bis-*p-Methoxyphenylthiohydantoin*, prepared from anisil and thiocarbamide, separates in colourless plates, m. p. 188°. E. F. A.

Electric Conductivity of Certain Dye-baths. LEO VIGNON (*Bull. Soc. chim.*, 1909, [iv], 5, 495—500. Compare this vol., i, 298).—Measurements have been made of the concentrations at which dye-baths containing orange II, roccellin, or magenta, dye wool, and of the electric conductivities of such baths. The results show that baths containing any one of these dyes are strongly ionised, and that these substances do not dye until the conductivity of the solution has attained a certain value. In practice this increase of conductivity can be secured by heating the bath, adding more dye, or by the addition of sulphuric acid, etc. Effective dyeing depends, not only on the intensity of the ionisation, but also on the nature of the ions present; thus magenta dyes wool in neutral or faintly acid solutions, but not in presence of sodium hydroxide. T. A. H.

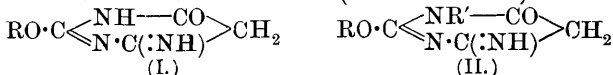
Combination of Silica with Methylene-blue. LOUIS PELET-JOLIVET and N. ANDERSEN (*Bull. Soc. chim.*, 1909, [iv], 5, 540—546).—In a previous investigation Pelet-Jolivet and Grand showed that amorphous silica, when placed in a solution of methylene-blue, absorbs the colouring matter, the amount absorbed depending on the concentration of the solution (*Rev. Mat. Col.*, 1907, August). In the present paper the composition of the precipitates formed when solutions of methylene-blue are added to solutions of water-glass are dealt with. These precipitates are not definite compounds, but merely mixtures of colouring matter, silica, and water, the relative proportion of each depending on the concentration of the solutions employed, according to the law of adsorption. Thus, when solutions of methylene-blue of different concentrations are added to a solution of water-glass of the same strength, the amount of methylene-blue in the precipitate formed increases with the strength of methylene-blue solution added. It is probable that, as shown by Kalensky in his experiments on the precipitation of water-glass solutions by ferric chloride, the active ions present have some influence on the composition of the precipitate formed, negative ions augmenting the quantity of positive colloid, and positive ions that of the negative

colloid. The fresh precipitates when washed yield colouring matter to water, slightly at first, and then in increasing quantities as the sodium chloride is washed out of the precipitate, but they yield dye to water much less readily after being dried at atmospheric temperature for some days.

Methylene-blue adsorbed by calcined precipitated silica is not entirely removed by water or by subsequent extraction with alcohol, although the latter never comes away quite colourless. The colouring matter dissolved by these solvents from such preparations differs in no respect from the original dye. These results are not in accordance with those obtained by Suida (*Zeit. Farb. Ind.*, 1907, November), who found that the precipitates yielded by magenta with solutions of water-glass were of constant composition. T. A. H.

Polyiodo-derivatives. LOUIS PELET-JOLIVET and H. SIEGRIST (*Bull. Soc. chim.*, 1909, [iv], 5, 626—628).—When to portions of a solution of methylene-blue or safranin varying quantities of a solution of iodine in potassium iodide are added, the amount of iodine which combines with the dye increases with the concentration of the initial mixture in iodine, but not quite regularly. If C represents the final concentration of free iodine, and x the iodine fixed by the dye, these have the relation $x = \beta C^{1/p}$, where $\beta = 2.6$ for methylene-blue and 1.75 for safranin, and $1/p = 0.085$ for methylene-blue and 0.12 for safranin. These periodides are therefore adsorption compounds. In estimating the iodine in the periodides, volumetric determination with sodium thio-sulphate was resorted to. This gives only the value I_x in the periodides, which may be represented by the general formula BI_xI_x . T. A. H.

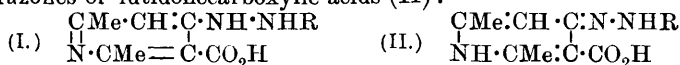
Preparation of 2-Alkyloxy-1-alkylpyrimidines. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 208639).—The 2-alkyl-



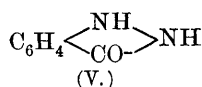
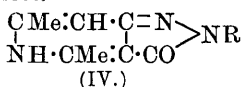
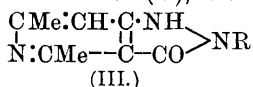
oxy-pyrimidines (I) are readily alkylated in position 1, and give rise to 2-alkyloxy-1-alkylpyrimidines (II), which are intermediate products in the hitherto unaccomplished synthesis of the 1-alkyl-xanthines.

4-Imino-2-methoxy-1-methyl-6-pyrimidone, m. p. 216°, results from the action of methyl sulphate and aqueous sodium hydroxide on 4-imino-2-methoxy-6-pyrimidone. F. M. G. M.

Some Derivatives of Ethyl 4-Chlorolutidine-3-carboxylate [Ethyl 4-Chloro-2:6-dimethylnicotinate]. AUGUST MICHAELIS (*Annalen*, 1909, 366, 324—407).—An extension of the investigations commenced by Michaelis and von Arend (*Abstr.*, 1901, i, 609; 1903, i, 292) and Michaelis and Hanisch (*Abstr.*, 1902, i, 823). The condensation of hydrazines with ethyl 4-chloro-2:6-dimethylnicotinate leads first to the formation of esters of acids, which may be regarded as arylhydrazinolutidinecarboxylic acids (I), or arylhydrazones of lutidonecarboxylic acids (II):

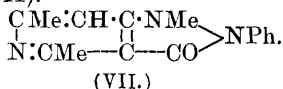
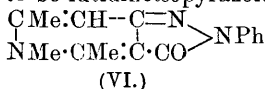


The latter assumption is the more probable, however, since the anhydrides of these compounds are yellow, a fact better represented by (IV) than (III), since benzoisopyrazolone, which undoubtedly has the constitution (V), is colourless.

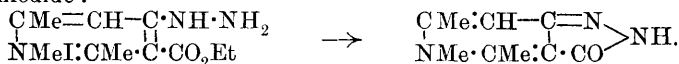


However, although the acids are probably lutidonehydrazoncarboxylic acids, nevertheless they react sometimes as hydrazinolutidinecarboxylic acids; thus, with phosphoryl chloride they yield 3-chloroindazoles, and when treated with mercuric oxide are converted into the corresponding azo-derivatives.

The lutidonehydrazoncarboxylic acids combine with alkyl iodides, forming compounds which, when acted on by alkali, lose hydrogen iodide with the formation of white, crystalline substances, which were formerly regarded as alkyl-lutidonopyrazolones (VI), but which are now shown to be lutidinoisopyrazolones (VII).



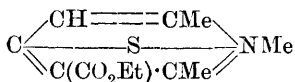
The alkyl-lutidonopyrazolones, in agreement with the constitution represented by (VI), are yellow substances. They are prepared by the action of sodium hydroxide on the hydrazino-ester formed by the condensation of hydrazines with ethyl 4-chloro-2:6-dimethylnicotinate methiodide:



I. *Preparation and Properties of Ethyl 4-Chloro-2:6-dimethylnicotinate*.—The formation of this ester by the action of phosphoryl chloride on ethyl aminocrotonate takes place through the intermediate formation of *ethyl 2:6-dimethyl-4-pyridone-3-carboxylate*, $\text{C}_{10}\text{H}_{13}\text{O}_3\text{N}$, since this substance is always obtained as a by-product, and is converted by phosphoryl chloride into ethyl 4-chloro-2:6-dimethylnicotinate; it crystallises in white prisms, m. p. 161° ; the corresponding acid has m. p. 251° (compare Collie, *Trans.*, 1891, 59, 176).

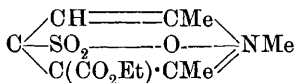
Ethyl 4-chloro-2:6-dimethylnicotinate methiodide, $\text{C}_{11}\text{H}_{15}\text{O}_2\text{NCI}$, prepared by the action of potassium iodide on the product of the interaction of ethyl chlorodimethylnicotinate and methyl sulphate, crystallises in white needles, m. p. 137° . *Ethyl 4-iodo-2:6-dimethylnicotinate methiodide*, $\text{C}_{11}\text{H}_{15}\text{O}_2\text{NI}_2$, prepared by heating the 4-chloro-ester with an excess of methyl iodide, forms pale yellow, hexagonal prisms, m. p. 194° .

[With WILHELM HEYDEN.]—II. *Thio-derivatives of Ethyl 4-Chloro-2:6-dimethylnicotinate*.—*Ethyl 1:4-thio-1:2:6-trimethylpyridine-3-carboxylate* (annexed formula), prepared by the action of potassium hydrogen sulphide on the condensation product of ethyl chlorodimethylnicotinate and methyl sulphate, crystallises in yellow, glistening plates or long, flat needles, m. p. 175° ; the hydrochloride, $\text{C}_{11}\text{H}_{15}\text{O}_2\text{NS}\cdot\text{HCl}$, forms glistening, white plates, m. p.



170°; the *platinichloride*, $(C_{11}H_{15}O_2NS)_2 \cdot H_2PtCl_6$, is a yellow powder, m. p. 215°; the *hydriodide* forms white needles, m. p. 140°; the *methiodide*, $C_{19}H_{18}O_2NSI$, crystallises in colourless, glistening needles, m. p. 185°. The thio-ester is oxidised by chlorine, hydrogen peroxide, etc., to the corresponding *trioxide* (annexed formula), crystallising in short, white, glistening needles; it carbonises without melting when heated. 1:4-*Thio*-1:2:6-*trimethylpyridine-3-carboxylic acid*,

$$C_9H_{11}O_2NS,$$

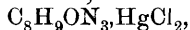


prepared by hydrolysing the ester with alcoholic potassium hydroxide, forms small, yellow, glistening crystals, m. p. 241°; the *ammonium* salt crystallises in slender, glistening needles; the *methiodide* forms white prisms, m. p. 230°; the *trioxide*, $C_9H_{11}O_5NS$, forms small, white crystals, decomposes above 200°, and yields a *mercury* salt, $(C_9H_{10}O_5NS)_2Hg$, a white, microcrystalline powder.

III. *Anilino-derivatives of Ethyl 4-Chloro-2:6-dimethylnicotinate*.—Aniline reacts energetically with the methiodide or methosulphate of ethyl chlorodimethylnicotinate, yielding ethyl 4-anilino-2:6-dimethylnicotinate, and also a crystalline substance, m. p. 233°, which is probably a mixture of the *methohydroxide* of ethyl 4-anilino-2:6-dimethylnicotinate and *ethyl 4-methylanilino-2:6-dimethylnicotinate*. Aniline and ethyl chlorodimethylnicotinate when heated together yield 4-anilino-2:6-dimethylnicotinic acid and its ethyl ester. *Ethyl 4-anilino-2:6-dimethylnicotinate*, $C_{16}H_{18}O_2N_2$, crystallises with $1H_2O$ in long, white needles, m. p. 80°; the *anhydrous* substance has b. p. 164°/15 mm.; the *hydrochloride*, $C_{16}H_{18}O_2N_2 \cdot HCl$, crystallises in prisms, m. p. 168—169°; the *platinichloride* crystallises in thin, red leaflets, m. p. 194° (decomp.); the *hydriodide* crystallises in needles, m. p. 187°, and when heated in a vacuum dissociates into anilinolutidine, ethyl iodide, and carbon dioxide.

4-*Anilino-2:6-dimethylnicotinic acid*, $C_{14}H_{14}O_2N_2$, crystallises with $1H_2O$ in glistening, white needles, m. p. 244°; the *silver* salt is a white, amorphous powder; the *methiodide*, $C_{16}H_{17}O_2N_2I$, forms white leaflets, m. p. 200°; the *platinichloride*, $(C_{15}H_{16}O_2N_2)_2 \cdot H_2PtCl_6$, of the corresponding methochloride forms reddish-yellow needles, m. p. 230°.

IV. *Hydrazine Derivatives of Ethyl 4-Chloro-2:6-dimethylnicotinate*. [With LUDWIG KRIEDEMAYER.]—Lutidonopyrazolone, described previously (*loc. cit.*) as hydrazinodimethylnicotinic anhydride, forms a *hydrochloride*, $C_8H_9ON_3 \cdot HCl$, white, glistening crystals, which decompose without melting when heated; the *mercurichloride*,

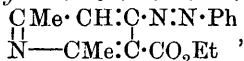


forms tufts of long, colourless needles, m. p. 240°. When lutidonopyrazolone is heated with methyl iodide at 150° for six hours, it yields *lutidonomethylpyrazolone methiodide*,

$$\begin{array}{c} \text{CMe} \cdot \text{CH} \cdot \text{C} \cdot \text{NMeI} \\ \text{NH} \cdot \text{CMe} \cdot \text{C} \text{---} \text{CO} \end{array} \text{NMe},$$
crystallising in slender, yellow needles, m. p. 254—255°.

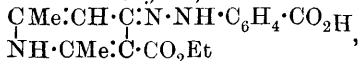
Lutidonephenylhydrazonocarboxylic acid (2:6-dimethyl-4-pyridone-phenylhydrazon-3-carboxylic acid) has been described previously (Michaelis and von Arend, *loc. cit.*); the *platinichloride* forms bright yellow needles, and decomposes without melting when heated. The

ethyl ester, $\begin{array}{c} \text{CMe} \cdot \text{CH} \cdot \text{C} \cdot \text{N} \cdot \text{NHPh} \\ | \\ \text{NH} \cdot \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array}$, crystallises in white or faintly yellow prisms, m. p. 141° , and when warmed in alcoholic solution with yellow mercuric oxide yields ethyl 4-benzeneazo-2:6-dimethylnicotinate,

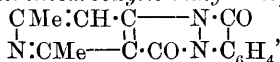


crystallising in dark red needles, m. p. 78° . The following derivatives of 2:6-dimethyl-4-pyridonephenylhydrazone-3-carboxylic acid were prepared by heating this substance with the corresponding halogen compound: *methiodide*, $\text{C}_5\text{H}_2\text{NMe}_2 \cdot \begin{array}{c} \text{CO}_2\text{H} \\ \diagup \\ \text{NMeI} \cdot \text{NHPh} \end{array}$, pale yellow leaflets, m. p. 288° ; *ethiodide*, $\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}_3\text{EtI}$, tufts of pale yellow needles, m. p. 218° ; *propiodide*, $\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}_3\text{PrI}$, yellow needles, m. p. 207° ; *benzylchloride*, $\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}_3\text{CH}_2\text{PhCl}$, white leaflets, m. p. 252° ; *phenacylbromide*, $\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}_3\text{Ph} \cdot \text{CO} \cdot \text{CH}_2\text{Br}$, white, transparent prisms, m. p. 288° .

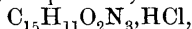
[With DIETRICH REINIGHAUS.]—Ethyl 2:6-dimethyl-4-pyridone-o-carboxyphenylhydrazone-3-carboxylate,



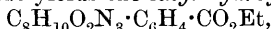
prepared by the condensation of ethyl chlorodimethylnicotinate and o-hydrazinobenzoic acid, crystallises in small, orange needles, sinters at 180° , and melts with the elimination of water and alcohol at 285° , the m. p. of the anhydride; the *ammonium* salt is a reddish-yellow, crystalline powder, m. p. $189-190^\circ$. The formation of the ester just described is accompanied by that of *lutidinobenzobisisopyrazolone* (o-carboxyphenylhydrazinolutidinecarboxylic anhydride),



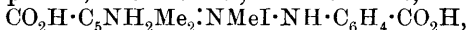
a pink, crystalline powder, m. p. 285° ; the *hydrochloride*,



forms brown, glistening leaflets, m. p. 285° (decomp.). The pyrazolone is hydrolysed by 10% aqueous sodium hydroxide, yielding 2:6-dimethyl-4-pyridone-o-carboxyphenylhydrazone-3-carboxylic acid, $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_3$, which crystallises in glistening, yellow needles, loses water when heated, and melts at 285° , the m. p. of the anhydride; the *hydrochloride*, $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_3\text{HCl}$, forms small, greyish-white crystals; the *platinichloride* forms golden-yellow, glistening leaflets; the *sodium hydrogen salt*, $\text{C}_{15}\text{H}_{14}\text{O}_4\text{N}_3\text{Na} \cdot 2\text{H}_2\text{O}$, crystallises in pale yellow needles; the *barium hydrogen salt*, $(\text{C}_{15}\text{H}_{14}\text{O}_4\text{N}_3)_2\text{Ba}$, forms yellow needles; the *hydrogen silver salt*, $\text{C}_{15}\text{H}_{14}\text{O}_4\text{N}_3\text{Ag}$, is a pale yellow powder, and when treated with ethyl iodide yields the *ethyl hydrogen ester*,



which crystallises in small, yellow needles and passes into the anhydride, m. p. 285° , when heated; the *methiodide*,

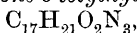


crystallises in white needles, m. p. 211° . The following compounds are prepared by methods similar to those employed in the formation of the analogous ortho-compounds: *ethyl 2:6-dimethyl-4-pyridone-m-carboxyphenylhydrazone-3-carboxylate*, yellow, crystalline powder, m. p.

300° (decomp.); the *platinichloride* forms small, golden-yellow crystals, m. p. 218° (decomp.); the *acid*, $C_{15}H_{14}O_4N_2 \cdot 2H_2O$, forms slender, white needles, m. p. 234°.

[With BENNO VON GHIEL.]—2:6-Dimethyl-4-pyridone-*p*-tolylhydrazone-3-carboxylic acid, $C_{14}H_{16}N_3 \cdot CO_2H$, prepared from ethyl chlorodimethylnicotinate and *p*-tolylhydrazine, forms a yellow, microcrystalline powder, m. p. 283°; it does not yield an anhydride when heated; the *ethyl ester*, $C_{14}H_{16}N_3 \cdot COEt$, forms faintly yellow, felted needles, m. p. 154°; the *hydrochloride*, $C_{15}H_{17}O_2N_3 \cdot HCl \cdot H_2O$, forms yellowish-white needles, m. p. 270°; the *platinichloride* crystallises in brown needles, and decomposes without melting when heated; the *mercurichloride*, $C_{15}H_{17}O_2N_3 \cdot HgCl_2$, forms white needles, m. p. 131°; the *methiodide*, $C_{15}H_{17}O_2N_3 \cdot MeI$, forms pale yellow leaflets, m. p. 236°.

Ethyl 2:6-dimethyl-4-pyridone-o-tolylhydrazone-3-carboxylate,



crystallises in white leaflets, m. p. 108°; the solution obtained by boiling the ester with aqueous sodium hydroxide when treated with carbon dioxide does not yield the corresponding acid, but the *anhydride*

(*lutidino-o-tolylpyrazolone*), $\begin{array}{c} CMe:CH \cdot C=N \\ | \\ NH \cdot CMe:C \cdot CO \end{array} > N \cdot C_6H_4Me$, yellow needles,

which decompose without melting above 310°; the *mercurichloride*, $C_{15}H_{15}ON_3 \cdot HgCl_2$, forms white or slightly pink needles, m. p. 223°; the *methiodide*, $C_{15}H_{15}ON_3 \cdot MeI$, crystallises in pale yellow leaflets, m. p. 268°.

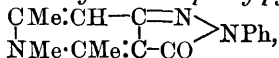
[With LUDWIG KRIEDEMAYER.]—2:6-Dimethyl-4-pyridone- β -naphthylhydrazone-3-carboxylic acid, $C_{18}H_{17}O_2N_3$, crystallises in yellow needles, m. p. 288°; the *hydrochloride* was analysed.

Ethyl 4-hydrazino-2:6-dimethylnicotinate methiodide, prepared by the action of hydrazine on ethyl 4-chloro-2:6-dimethylnicotinate methiodide, forms yellow needles, m. p. 247°, and is converted by aqueous sodium

hydroxide into *methyl-lutidonopyrazolone*, $\begin{array}{c} CMe:CH-C=N \\ | \\ NMe \cdot CMe:C \cdot CO \end{array} > NH$,

which crystallises with $4H_2O$ in slender, yellow needles, m. p. above 360°; the *hydrochloride* of the latter compound ($1H_2O$) forms white crystals, melting above 360° with elimination of methyl chloride; the *platinichloride*, $(C_9H_{11}ON_3)_2 \cdot H_2PtCl_6$, forms brownish-red needles, m. p. above 360°; the *hydriodide* ($1\frac{1}{2}H_2O$) forms white needles, and loses methyl iodide without melting when heated above 360°.

Ethyl 4-phenylhydrazino-2:6-dimethylnicotinate methiodide forms thick, yellowish-red prisms, m. p. 203°, and when treated with aqueous sodium hydroxide yields *methyl-lutidonophenylpyrazolone*,

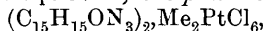


which forms yellow crystals, m. p. 258°; the *hydrochloride* ($3H_2O$) of the latter substance crystallises in white needles, m. p. 255°; the *platinichloride*, $(C_{15}H_{15}ON_3)_2 \cdot H_2PtCl_6$, is a yellowish-red powder, m. p. above 360°; the *hydriodide* ($2H_2O$) forms colourless needles, m. p. 230°; the *methiodide* ($1H_2O$) has m. p. 145°; the *anhydrous substance* has m. p. 220°.

Lutidinodimethylisopyrazolone, $\begin{array}{c} \text{CMe} \cdot \text{CH} \cdot \text{C} \cdot \text{NMe} \\ | \quad | \\ \text{N} \cdot \text{CMe} - \text{C} - \text{CO} \end{array} \rangle \text{NMe}$, prepared by

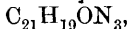
the action of aqueous sodium hydroxide or silver oxide on the product of the interaction of methyl iodide and lutidonopyrazolone, crystallises with $2\text{H}_2\text{O}$ in white, glistening prisms, m. p. 92° ; the *anhydrous* substance has m. p. 167° ; the *hydrochloride*, $\text{C}_{10}\text{H}_{13}\text{ON}_3\text{HCl}$, is a crystalline mass, m. p. above 360° ; the *platinichloride* forms stout, yellow needles, m. p. 230° ; the *methiodide*, $\text{C}_{10}\text{H}_{13}\text{ON}_3\text{MeI}$, forms pale yellow needles, m. p. 276° , and when treated with a concentrated aqueous solution of sodium hydroxide yields *lutidinodimethylpyrazolone-methylammonium hydroxide*; the latter substance, when treated with hydrochloric acid and platinum chloride, yields the *methochloride platinichloride*, reddish-yellow crystals, m. p. 255° (decomp.).

[With THILO MÜHLBERG.]—*Lutidinophenylmethylisopyrazolone* (*lutidinoantipyrine*), $\begin{array}{c} \text{CMe} \cdot \text{CH} \cdot \text{C} \cdot \text{NMe} \\ | \quad | \\ \text{N} \cdot \text{CMe} - \text{C} - \text{CO} \end{array} \rangle \text{NPh}$, prepared by the action of sodium hydroxide on 2:6-dimethyl-4-pyridone-phenylhydrazone-3-carboxylic acid methiodide, crystallises in white leaflets or needles, m. p. 154° ; it also crystallises with $12\text{H}_2\text{O}$ in broad needles; the *hydrochloride*, $\text{C}_{15}\text{H}_{15}\text{ON}_3\text{HCl}$, forms white, glistening leaflets, m. p. $286\text{--}287^\circ$ (decomp.); the *platinichloride* ($1\text{H}_2\text{O}$) forms slender, golden-yellow needles, which decompose without melting when heated; the methiodide is identical with the methiodide of methyl-lutidinophenylpyrazolone; the *methochloride*, $\text{C}_{15}\text{H}_{15}\text{ON}_3\text{MeCl} \cdot \text{H}_2\text{O}$, forms slender, white needles, m. p. 174° ; the *platinichloride*,

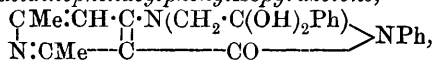


forms small, golden-yellow crystals, and decomposes without melting at high temperatures; the *ethiodide*, $\text{C}_{15}\text{H}_{15}\text{ON}_3\text{EtI} \cdot \text{H}_2\text{O}$, forms leaflets, m. p. 200° ; the *propiodide*, $\text{C}_{15}\text{H}_{15}\text{ON}_3\text{PrI}$, crystallises in leaflets, m. p. 270° . The parent substance when treated with bromine in glacial acetic acid yields the *dibromide*, $\begin{array}{c} \text{CMe} \cdot \text{CH} \cdot \text{C} \cdot \text{NMe} \\ | \quad | \\ \text{NBr}_2 \cdot \text{CMe} \cdot \text{C} - \text{CO} \end{array} \rangle \text{NPh}$, crystallising in yellowish-red needles, m. p. 180° (decomp.). A *tetraiodide*, crystallising in red needles, m. p. 182° , was also prepared.

The following compounds are prepared by methods similar to those already described. *Lutidinophenylethylisopyrazolone*, $\text{C}_{16}\text{H}_{17}\text{ON}_3$, forms slender, white needles, m. p. 132° ; the *dibromide*, $\text{C}_{16}\text{H}_{17}\text{ON}_3\text{Br}_2$, forms dark orange crystals, m. p. 180° . *Lutidinophenylpropylisopyrazolone*, $\text{C}_{17}\text{H}_{19}\text{ON}_3$, crystallises in small, slender needles, m. p. 128° ; the *methiodide* has m. p. 228° . *Lutidinophenylbenzylisopyrazolone*,



forms white needles, m. p. 133° ; the *methiodide* forms yellow needles, m. p. 230° . *Lutidinophenacylphenylisopyrazolone*,

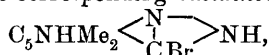


crystallises with $2\text{H}_2\text{O}$ in colourless, transparent prisms, m. p. 143° ; it crystallises from alcohol in anhydrous, colourless leaflets, m. p. 180° . The molecule of water combined with the phenacyl radicle cannot be removed without destroying the substance. *Lutidinophenylmethylisopyrazolone*, $\text{C}_{16}\text{H}_{17}\text{ON}_3$, forms snow-white leaflets, m. p.

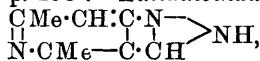
145°; the corresponding *o*-tolyl derivative forms white needles, m. p. 132°.

V. *Indazoles and Chloroindazoles of Lutidines*.—The lutidone-hydrazonecarboxylic acids, when heated with phosphoryl chloride or bromide, yield the corresponding chloro- or bromo-indazoles, which, when treated with zinc dust and acetic acid, yield the indazoles.

Lutidino-3-chloroindazole hydrochloride, $C_8H_8N_3Cl \cdot HCl$, forms colourless needles, m. p. 310°; the *platinichloride* ($2H_2O$) is a reddish-yellow crystalline powder; the corresponding *lutidinobromoindazole*,



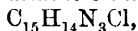
forms white needles, m. p. 253°. *Lutidinoindazole*,



prepared by reducing the bromo-, but not the chloro-, derivative, forms aggregates of needles, m. p. 190°.

[With LUDWIG KRIEDEMAYER.]—The following lutidino-3-chloro-2-alkylindazoles are prepared by heating lutidino-3-chloroindazole with alcoholic potassium hydroxide and alkyl iodide. *Lutidino-3-chloro-2-methylindazole*, $C_5NHMe_2 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ | \\ \text{C} \\ | \\ \text{Cl} \end{array} \text{CMe}$, forms white needles,

m. p. 74°; the *platinichloride* crystallises in bright yellow needles, m. p. 240° (decomp.). *Lutidino-3-chloro-2-ethylindazole*, $C_{10}H_{12}N_3Cl$, has m. p. 118°; the *platinichloride* ($1H_2O$) forms red crystals, which swell at 219°, m. p. 224°. *Lutidino-3-chloro-2-benzylindazole*,

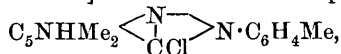


crystallises in white needles, m. p. 95°.

[With DIETRICH REINTGENHAUS.]—*Lutidino-3-chloro-2-m-carboxyphenylindazole*, $C_5NHMe_2 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ | \\ \text{C} \\ | \\ \text{Cl} \end{array} \text{N} \cdot C_6H_4 \cdot CO_2H$, is a white, crystalline

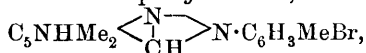
powder, m. p. 195° (decomp.); the *sodium salt* ($1H_2O$) was prepared; the *methiodide* crystallises in small, white needles, m. p. 239° (decomp.); the *ethyl ester*, $C_{14}H_{11}N_3Cl \cdot CO_2Et$, forms yellowish-white crystals, m. p. 124°. *Lutidino-2-m-carboxyphenylindazole*, $C_{15}H_{13}O_2N_3$, crystallises with $2H_2O$ in white, microscopic crystals, m. p. 165°.

[With BENNO VON GHIEL.]—*Lutidino-3-chloro-2-p-tolylindazole*,



forms white, rhombohedral crystals, m. p. 174°; the *methiodide* crystallises in slender, pale yellow needles, m. p. 246—247°; the *methochloride* has m. p. 231—232°. The corresponding *3-bromo-compound*, $C_{15}H_{14}N_3Br$, forms white needles, m. p. 161°.

Lutidino-2-p-tolylindazole, $C_{15}H_{15}N_3$, crystallises in white, felted needles, m. p. 131—132°; the *hydrochloride* forms slender, white needles, m. p. 293°; the *methiodide* crystallises in long needles, m. p. 252°. *Lutidinobromo-2-p-tolylindazole*,



1-Acetyl-amino-2 : 5-dimethyl-1 : 3 : 4-triazole, $\text{NHAc} \cdot \text{N} \begin{smallmatrix} \text{CMe:N} \\ \text{CMe:N} \end{smallmatrix}$

separates from acetone in prismatic crystals, m. p. 163°.

1-m-Nitrobenzylidene-amino-2 : 5-dimethyl-1 : 3 : 4-triazole,



prepared by the action of *m*-nitrobenzaldehyde on 1-amino-2 : 5-dimethyl-1 : 3 : 4-triazole in presence of piperidine, separates from benzene in shining crystals, m. p. 183°. T. H. P.

Quinonoid Compounds. XIII. Aniline-Black. II. RICHARD WILLSTÄTTER and STEFAN DOROGI (*Ber.*, 1909, 42, 2147—2168. Compare *Abstr.*, 1907, i, 641).—The authors have undertaken the study of the constitution and mode of formation of aniline-black with the object of explaining its formation as an intermediate product in the oxidation of aniline to benzoquinone. It is found that 1 molecule of aniline requires 1.27 atoms of oxygen for its oxidation to aniline-black by means of potassium dichromate and sulphuric acid at 5°; a very pure form of aniline-black can be obtained by using only sufficient dichromate to oxidise about a quarter of the total aniline present; by this means over oxidation of the aniline-black is prevented; the precipitated aniline-black sulphate when filtered off and washed with water forms a chrome-green powder; it was further purified by shaking for twelve to twenty-four hours with 100 times its weight of 2*N*-sulphuric acid and then boiling for six hours more with fresh acid, and was finally converted into the colour base by adding it to a large excess of boiling 2*N*-ammonia solution. Aniline-black, $\text{C}_{48}\text{H}_{36}\text{N}_8$, thus prepared is a dark blue powder, the composition of which may be expressed by the formula :

$\text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}$. When heated with 17% sulphuric acid for twelve hours in a sealed tube at 200°, it loses one-eighth part of its nitrogen in the form of ammonia, according to the equation : $\text{C}_{48}\text{H}_{36}\text{N}_8 + \text{H}_2\text{O} = \text{C}_{48}\text{H}_{35}\text{ON}_7 + \text{NH}_3$. The resulting product is a much darker aniline-black; a description of this substance and of its salts is reserved for a future communication.

The aniline-black of the composition $\text{C}_{48}\text{H}_{36}\text{N}_8$ yields green salts, the *hydrochloride* and *sulphate* having the formulæ $\text{C}_{48}\text{H}_{36}\text{N}_8 \cdot 3\text{HCl}$ and $\text{C}_{48}\text{H}_{36}\text{N}_8 \cdot 2\text{H}_2\text{SO}_4$ respectively; a second sulphate of the formula $\text{C}_{48}\text{H}_{36}\text{N}_8 \cdot 5\text{H}_2\text{SO}_4$ is obtained by shaking the former sulphate with an ethereal solution of sulphuric acid; it is an almost black solid. The authors have also made quantitative measurements of the amount of benzoquinone produced by the oxidation of *p*-aminophenol, *p*-phenylenediamine, aniline, aniline-black, benzoquinonemonoanil, and phenylhydroxylamine with dichromate and sulphuric acid and with lead peroxide and sulphuric acid. P. H.

[Cain's Theory of Diazonium and Ammonium Salts.] ARTHUR HANTZSCH (*Ber.*, 1909, 42, 2137—2138).—Polemical. A final reply to Cain (this vol., i, 445). W. H. G.

***p*-Nitrobenzenediazonium Chloride.** HANS T. BUCHERER (*Ber.*, 1909, 42, 1852—1853).—A reply to Schwalbe (this vol., i, 445).

C. H. D.

[1-Diazo-2-oxynaphthalene-3-carboxylic Acid and its Azo-derivatives.] BASLER CHEMISCHE FABRIK (D.R.-P. 206698).—Diazo-2-oxynaphthalene-3-carboxylic acid when introduced in paste form into alkaline solutions of α - and β -naphthol, resorcinol, *m*-hydroxydiphenylamine, *m*-phenylenediamine, and other similarly reactive phenols and amines gives rise to azo-dyes, which are sufficiently soluble to dye wool and yield fast shades on chroming.

Nitro-1-diazo-2-oxynaphthalene-3-carboxylic acid, light yellow needles from methyl alcohol and ethyl acetate, m. p. 212—213°, is obtained by nitrating the foregoing diazoimide with a mixture of nitric and sulphuric acids at 0—5°; it gives rise to similar azo-dyes.

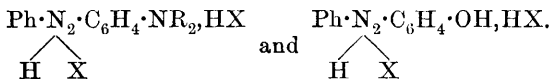
F. M. G. M.

Salts of Azobenzene, Amino- and Hydroxy-azo-compounds with Mineral Acids. ARTHUR HANTZSCH (*Ber.*, 1909, 42, 2129—2135. Compare Hantzsch and Hilscher, *Abstr.*, 1908, i, 484).—An optical examination of the salts of azobenzene, *p*-aminoazobenzene derivatives, and *p*-hydroxyazobenzene derivatives with mineral acids. It is shown that these salts belong to three widely different types:

(1) Yellow ammonium salts, $\text{Ar}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2\text{HX}$, optically similar to azobenzene.



(2) Dark yellow azo-salts, $\text{Ar}\cdot\text{N}_2\cdot\text{Ar}$. Solutions of azobenzene in indifferent solvents give a different absorption spectrum to solutions of this substance in strong acids. The absorption spectrum of the latter is similar to that of aminoazobenzene and hydroxyazobenzene derivatives in strong acids, so that these substances are present as salts having the formulæ:



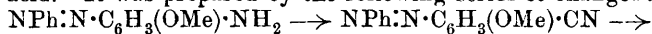
(3) Violet quinonoid salts, $\text{Ar}\cdot\text{NH}\cdot\text{N}:\text{C}_6\text{H}_4:\text{NR}_2\text{X}$, the absorption spectrum of which is quite different from the spectra of the preceding salts.

A violet, crystalline *hydrobromide* of *p*-hydroxyazobenzene, $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH,HBr}$, has been prepared by passing hydrogen bromide into an ethereal solution of the azo-compound; it probably has the quinonoid oxonium formula: $\text{Ph}\cdot\text{NH}\cdot\text{N}:\text{C}_6\text{H}_4:\text{O} < \begin{array}{c} \text{H} \\ \text{Br} \end{array}$.

W. H. G.

Benzeneazosalicylic Acid with the Carboxyl Group in the para-Position. HERMANN FINGER and E. WILNER (*J. pr. Chem.*, 1909, [ii], 79, 451—453).—An account of the preparation of the simplest

member of a class of important dyes, namely, *p*-benzeneazosalicylic acid. It was prepared by the following series of changes :



$\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CN} \longrightarrow \text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}$,
but was not obtained perfectly free from the corresponding nitrile.

Benzeneazo-*o*-anisidine, when diazotised and treated with potassium cuprous cyanide, yields 4-cyano-3-methoxy-1-azobenzene, $\text{C}_{14}\text{H}_{11}\text{ON}_3$, obtained as a mass of red needles having a characteristic odour. The latter substance is converted by treatment with aluminium chloride in carbon tetrachloride into 4-cyano-3-hydroxy-1-azobenzene, $\text{C}_{13}\text{H}_9\text{ON}_3$, which crystallises in small, reddish-yellow needles, and is not completely hydrolysed even by boiling with alcoholic potassium hydroxide for twenty hours ; the *acid*, contaminated with some of the nitrile, was obtained as a deep red, crystalline substance. W. H. G.

Influence of Proteins on the Solubility of Electrolytes.

WOLFGANG PAULI and MAX SAMEC (*Biochem. Zeitsch.*, 1909, 17, 235—256).—Solubility determinations were made at 25°, in flasks placed in an Ostwald thermostat with the usual precautions, of a number of salts in pure water, in ox-serum, purified from mineral salts by many weeks dialysis, and in 4% and 10% gelatin. The serum contained 2.23% protein and less than 0.005% ash.

Easily soluble salts, such as ammonium chloride, magnesium chloride, and ammonium thiocyanate, were less soluble in the protein solutions. Calcium sulphate is slightly more soluble in serum than in pure water, calcium phosphate and calcium carbonate relatively much more so, and silica and uric acid even more so. The least soluble salts showed proportionally the greatest increase in solubility. The same holds, although to a less extent, for solutions in 1.5% gelatin. Witte's peptone behaved somewhat differently ; it contained 0.44% ash, and increased the solubility only of calcium carbonate, the other salts being slightly less soluble in it than in water. E. F. A.

Hydrolysis of Serum-globulin by Alkalis. H. LAMPEL and ZDENKO H. SKRAUP (*Monatsh.*, 1909, 30, 363—375).—The hydrolysis of serum-globulin from horse blood by warm 6% sodium hydroxide is quite similar to that of egg-albumin (this vol., i, 340). The products being 11% of *globulin-protalbic acid*, precipitated by dilute sulphuric acid, 21% of *globulin-lysabic acid*, precipitated by ammonium sulphate, and 6% of *globulin-peptone*, soluble in a solution of ammonium sulphate.

The three products and the original serum-globulin have been hydrolysed by 33% sulphuric acid ; the table shows the results in parts % :

	Serum.	Protalbic acid.	Lysabic acid.	Peptone.
Histidine	1.7	1.5	1.7	1.5
Arginine	3.7	0.0	0.0	0.0
Lysine	4.3	3.9	4.4	4.4
Tyrosine	3.1	4.4	2.5	1.2
Proline	3.0	3.2	2.9	2.3
Phenylalanine	3.6	1.0	2.7	1.8
Glutamic acid	4.4	—	1.9	0.0
Amino-acids	18.5	20.4	21.2	13.5

Colour reactions with α -naphthol and thymol indicate that the carbohydrate content of the protalbic acid is very much smaller than that of the peptone. C. S.

The Relation of Different Acids to the Precipitation of Casein and to the Solubility of Cheese Curds in Salt Solution. JOHN L. SAMMIS and EDWIN B. HART (*J. Biol. Chem.*, 1909, 6, 181—187. Compare Abstr., 1905, i. 498).—Experiments have been made by adding 0.1*N*-solutions of different acids to 10 c.c. of a 10% solution of casein in lime water, and observing in each case how much acid was required (1) to remove the red colour of the phenolphthalein indicator added; (2) to cause visible separation of a precipitate; (3) to cause complete flocculation of the precipitate; (4) to give a precipitate completely and readily soluble in 5% salt solution; (5) to give a precipitate quite soluble in the salt solution. The amount of acid required varies not merely with the acid used, but also with the temperature. The acids used were lactic, oxalic, acetic, and phosphoric. The age of the casein solution is also an important factor. The solubility of the precipitate in 5% salt solution changes completely when the precipitate is kept for a few minutes before decanting.

The solubility of cheese curd in 5% solutions of sodium, potassium, magnesium, ammonium, barium, and calcium chlorides has been determined. The curd is very sparingly soluble in barium and calcium chloride solutions, but readily soluble in sodium, potassium, and ammonium chloride solutions. J. J. S.

A Stable Derivative of Hæmochromogen. The Carbon Monoxide Capacity of Reduced Acid Hæmatin. J. A. MILROY (*J. Physiol.*, 1909, 38, 384—391, 392—400).—When hæmatin dissolved in glacial acetic acid is reduced with aluminium in the presence of nickel acetate, a stable pigment is formed; this appears to be a derivative of hæmochromogen, in which nickel has largely replaced the iron. It is not altered by exposure to the air, and does not unite with carbon monoxide.

Reduced acid hæmatin is capable of uniting with carbon monoxide; its specific capacity for this gas is about 355—356 c.c. Some spectroscopic evidence is adduced for the view that the reduction of acid hæmatin takes place in two stages. W. D. H.

Preparation of Hæmatoporphyrin and other Blood Derivatives. FRIEDRICH ESCHBAUM (*Ber. deut. pharm. Ges.*, 1909, 19, 284—292).—Hæmatoporphyrin may be prepared by adding 6 grams of goat's blood to 100 grams of sulphuric acid, heating until a clear solution is obtained, cooling, and pouring the mixture into three times its volume of alcohol. To this liquid enough of an alcoholic solution of potassium hydroxide is added to just neutralise the acid. The solution is then decanted from the precipitated potassium sulphate and evaporated to dryness. This preparation gives the characteristic spectra of hæmatoporphyrin in neutral, acid, or alkaline solution. Descriptions of the methods of preparing methæmoglobin, hæmatin, hæmochromogen, carbonylhæmoglobin, sulphohæmoglobin, and cyano-

hæmoglobin, and the behaviour of these substances with Stokes' reagent, and methods of recognising them are given.

The author is of opinion that the formation of sulphohæmoglobin does not take place in cloacal poisoning, since in his experience this substance cannot be detected in blood withdrawn from blood-vessels in such cases. Similarly, cyanohæmoglobin cannot be detected in the blood of dogs poisoned with hydrocyanic acid, nor can it be prepared by adding the acid to unchanged blood. Methæmoglobin is readily detected in blood withdrawn from the fingers of persons engaged in working with aniline or phenylhydrazine.

T. A. H.

The Pigment of Blood. OSCAR PIŁOTY (*Annalen*, 1909, 366, 237—276. Compare Küster, Abstr., 1901, i, 298; 1902, i, 845; 1904, i, 357; Nencki and Zaleski, Abstr., 1901, i, 434; Zaleski, Abstr., 1903, i, 217).—An investigation of the degradation products of hæmatoporphyrin.

It has been found possible to obtain hæmopyrrole, one of the reduction products of hæmatoporphyrin, in a pure state, and also to isolate two other substances formed simultaneously with hæmopyrrole. One of these substances is designated hæmopyrrolecarboxylic acid, and has the formula $\text{NH} \begin{array}{l} \text{CH:CMe} \\ \text{CH:C} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{H} \end{array}$; the nature of the side-chain and its position in the pyrrole nucleus is, however, not yet definitely settled.

Hæmopyrrole and hæmopyrrolecarboxylic acid are derived from two distinct portions of the hæmatoporphyrin molecule, since the molecule of the compound remaining after the elimination of these substances contains either 14 or 17 carbon atoms. This compound, named provisionally hæmatopyrrolidinic acid, has not been isolated in a pure state, and analyses of its salts have not led to definite conclusions as to its chemical composition. However, when it is oxidised it yields a substance, which is probably a derivative of a hydropyrrole, and hæmopyrrolecarboxylic acid, which is further oxidised to hæmatic acid.

When hæmatoporphyrin is reduced gently with zinc and hydrochloric acid, it yields a pigment, named deoxyhæmatoporphyrin, which probably has the formula $\text{C}_{34}\text{H}_{38}\text{O}_5\text{N}_4$, and breaks down when treated with energetic reducing agents into hæmopyrrole, hæmopyrrolecarboxylic acid, and hæmatopyrrolidinic acid. The products of reduction just mentioned are rapidly acted on by atmospheric oxygen with the formation of various brown substances. It is extremely probable that Hoppe-Seyler's urobilin (Abstr., 1875, 96) is a mixture of these substances.

Hæmopyrrole is a colourless oil with a faint blue fluorescence, b. p. $86-87^\circ/23$ mm. (compare Nencki and Zaleski, *loc. cit.*). It is converted by nitrous acid into two substances, one of which forms crystals, m. p. 66° , and is probably the *imide* of methylethylmaleic acid, whilst the other crystallises in almost colourless prisms, m. p. $206-207^\circ$, and is probably the *oxime*, $\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2$, of the former substance.

Hæmopyrrolecarboxylic acid, $\text{C}_9\text{H}_{13}\text{O}_2\text{N}$, crystallises in tufts of white, slender, pointed needles, m. p. 125° ; the *picrate*, $\text{C}_{15}\text{H}_{16}\text{O}_9\text{N}_4$, forms

yellow, prismatic leaflets, sinters at 140° , m. p. 148° ; the *methyl* ester, $C_{10}H_{15}O_2N$, crystallises in long, slender needles, m. p. 56° . An ethereal solution of the acid, when exposed to the action of dry air, deposits a *substance*, $C_{18}H_{24}O_4N_2$ (?), obtained as a brownish-red powder, a solution of which in alcohol quickly changes from brown to green when exposed to the air. Another *substance*, $C_{18}H_{22}O_4N_2$, obtained as a violet powder, was isolated from a mixture of coloured substances obtained by the prolonged action of the air on an ethereal solution of the acid. Nitrous acid acts on hæmopyrrolecarboxylic acid, yielding hæmatic acid and a substance which is probably the *oxime*, $C_8H_{10}O_4N_2$, of hæmatic acid; it crystallises in colourless leaflets, commences to sinter at 221° , m. p. 242° (decomp.).

Deoxyhaematoporphyrin, $C_{34}H_{38}O_5N_4$, is an amorphous, granular, brown powder. An isomeric *substance*, $C_{34}H_{38}O_5N_4$, is obtained as a blue powder by reducing hæmatoporphyrin with zinc dust and glacial acetic acid.

Haematopyrrolidinic acid could not be crystallised; the *picrate*, $(C_{17}H_{28}O_2N_2)_2(C_6H_3O_7N_3)_3$ or $C_{14}H_{22}O_2N_2, C_6H_3O_7N_3$, is a lemon-yellow, amorphous powder, which commences to carbonise at 125° . The acid when oxidised with manganese dioxide and sulphuric acid yields hæmatic acid and a *substance*, obtained as a colourless oil, having an odour like piperidine; the *picrate* is an amorphous powder.

W. H. G.

Inosic Acid. III. PHŒBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1909, 42, 1198—1203. Compare this vol., i, 164; Haiser and Wenzel, *Abstr.*, 1908, i, 561).—The authors have finally succeeded in obtaining the pentose derived from inosine in a crystalline condition, and have in consequence been enabled to support their contention that it is neither *l*-xylose, as stated by Neuburg and Brahn (*Abstr.*, 1908, i, 1029), nor *r*-arabinose, as argued by Bauer (*Abstr.*, 1907, i, 1098). It is probably either *d*-ribose or *d*-arabinoketose.

The pentose was prepared from carnine by the method of Haiser and Wenzel (*loc. cit.*), and crystallised from hot absolute alcohol. It forms microscopic plates, m. p. 86 — 87° (corr.), $[\alpha]_D -19.5^{\circ}$ in water. A solution of 0.1006 gram of the phenylosazone in 5 c.c. of pyridine alcohol gave α_D 1.16° in a 1-dm. tube. The *phenylbenzylhydrazones*, $C_{18}H_{22}O_4N_2$, has m. p. 127 — 128° (corr.), $[\alpha]_D -26.46^{\circ}$ in alcohol.

W. H. G.

Carnine and Inosic Acid. III. FRANZ HAISER and FRANZ WENZEL (*Monatsh.*, 1909, 30, 377—386. Compare this vol., i, 322).—The pentose obtained from inosine has definitely been identified with *d*-lyxose by the comparison of the *phenylbenzylhydrazones*, m. p. 127° and 128° respectively.

The molecular formula of inosic acid is proved to be $C_{10}H_{13}O_8N_4P$ in two ways. The increase of the equivalent conductivity of the sodium salt between the dilutions 32 and 1024 shows that inosic acid is dibasic. The molecular weight by the cryoscopic method of inosic acid in aqueous solution has been found in two experiments to be 256.8 and 273.5; applying the correction for ionic dissociation, determined from

the relation $\alpha = \mu/\mu_\alpha$, the preceding values become 350.9 and 362.9, the theoretical value being 348. C. S.

Inosic Acid. CARL NEUBERG and R. BRAHN (*Biochem. Zeitsch.*, 1909, 17, 293—296. Compare Abstr., 1908, i, 1029; Haiser and Wenzel, this vol., i, 322).—Polemical. The authors uphold the view that the sugar obtained on hydrolysing inosic acid is *l*-xylose. E. F. A.

The Pentose in Nucleic Acids. PHÆBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1909, 42, 2102—2106).—The pentose obtained from inosic acid (compare preceding abstracts), which it is proposed to designate provisionally *carnose*, is in all probability also present in guanylic acid obtained from the liver and the pancreas, likewise in the nucleic acid from yeast; at least, the osazone of the sugar obtained from each acid has the same properties. It is further shown that *carnose* is not *d*-lyxose, as suggested by Haiser and Wenzel (this vol., i, 322), since lyxose yields a xylosazone quite different from the osazone of *carnose*.

The following derivatives of *carnose* have been prepared: *phenylhydrazone*, long, silky needles, m. p. 124—127°, $[\alpha]_D^{20} + 4.53^\circ$ (in alcohol); *p*-*bromophenylhydrazone*, colourless, silky needles, which sinter at 168°, m. p. 172—173° (decomp., corr.), $[\alpha]_D^{20} - 5.69^\circ$ (in alcohol).

W. H. G.

Yeast Nucleic Acid. PHÆBUS A. LEVENE (*Biochem. Zeitsch.*, 1909, 17, 120—131).—Yeast nucleic acid was obtained as a snow-white powder, $[\alpha]_D$ about $+36^\circ$ in 10% ammonia, having the composition $C_{33}H_{50}O_{29}N_{15}P_4$. It yields about 20% of its weight as bases, consisting of adenine, guanine, uracil, and cytosine, present in equimolecular quantities. The only carbohydrate present is a pentose, of which the nature has not been identified. On alkaline hydrolysis, phosphoric acid is eliminated, but no reducing substance obtained; complexes of sugar and base are formed of glucosidic character, which are resistant towards alkalis, but easily hydrolysed by acids. By partial hydrolysis with dilute sulphuric acid, a complex, consisting of phosphoric acid-pentose-uracil, was obtained. E. F. A.

Hydrolysis of Proteins by Acids. HENRI MATHIEU (*Compt. rend.*, 1909, 148, 1218—1221).—The hydrolysis of gelatin has been effected by sulphuric, hydrochloric, and oxalic acids, and Siegfried's coefficient, N/CO_2 , determined from time to time in the product (Abstr., 1908, i, 379). By plotting the value of this coefficient against the time, a characteristic discontinuous curve is obtained. This throws light on the course of hydrolysis by facilitating the determination of the successive stages at which the various amino-acids are produced.

W. O. W.

Soluble Chitin. CARL L. ALSBERG and C. HEDBLÖM (*Proc. Amer. Soc. Biol. Chem.*, 1908, xlv; *J. Biol. Chem.*, 6).—Chitin from *Limulus* resembles other chitins in composition. If treated with 10% hydro-

chloric acid at room temperature for nine months, it gelatinises and forms a colloidal solution. The colloidal material loses its power of being coloured by iodine. The solutions are irreversible. Soluble chitin does not reduce Fehling's solution ; its percentage of oxygen is increased ; it dialyses very slowly. W. D. H.

Action of Alkalis on Protein. I. ALBRECHT KOSSEL and FR. WEISS (*Zeitsch. physiol. Chem.*, 1909, 59, 492—498).—When protamines, for example, clupeine, are left in contact with 0.5*N*-sodium hydroxide solution at the ordinary temperature, a diminution of the laevorotation is observed, for example, from -2.6° to 0.5° at the end of seven days. This is probably due to a process of racemisation, since the product when hydrolysed by acids yields *dl*-arginine, whereas clupeine itself yields an active arginine. By the prolonged action of barium hydroxide solution on clupeine at 40° , *dl*-ornithine is obtained. Experiments have shown that *d*-ornithine and *d*-arginine themselves are not racemised by the action of alkalis, so that the arginine groups appear to be more reactive towards racemising agents when present as part of a protein molecule.

Some of the higher proteins, for example, gelatin, react with alkalis in much the same manner as clupeine. The ornithine was isolated as the *sulphate*, $2\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{SO}_4$, m. p. 213° . J. J. S.

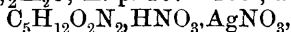
Action of Alkalis on Proteins. II. ALBRECHT KOSSEL and FR. WEISS (*Zeitsch. physiol. Chem.*, 1909, 60, 311—316. Compare preceding abstract).—By the action of 0.5*N*-sodium hydroxide solution on clupeine, a clupeone is obtained, which can be precipitated by the silver sulphate-baryta method. The product differs from the clupeone obtained by the action of dilute acids on clupeine ; for example, it yields less arginine, but more amino-acids, and when completely hydrolysed by acids the alkali-clupeone yields a substance which is precipitated by phosphotungstic acid, but not by the silver-baryta process.

The alkali-clupeone does not contain free ornithine, but when hydrolysed by dilute acids yields *dl*-ornithine. The formation of this product is regarded as further evidence in favour of the view that alkali produces racemisation in the protein molecule. J. J. S.

Salts of Inactive Ornithine. FR. WEISS (*Zeitsch. physiol. Chem.*, 1909, 59, 499—505. Compare E. Fischer, *Abstr.*, 1901, i, 192 ; Riesser, *ibid.*, 1907, i, 77 ; Ackermann, 1908, i, 774).—*dl*-Ornithine was prepared by the action of barium hydroxide solution on clupeine (compare preceding abstracts). The *nitrate*, $\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2 \cdot \text{HNO}_3$, is deposited as crystalline needles from aqueous alcohol, and has m. p. 183° . The *hydrochloride*, $\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2 \cdot \text{HCl}$, forms slender needles, m. p. 215° . The *oxalate*, $2\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{C}_2\text{O}_4$, forms crystalline plates, m. p. 218° . The *picrate*, $\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, does not contain water of crystallisation, and has m. p. 195° (Riesser gives 170°). The *picrolonate*, $\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2 \cdot \text{C}_{10}\text{H}_8\text{O}_5\text{N}_4 \cdot 1.5\text{H}_2\text{O}$, forms long, yellow needles, m. p. 220° — 221° (decomp.). The *acetate*,
 $\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2 \cdot \text{C}_2\text{H}_4\text{O}_2$,

is not so characteristic as the acetate of *d*-ornithine. It forms plates, m. p. 163—164°, and is readily soluble.

The compounds $2\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2, \text{CuSO}_4, \text{H}_2\text{O}$, m. p. 204—205° (decomp.), $2\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2, \text{Cu}(\text{NO}_3)_2, \frac{1}{2}\text{H}_2\text{O}$, m. p. 167—168°, and



which darkens at 130°, have been prepared.

J. J. S.

Inhibition and Reactivation of Enzyme Action by Mercuric Chloride. S. HATA (*Biochem. Zeitsch.*, 1909, 17, 156—187).—Mercuric chloride inhibits the action of pepsin, trypsin, rennet, ptyalin, the proteolytic enzyme of the liver, and enzymes which decompose hydrogen peroxide. The opposite action was never observed. The action of the enzymes is, however, restored by agents which precipitate mercury from solution. The enzymes are precipitated by mercuric chloride with greater difficulty than the proteins which accompany them; this may be used to separate enzymes from protein, and they may then be reactivated by precipitating the mercury with potassium sulphide.

W. D. H.

Influence of Reaction of the Medium on the Activity of Maltases from Maize. R. HUERRE (*Compt. rend.*, 1909, 148, 1121—1123. Compare this vol., ii, 258, 338).—Variation of the reaction of the solution by addition of sulphuric acid or potassium hydroxide has considerable influence on the action of the enzymes in maize extract. Some species of maize contain maltases which only exert their maximum activity in an alkaline solution, whilst others require a neutral or feebly acid medium. The author's experiments confirm his previous conclusions as to the plurality of maltases in maize.

W. O. W.

Chemistry of the Higher Fungi. III. Fungus Diastase. JULIUS ZELLNER (*Monatsh.*, 1909, 30, 231—246. Compare Abstr., 1909, ii, 175).—Amylolytic enzymes are widely distributed in fungi which grow on wood, and remain active for a prolonged period in the dried fungi. The ferment activity is easily impaired by dilute inorganic acids and bases; dilute organic acids have an accelerating influence. The diastatic action is most rapid at 40—60°, the optimum temperature being at about 50°; the ferment is destroyed at 70°. The diastatic power of fungi is relatively small in comparison with that of barley malt. The products of action are at first dextrins, and finally dextrins and dextrose; maltose if formed is probably destroyed by maltases in the fungus sap. The fungus enzyme is without action on inulin and arabin.

E. F. A.

***p*-Iodophenylarsinic Acid and Arsenious *p*-Iodophenyl Iodide.** EFISIO MAMELI and A. PATTÀ (*Boll. Soc. Med.-Chirurg. Pavia*, 1909).—Substitution of the amino-group of *p*-aminophenylarsinic acid (compare Ehrlich and Bertheim, Abstr., 1907, i, 812) by iodine by Sandmeyer's reaction leads to the formation of various compounds, of which the authors here describe the following.

p-Iodophenylarsinic acid, $C_6H_4I \cdot AsO(OH)_2$, is an infusible substance, crystallising from alcohol, acetone, or acetic acid in shining, white needles and exhibiting the characteristic reactions of the phenylarsinic acids.

Arsenious *p*-iodophenyl iodide, $C_6H_4I \cdot AsI_2$, which can also be obtained directly from *p*-iodophenylarsinic acid by heating for a short time or by prolonged contact with concentrated hydriodic acid, crystallises from acetic acid in golden-yellow needles or scales, m. p. 80° .

The therapeutic uses of these two products and of the others obtained are being investigated. T. H. P.

Magnesium Derivatives of Xylyl Bromides. PAUL CARRÉ (*Compt. rend.*, 1909, 148, 1108—1110; *Bull. Soc. chim.*, 1909, [iv], 5, 486—489. Compare Tiffeneau, *Abstr.*, 1903, i, 819; 1904, i, 48).—The chief product formed when magnesium acts on an ethereal solution of a xylyl bromide is the corresponding dimethyldibenzyl (Moritz, *Abstr.*, 1899, i, 910); only a small quantity of the organo-magnesium compound is formed. Magnesium *m*-xylyl bromide reacts with formaldehyde giving Kling's *m*-tolylethyl alcohol, b. p. $112\text{--}113^\circ/10$ mm. (*Abstr.*, 1908, i, 980); its *acetyl* derivative has b. p. $115\text{--}116^\circ/18$ mm. The following alcohols have been prepared in the same way: *m*-Tolylisopropyl alcohol, $C_7H_7 \cdot CH_2 \cdot CHMe \cdot OH$, b. p. $119\text{--}120^\circ/18$ mm. Its *acetyl* derivative has b. p. $116\text{--}117^\circ/20$ mm.; the benzoyl derivative has b. p. $188\text{--}190^\circ/12$ mm. *m*-Tolyl-*tert*-butyl alcohol, $C_7H_7 \cdot CH_2 \cdot CMe_2 \cdot OH$, b. p. $107\text{--}108^\circ/10$ mm., has an odour resembling that of terpineol; its *acetyl* derivative has b. p. $119\text{--}120^\circ/16$ mm. *o*-Tolyl-*tert*-butyl alcohol has b. p. $125\text{--}126^\circ/22$ mm. W. O. W.

Action of Magnesium Phenyl Bromide on Styrene. EZIO COMANDUCCI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 245—248).—When cinchonine (cinchotoxine) (1 mol.) is treated with magnesium phenyl bromide (4 mols.) in ethereal solution, the ether, when distilled off, is found to be accompanied by an amount of benzene corresponding with about 1 mol. of magnesium phenyl bromide; similarly, when magnesium α -naphthyl bromide is used, a corresponding amount of naphthalene distils over. The vinyl group of the cinchonidine evidently reacts with the organo-magnesium compound in the same way as does acetylene (compare Oddo, *Abstr.*, 1907, i, 549): $CHR:CH_2 + MgPhBr = CHR:CH \cdot MgBr + C_6H_6$ and $CHR:CH_2 + Mg(C_{10}H_7)Br = CHR:CH \cdot MgBr + C_{10}H_8$.

This reaction is not confined to complex compounds containing a vinyl group, since with magnesium phenyl bromide and styrene, benzene is obtained. T. H. P.

Organic Chemistry.

Preparation of Hydrocarbons by Electrolytic Reduction of Acetoacetic Esters. JULIUS TAFEL and WILHELM JÜRGENS (*Ber.*, 1909, 42, 2548—2556).—It was shown by Tafel and Hahl (Abstr., 1907, i, 765) that β -benzylbutane is obtained by the electrolytic reduction of ethyl benzylacetoacetate, and it is now found that the reaction may be extended to ethyl acetoacetate and its substituted derivatives, only failing in the case of ethyl diacetylsuccinate, which is reduced to ethyl diethylsuccinate, no hydrocarbon being produced.

Aqueous-alcoholic sulphuric acid is used as solvent, and a lead cylinder as cathode, enclosed in a porcelain cell with gas-tight lead cap and condenser. A high current density (up to 0.76 ampere per sq. dm.) and high temperature are necessary. The current concentration is from 100 to 500 amperes per litre of cathode solution. The products are purified by fractional distillation.

Ethyl acetoacetate yields butane. γ -Methylhexane, from ethyl propylacetoacetate, has b. p. 98—99°/748 mm., D_4^{19} 0.684 (compare Welt, Abstr., 1895, ii, 97); ethyl butylacetoacetate yields γ -methylheptane; ethyl isobutylacetoacetate yields $\beta\delta$ -dimethylhexane, b. p. 117—118°/751 mm., D_4^{19} 0.698 (compare Clarke, Abstr., 1908, i, 593). γ -Methyl- γ -ethylpentane, from ethyl diethylacetoacetate, has b. p. 118.5—119°/750 mm., D_4^{19} 0.713, n_D^{19} 1.4028. β -Benzylbutane has b. p. 203—204°/750 mm., D_4^{19} 0.860 (compare Tafel and Hahl, *loc. cit.*). β -Benzyl- β -methylbutane, from ethyl benzylmethylacetoacetate, has b. p. 214.5°/753 mm., D_4^{19} 0.860, n_D^{19} 1.4882. C. H. D.

Catalytic Actions of Colloidal Metals of the Platinum Group. VII. The Reduction of Ethylene. CARL PAAL and WILHELM HARTMANN (*Ber.*, 1909, 42, 2239—2244. Compare Abstr., 1908, i, 599; this vol., i, 358, 381).—On shaking ethylene and hydrogen together with palladium hydrosol, reduction of the ethylene to ethane takes place quantitatively. C. H. D.

***n*-Butinene and Some of its Derivatives.** GEORGES DUPONT (*Compt. rend.*, 1909, 148, 1522—1524. Compare Bruylants, *Ber.*, 1875, 8, 412).— $\beta\beta$ -Dichlorobutane has b. p. 102—104°, m. p. -74°, n_D 1.4295. β -Chloro- Δ^a -butylene has b. p. 61—62°, n_D 1.4168.

n - Δ^a -Butinene (ethylacetylene), obtained with difficulty by Bruylant's process, is prepared by the following method with good yields. The vapour of *n*-butyl alcohol is passed over heated alumina (Senderens, Abstr., 1908, i, 494), and the butylene absorbed by bromine. The butylene dibromide is then allowed to react at 180° with dry potassium hydroxide moistened with alcohol. Details are given for the preparation of *n*-butyl alcohol by a modification of Grignard's method.

n - Δ^a -Butinene is a liquid, b. p. 18.5°, m. p. -130°, D_0 0.668, n_D 1.3962 (compare Wislicenus, Abstr., 1901, i, 2). With bromine

it forms the dibromide, $\text{CBrEt}\cdot\text{CHBr}$, b. p. 150° , m. p. -49.5° , D_0 1.887, and a tetrabromide, which sublimes at 200° (compare Caventou, *Annalen*, 1863, 127, 93). The copper derivative when treated with iodine yields $\alpha\beta$ -tri-iodo- Δ^4 -butylene, $\text{CI}\cdot\text{Et}\cdot\text{Cl}_2$, m. p. 26° . When oxidised with potassium ferricyanide, it yields octadi-inene, $\text{CEt}:\text{C}:\text{C}:\text{CEt}$, a pale yellow liquid, b. p. $163-164^\circ$, D_0 0.826, n_D 1.4968. When this is heated with alcoholic mercuric chloride, it forms *octan- γ -dione*, $\text{COEt}\cdot\text{CH}_2\cdot\text{COPr}^a$, characterised by a copper derivative, m. p. 158.5° .

Carbon dioxide reacts with butinene magnesium bromide, forming *n*-butinene- α -carboxylic acid; the ethyl ester has b. p. $67-68^\circ/18$ mm., D_0 0.962, and forms a compound with piperidine, $\text{C}_{12}\text{H}_{21}\text{O}_2\text{N}$, b. p. $165-166^\circ/17$ mm., n_D 1.5246; by hydrolysis of the latter, ethyl propionylacetate is obtained.

α -Phenyl Δ^8 -pentin- n - α -ol, $\text{OH}\cdot\text{CHPh}\cdot\text{C}:\text{CEt}$, b. p. $137-138^\circ/16$ mm., D_0 1.037, n_D 1.5455, is prepared by the action of benzaldehyde on the above magnesium compound; its benzoyl derivative has m. p. 59° . It forms a di-iodide, $\text{CEtI}\cdot\text{Cl}\cdot\text{CHEt}\cdot\text{OH}$, m. p. 196° . When acetone reacts with butinene magnesium bromide, *α -methyl- Δ^7 -hexinen- β -ol*, $\text{CHMe}_2\text{OH}\cdot\text{C}:\text{CEt}$, is formed. This has b. p. $145-147^\circ$, D_0 0.962, n_D 1.4411.

W. O. W.

Action of Metallic Oxides on Methyl Alcohol. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1909, 148, 1734-1736. Compare Abstr., 1908, i, 594, 713; Senderens, this vol., i, 127).—Methyl alcohol is less readily decomposed by finely divided copper than other primary alcohols; formaldehyde is produced at 280° , but at 360° complete decomposition into hydrogen and carbon monoxide occurs. Chromic oxide and tungsten dioxide at 300° give a mixture of methyl ether and formaldehyde with some hydrogen and carbon monoxide. With the oxides of glucinum, zirconium, zinc, uranium, molybdenum, vanadium, lead, tin, cadmium, and ferric oxide, the predominating action is one of dehydrogenation, with further decomposition of the formaldehyde so produced. The action is most rapid in the case of stannic oxide, but the velocity of reaction depends, in each case, on the method of preparation of the oxide.

W. O. W.

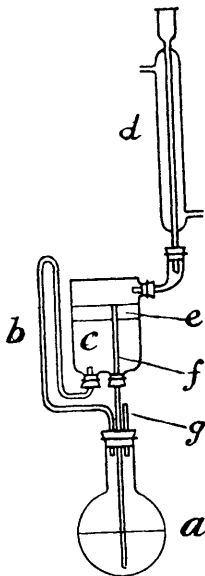
Action of Some Organo-magnesium Compounds on α -Methylpentan- δ -one. F. BODROUX and FELIX TABOURY (*Compt. rend.*, 1909, 148, 1675-1677).—The reaction between organo-magnesium compounds and α -methylpentan- δ -one is accompanied by the liberation of a saturated hydrocarbon corresponding with the magnesium derivative employed. Treatment of the product with hydrogen chloride yields a complex mixture containing a tertiary alcohol and the corresponding ethylenic hydrocarbon, with compounds of indefinite b. p. and much unaltered ketone. Magnesium ethyl iodide forms *$\beta\delta$ -dimethylhexan- δ -ol*, $\text{CH}_2\text{Pr}^b\cdot\text{CMeEt}\cdot\text{OH}$, b. p. $151-153^\circ/750$ mm., D^{15}_0 0.830, n^{15}_D 1.4286. The following new compounds are also mentioned: *$\beta\delta$ -dimethylheptan- δ -ol*, $\text{CH}_2\text{Pr}^b\cdot\text{CMePr}^a\cdot\text{OH}$, b. p. $170-171^\circ/750$ mm., D^{20}_0 0.826, n^{15}_D 1.4318; *$\beta\delta\zeta$ -trimethylheptan- δ -ol*, $\text{OH}\cdot\text{CMe}(\text{CH}_2\text{Pr}^b)_2$, b. p. $180-182^\circ/753$ mm., D^{21}_0 0.823, n^{18}_D 1.4334. Phenyl magnesium bromide gives (1) *β -phenyl- γ -methylpentan- β -ol*, $\text{CHMeEt}\cdot\text{CMePh}\cdot\text{OH}$, b. p. $125-128^\circ/18$ mm., D^{18}_0 0.952, n^{18}_D 1.5157; (2) *β -phenyl-*

δ -methyl- Δ^8 -pentene, $\text{CHPr}^\beta\text{:CMePh}$, b. p. $216\text{--}220^\circ/738$ mm., $111\text{--}115^\circ/18$ mm., D^{16}_4 0.909, n^{18}_D 1.5231; (3) $\delta\xi$ -dimethyl- Δ^a -hepten- δ -ol, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CMe(OH)}\cdot\text{CH}_2\text{Pr}^\beta$, b. p. $180\text{--}182^\circ/753$ mm., D^{21}_4 0.823, n^{19}_D 1.4443; this compound has also been obtained, together with propylene, by treating an ethereal solution of allyl bromide and methylpentanone with magnesium. W. O. W.

Action of Organo-magnesium Compounds on β -Hydroxy- α -methylbutaldehyde. PAUL ABELMANN (*Ber.*, 1909, 42, 2500—2505).—The interaction of magnesium methyl iodide (2 mols.) and β -hydroxy- α -methylbutaldehyde leads to the formation of γ -methylpentan- $\beta\delta$ -diol, $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{OH}$, b. p. $104\text{--}105^\circ/12.5$ mm. (diacetate, b. p. $107\text{--}109^\circ/19$ mm.); when an excess of magnesium methyl iodide ($2\frac{1}{2}$ mols.) is used, the product is contaminated with β -methylbutane- $\alpha\gamma$ -diol, obtained by the reduction of the original aldehyde. In a similar manner β -hydroxy- α -methylbutaldehyde reacts with magnesium ethyl bromide to form ultimately γ -methylhexane- $\beta\delta$ -diol, $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CHEt}\cdot\text{OH}$, b. p. $112\text{--}113^\circ/10$ mm. (diacetate, b. p. $103\text{--}105^\circ/10$ mm.), and with magnesium propyl bromide to form γ -methylheptane- $\beta\delta$ -diol, $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CHPr}^a\cdot\text{OH}$, b. p. $122\text{--}123^\circ/15.5$ mm. (diacetate, b. p. $113\text{--}114^\circ/10$ mm.). C. S.

Ether Purifying and Extraction Apparatus.

RODOLFO FRITSCH (*Chem. Zeit.*, 1909, 33, 759—760).—The apparatus described enables large quantities of ether to be purified from alcohol in an expeditious and economical manner. In the accompanying figure, *a* represents a flask containing ether, which is heated to boiling on a water-bath; the vapour passes through tube *b* to the inverted Woulffe bottle containing a solution of calcium chloride, *c*, through which it passes, becoming partially condensed—any escaping vapour being condensed in *d*. A layer of ether, *e*, accumulates on the surface of *c*, and is automatically returned to *a* by a siphon, indicated by tube *f*. When once set in operation this purifying process becomes continuous and requires little attention; care must, however, be taken when completed, and the source of heat removed, to open the side-tube *g* at once, so as to prevent the calcium chloride solution entering the flask by tube *b*. It will be readily seen that this apparatus is also suitable for extraction purposes, the liquid to be extracted by ether taking the place of the calcium chloride solution. J. V. E.



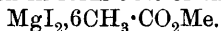
The Nitrogenous Radicle of Lecithin and other Phosphatides. HUGH MACLEAN (*Bio-Chem. J.*, 1909, 4, 240—257).—Further work is recorded which confirms the author's previous con-

clusion that choline is not the only nitrogen-containing group in lecithin; probably part of the nitrogen is in the form of amino-acid. The usually accepted formula for lecithin cannot therefore be correct. Lecithins from various sources, although often giving similar results on elementary analysis, differ in the amount of choline they yield.

W. D. H.

The Solubility of the Molecular Compounds of Magnesium Bromide and Iodide in the Organic Compounds from which They are Formed. BORIS N. MENSCHUTKIN (*Zeitsch. anorg. Chem.*, 1909, 62, 395—404. Compare Abstr., 1907, i, 19, 395; this vol., i, 82, 89).—The solubility curves obtained in the author's investigations are compared and plotted uniformly. They may be grouped in four classes, which, however, are not sharply distinguished.

The more stable the compound of the magnesium salt with an organic compound is, the more nearly its solubility curve resembles that of the hexahydrate in water. The solubility curves of the less stable compounds approach in form that of the compound



The order in which the organic compounds arrange themselves resembles that found by Walden (Abstr., 1906, ii, 527) for the solubility of metallic iodides and quaternary ammonium iodides in organic solvents, but is quite different from that obtained by Étard (Abstr., 1894, ii, 443) from solubility measurements of mercuric chloride.

C. H. D.

Theory of Hydrolysis of Fats and Oils. J. KELLNER (*Chem. Zeit.*, 1909, 33, 661—662. Compare this vol., i, 357).—The hydrolysis of fats by means of Twitchell's reagent, like the autoclave process, is to some extent a bi- and ter-molecular reaction, although the formation of the mono- and di-glycerides does not occur to the same extent as in the latter process.

The hydrolysis by means of the ferment of castor-oil seeds also gives rise to the formation of mono- and di-glycerides, although to a still less extent.

L. DE K.

Glycerol Esters of Stearolic and Behenolic Acids. H. QUENSELL (*Ber.*, 1909, 42, 2440—2452).—The existence in nature of glycerides of acids containing a triple linking has not yet been firmly established; compounds of this type have now been synthesised for the first time; they readily form additive compounds with one molecular proportion of chlorine or bromine, but react with two molecular proportions only on prolonged exposure in sunlight; they, however, never react with more than one molecule of iodine. Similarly, they only add on one molecule of iodine chloride for each acid radicle they contain.

Glycerol α -monostearolate, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_{17}\text{H}_{31}$, prepared by heating together equal parts of stearolic acid and anhydrous glycerol for five hours at 160—170°, or by heating in an oil-bath a mixture of sodium stearolate and α -monochlorohydrin in a stream of carbon dioxide, crystallises from alcohol in colourless leaflets, m. p. 40.5°.

Glycerol aa'-distearolate, $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{31})_2$, by heating *aa'*-dichlorohydrin with excess of sodium stearolate in a sealed tube for eight hours at 180° , or by heating anhydrous glycerol with an excess of stearolic acid under a pressure of 12 mm. for eight hours at 190° , crystallises from alcohol; m. p. $38\cdot5^\circ$.

Glycerol $\alpha\beta$ -distearolate, $\begin{array}{c} \text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{31} \\ | \\ \text{CH}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{31} \\ | \\ \text{CH}_2\cdot\text{OH} \end{array}$, by heating $\alpha\beta$ -dibromo-

hydrin with an excess of sodium stearolate for six hours in a sealed tube at 175° , crystallises from light petroleum, and has m. p. 40° .

Glyceryl tristearolate, $\text{C}_3\text{H}_5(\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{31})_3$, by heating trichlorohydrin with a slight excess of sodium stearolate in a sealed tube at 190 – 200° , does not crystallise well; it separates from alcohol in aggregates, which retain a good deal of solvent, and was dried at 60° for analysis; it has m. p. 29° .

Epistearolhydrin, $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH} > \text{O} \\ | \\ \text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{31} \end{array}$, by heating epichlorohydrin

with sodium stearolate for eight hours at 160° , crystallises from alcohol in small, colourless scales, m. p. 36° .

Glycerol α -monobehenolate, $\text{C}_{25}\text{H}_{46}\text{O}_4$, the constitution of which is similar to that of the corresponding stearyl derivative, was prepared by heating α -monochlorohydrin with sodium behenolate for six hours at 160° ; it crystallises from alcohol in colourless leaflets, m. p. $50\cdot5^\circ$.

Glycerol aa' -dibehenolate, $\text{C}_{47}\text{H}_{84}\text{O}_5$, by heating *aa'*-dichlorohydrin with sodium behenolate in a sealed tube for six hours at 180° , crystallises from light petroleum; m. p. 42° .

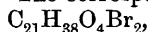
Glycerol $\alpha\beta$ -dibehenolate, $\text{C}_{47}\text{H}_{84}\text{O}_5$, prepared as above from $\alpha\beta$ -dibromohydrin, crystallises from alcohol, m. p. 43° .

Glyceryl tribehenolate, $\text{C}_{69}\text{H}_{122}\text{O}_6$, m. p. 41° , was obtained by heating trichlorohydrin with sodium behenolate in an atmosphere of carbon dioxide for ten hours at 240° , or by heating the acid with anhydrous glycerol under a pressure of 1 mm. for eighteen hours at 205 – 210° ; it separates from alcohol in colourless leaflets.

Epibehenolhydrin, $\text{C}_{25}\text{H}_{44}\text{O}_3$, by heating sodium behenolate with epichlorohydrin in a sealed tube for eight hours at 180° , crystallises from alcohol or light petroleum in colourless leaflets, m. p. 43° .

The iodine value of most of the above compounds was determined by Waller's modification of Hübl's method, and the *trichloriodide* of *glyceryl tribehenolate*, $\text{C}_{69}\text{H}_{122}\text{O}_6\text{Cl}_3\text{I}_3$, and *dichloriodide* of *glycerol dibehenolate*, $\text{C}_{47}\text{H}_{84}\text{O}_5\text{Cl}_2\text{I}_2$, were isolated and analysed.

Glyceryl monostearolate dichloride, $\text{C}_{21}\text{H}_{38}\text{O}_4\text{Cl}_2$, prepared by exposing to daylight a chloroform solution of a mixture of glycerol monostearolate with a slight excess over one molecular proportion of chlorine, forms a heavy oil. The corresponding *dibromide*,



obtained by the action of bromine in presence of iron filings or ferric chloride on monostearol glycerol in carbon disulphide solution, is a pleasant smelling, heavy oil.

The *di-iodide*, $\text{C}_{21}\text{H}_{38}\text{O}_4\text{I}_2$, prepared by the interaction of its

generators in carbon disulphide solution for four to five days in presence of ferrous or aluminium iodides, separates from alcohol in yellow aggregates, m. p. 33° .

The *tetrabromide*, $C_{21}H_{38}O_4Br_4$, produced by the action of two molecular proportions of bromide on the glycerol monostearolate for a week, is an unstable oil.

The *hexabromide* of glyceryl tristearolate, $C_{37}H_{98}O_6Br_6$, was also prepared.

Glycerol monobehenolate dibromide, $C_{25}H_{46}O_4Br_2$, prepared in carbon disulphide solution in presence of metallic iron, is a light-coloured oil; the corresponding *di-iodide*, $C_{25}H_{46}O_4I_2$, produced from its generators in the course of a week, is a thick oil, which solidifies on cooling.

Glycerol dibehenolate tetrachloride, $C_{47}H_{84}O_5Cl_4$, prepared in chloroform solution, is a thick oil. P. H.

Synthesis of β -Ketonic Esters by means of Ethyl Diazoacetate. II. FRITZ SCHLOTTERBECK (*Ber.*, 1909, 42, 2565—2573. Compare Abstr., 1907, i, 676).—The synthesis of β -ketonic esters from aldehydes and ethyl diazoacetate is only possible when the aldehyde contains negative substituents. Ethyl diazopropionate or diazoacetophenone may also be used.

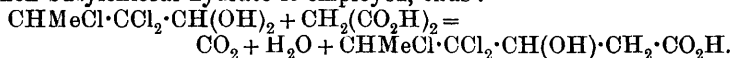
Ethyl di- γ -chloroacetoacetate, from freshly prepared dichloroacetaldehyde, has b. p. $203\text{--}205^{\circ}/761$ mm. *Ethyl γ -chloroacetoacetate*, from chloroacetaldehyde, has b. p. $95^{\circ}/0.8$ mm.

The chloro-esters obtained by Haller and Held (Abstr., 1887, 799) and by Genvresse (Abstr., 1889, 122) are not, as supposed, γ -derivatives, but α -derivatives, as shown by Hantzsch (Abstr., 1894, i, 171, 227); the above γ -chloro-esters are therefore new.

Ethyl tri- γ -bromoacetoacetate, $CBr_3 \cdot CO \cdot CH_2 \cdot CO_2Et$, has b. p. $158^{\circ}/14$ mm. *Ethyl $\gamma\delta$ -dichloropropionylacetate*, $CH_2Cl \cdot CHCl \cdot CO \cdot CH_2 \cdot CO_2Et$, from $\alpha\beta$ -dichloropropaldehyde, has b. p. $38^{\circ}/0.2$ mm. *Ethyl $\gamma\gamma\delta$ -trichlorobutyrylacetate*, from butyl chloral, has b. p. $149^{\circ}/20$ mm.

Ethyl *p*-nitrobenzoylacetate is obtained from *p*-nitrobenzaldehyde with some difficulty, and is purified by conversion into the barium derivative and decomposition of this with sulphuric acid while suspended in ether. C. H. D.

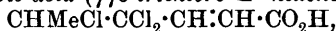
Condensation of Butylchloral and Butylchloral Hydrate with Malonic Acid. ADOLF RIEDEL and ERICH STRAUBE (*Annalen*, 1909, 367, 40—51).—The condensation of butylchloral with malonic acid proceeds in a manner analogous with that observed by von Garzarolli-Thurnlackh with chloral and malonic acid (compare Abstr., 1892, 429), in that carbon dioxide is eliminated with the formation of a β -hydroxycarboxylic acid. The reaction proceeds more smoothly when butylchloral hydrate is employed, thus:



$\gamma\gamma\delta$ -Trichloro- β -hydroxy-n-hexoic acid, $C_6H_9O_3Cl_3$, prepared by heating butylchloral hydrate, malonic acid, and pyridine together on a water-bath and treating the product with dilute sulphuric acid, crystallises in large, hexagonal leaflets and long, rectangular prisms, m. p. 102° ;

the *sodium* salt ($3\text{H}_2\text{O}$) forms long, white needles, m. p. 91° ; the *methyl* ester, $\text{C}_7\text{H}_{11}\text{O}_3\text{Cl}_3$, is a viscid, colourless oil with an aromatic odour, b. p. $150^\circ/12$ mm.; the *ethyl* ester, $\text{C}_8\text{H}_{13}\text{O}_3\text{Cl}_3$, is a colourless oil, b. p. $138^\circ/13$ mm., which slowly solidifies, forming large, four-sided leaflets.

Trichlorohydrosorbic acid ($\gamma\delta$ -trichloro- Δ^a -hexenoic acid),

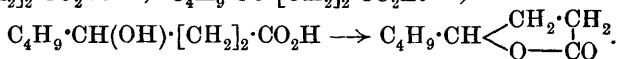
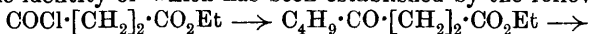


is prepared by treating anhydrous sodium $\gamma\delta$ -trichloro- β -hydroxy-*n*-hexoate with acetic anhydride; it crystallises in colourless needles, m. p. 78° ; the *chloride*, $\text{C}_6\text{H}_6\text{OCl}_4$, is a colourless liquid, b. p. $109^\circ/10$ mm.; the *amide*, $\text{C}_6\text{H}_7\text{ONCl}_3$, crystallises in long, white needles, m. p. 90° ; the *methyl* ester, $\text{C}_7\text{H}_9\text{O}_2\text{Cl}_3$, is a colourless oil with a fruity odour, b. p. $122^\circ/9$ mm.; the *ethyl* ester, $\text{C}_8\text{H}_{11}\text{O}_2\text{Cl}_3$, is a colourless oil, b. p. $129^\circ/11$ mm. The acid is oxidised by potassium permanganate to $\alpha\alpha\beta$ -trichlorobutyric acid, and reduced by sodium amalgam and water to *n*-hexoic acid. Treatment with zinc dust and dilute alcohol leads to the formation of γ -chlorosorbic acid, $\text{CHMe}\cdot\text{CCl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, crystallising in long, white needles, m. p. 116° ; the *ethyl* ester, $\text{C}_8\text{H}_{11}\text{O}_2\text{Cl}$, is a colourless oil with a peppermint-like odour, b. p. $138^\circ/13$ mm.; it solidifies in a freezing mixture, forming glistening leaflets.

W. H. G.

Lactonisation of Acid Alcohols. EDMOND É. BLAISE and A. KÖHLER (*Compt. rend.*, 1909, 148, 1772—1774).— ζ -Lactones appear to be incapable of existence, since reactions which might be expected to result in their formation are accompanied by migration of the hydroxyl group. In order to ascertain the limit of lactone formation the following hydroxy-acids have been prepared by reducing the corresponding ketonic acids (this vol., i, 204) by means of zinc and potassium hydroxide in presence of platinum.

ϵ -Hydroxyoctanoic acid, $\text{OH}\cdot\text{CHEt}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$, is a viscous liquid which yields, on distillation in a vacuum, ϵ -octolactone, $\text{C}_8\text{H}_{14}\text{O}_2$, b. p. 114 — $115^\circ/10$ mm.; sulphuric acid (50%) converts it into γ -*n*-octolactone, the identity of which has been established by the following synthesis:



ζ -Hydroxynonanoic acid, $\text{OH}\cdot\text{CHEt}\cdot[\text{CH}_2]_5\cdot\text{CO}_2\text{H}$, has b. p. $204^\circ/25$ mm., and does not form a lactone on distillation; sulphuric acid, however, converts it into γ -nonolactone, $\text{C}_9\text{H}_{16}\text{O}_2$, b. p. 137 — $138^\circ/14$ mm.

W. O. W.

$\gamma\gamma'$ -Diketonic Acids. JAMES B. GARNER, GUY A. REDDICK, and GAIL J. FINK (*J. Amer. Chem. Soc.*, 1909, 31, 667—669).—The sodium derivatives of β -diketones react with α -brominated esters, best at temperatures near the b. p. of the ester, to form $\gamma\gamma'$ -diketonic esters: $\text{R}\cdot\text{CO}\cdot\text{CHNa}\cdot\text{CO}\cdot\text{R}' + \text{CHR}''\text{Br}\cdot\text{CO}_2\text{Et} =$



where $\text{R} = \text{Me}$, $\text{R}' = \text{Me}$ or Ph , and $\text{R}'' = \text{H}$, Me , or Et . The resulting $\gamma\gamma'$ -diketonic esters are yellow liquids, which develop intense colorations with ferric chloride, reduce gold, silver, and platinum salts, and form unstable monophenylhydrazones, which readily lose water to form red,

viscous pyrazoles. All the esters respond to Knorr's pyrazoline reaction. The following new compounds have been prepared: *Ethyl $\beta\beta$ -diacetylpropionate*, $\text{CHAc}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, b. p. $165^\circ/55$ mm.; *oxime*, m. p. 120° , and the *pyrazole*, $\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}_2$, b. p. $242^\circ/83$ mm. *Ethyl $\beta\beta$ -diacetyl- α -ethylpropionate*, $\text{CHAc}_2 \cdot \text{CHEt} \cdot \text{CO}_2\text{Et}$, b. p. $205^\circ/27$ mm., and the *pyrazole*, b. p. $237^\circ/45$ mm. *Ethyl $\beta\beta$ -diacetyl- $\alpha\alpha$ -dimethylpropionate*, $\text{CHAc}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$, b. p. $180^\circ/22$ mm., and the *pyrazole*, $\text{C}_{17}\text{H}_{22}\text{O}_2\text{N}_2$, b. p. $215^\circ/20$ mm. *Ethyl β -benzoyl- β -acetylpropionate*, $\text{CHAcBz} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, b. p. $194^\circ/44$ mm., forms a colourless, unstable *phenylhydrazone*, m. p. 101 — 106° , which readily changes into the *pyrazole* derivative, $\text{C}_{18}\text{H}_{16}\text{O}_3\text{N}_2$, b. p. $270^\circ/47$ mm. *Ethyl β -benzoyl- β -acetyl- α -methylpropionate*, $\text{CHAcBz} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$, b. p. $205^\circ/69$ mm., and the *pyrazole*, $\text{C}_{19}\text{H}_{18}\text{O}_3\text{N}_2$, b. p. 250 — $253^\circ/55$ mm. *Ethyl β -benzoyl- β -acetyl- α -ethylpropionate*, $\text{CHAcBz} \cdot \text{CHEt} \cdot \text{CO}_2\text{Et}$, b. p. $198^\circ/37$ mm., and the *pyrazole*, $\text{C}_{20}\text{H}_{20}\text{O}_3\text{N}_2$, b. p. 250 — $253^\circ/46$ mm. C. S.

Digitoxonic and Digitalonic Acid. HEINRICH KILIANI (*Ber.*, 1909, 42, 2610—2611).—Pure digitoxonic acid has been prepared through its crystalline phenylhydrazide with the object of determining whether it could be obtained in crystalline form; a syrupy residue, consisting for the most part of lactone, however, showed no signs of crystallisation after fourteen days. The *potassium*, *lead*, and especially *silver* salts were, however, found to be crystalline; the free acid liberated from the pure silver salt could not be made to crystallise, from which it appears that the phenylhydrazide still remains the only suitable derivative for the identification of this acid, with the possible exception of the silver salt, which forms stout, rhombic plates.

The lactone of digitalonic acid can be conveniently separated from gluconic acid (compare Abstr., 1892, 1241) by shaking a syrupy mixture of the two substances with three times its volume of a mixture of one part of alcohol with four parts of ether; after allowing the precipitate to settle, the ethereal solution is siphoned off and allowed to evaporate spontaneously, when the pure lactone remains. The *phenylhydrazide* of digitalonic acid, obtained by mixing the lactone with phenylhydrazine in alcoholic solution, separates, after twenty-four hours, in the form of stout plates; it crystallises from a mixture of methyl alcohol with a large excess of absolute ether, and has m. p. 174° . P. H.

Thionyltartaric Acid Esters. EMIL SCHILLER (*Ber.*, 1909, 42, 2017—2020).—Ethyl tartrate and thionyl chloride in molecular quantities react at the ordinary temperature, or on warming to 50° , to form ethyl thionyltartrate, $\text{SO} \begin{smallmatrix} \diagup \text{O} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \\ \diagdown \text{O} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$. This and corresponding esters are colourless, odourless, syrupy compounds, hydrolysed on long boiling with water, and are more easily volatile than the corresponding acid esters.

Methyl thionyltartrate has b. p. $157.5^\circ/12.3$ mm., $274^\circ/770$ mm., $D_{19.5}^{20} 1.4425$, $[\alpha]_D^{18} - 61^\circ$.

Ethyl thionyltartrate has b. p. $167^\circ/11.5$ mm., $279^\circ/770$ mm., $D_{19.5}^{20} 1.3257$, $[\alpha]_D - 56.7^\circ$.

n-Propyl thionyltartrate has b. p. $176^{\circ}/12$ mm., $295^{\circ}/770$ mm., $D_{19.5}^{1.2378}$, $[\alpha]_D -18.5^{\circ}$.

Methyl thionylacetate has b. p. $158.5^{\circ}/12.2$ mm., $276^{\circ}/770$ mm., $D_{19.5}^{1.4648}$. E. F. A.

Conversion of Aldehydes into Ketones by Diazomethane. II. FRITZ SCHLOTTERBECK (*Ber.*, 1909, 42, 2559—2564. Compare Abstr., 1907, i, 185).—The reaction previously described has been extended to negatively substituted aldehydes, and furnishes a means of obtaining substituted ketones not otherwise obtainable.

Tri- α -chloroacetone, $\text{CCl}_3 \cdot \text{COMe}$, prepared by adding ethereal diazomethane to chloral in absolute ether, cooling with a freezing mixture, forms a colourless, mobile liquid with somewhat sweet smell, b. p. $149^{\circ}/764$ mm. The trichloroacetone described in the literature is mainly the unsymmetrical compound.

By adding a further quantity of chloral in the above preparation, *s*-trichloroacetonechloral, $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CCl}_3$, may be obtained in white crystals, m. p. 88° .

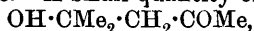
$\alpha\beta$ -Dibromopropionaldehyde, from acraldehyde and bromine, reacts with diazomethane to form methyl $\alpha\beta$ -dibromoethyl ketone,



b. p. $53^{\circ}/0.2$ mm., a colourless oil with pleasant odour.

$\alpha\beta$ -Dichloropropaldehyde, b. p. $25^{\circ}/0.2$ mm., yields methyl $\alpha\beta$ -dichloroethyl ketone, $\text{CHCl} \cdot \text{CHCl} \cdot \text{COMe}$, a colourless, mobile liquid, b. p. $30-40^{\circ}/0.2$ mm. C. H. D.

Condensation of Acetone by Calcium Oxide. ALFRED HOFFMAN (*J. Amer. Chem. Soc.*, 1909, 31, 722—724).—By boiling acetone in a Soxhlet apparatus containing calcium oxide in the extraction cup, a condensation product is obtained consisting almost entirely of mesityl oxide. A small quantity of diacetone,



is also formed, which becomes the sole product when calcium hydroxide is used as the condensing agent. Dry acetone and pure calcium oxide do not react at $105-110^{\circ}$, but in the presence of a trace of the hydroxide a viscous syrup of the higher condensation products is obtained. Calcium hydroxide and acetone give only a small quantity of diacetone. Dry mesityl oxide, alone or in the presence of acetone, reacts with calcium oxide only when the hydroxide is present.

The experiments show that the formation of mesityl oxide proceeds in two stages, and that the production of isophorone and the xylitones is due to the secondary condensation of mesityl oxide with acetone or with itself. C. S.

Products of the Reaction between Lactose and Calcium Hydroxide. HEINRICH KILIANI and FRITZ EISENLOHR (*Ber.*, 1909, 42, 2603—2610. Compare Abstr., 1908, i, 715).—The acid extract II (*loc. cit.*) has been examined once more, and found to contain isosaccharin. The dibasic acid, $\text{C}_6\text{H}_{10}\text{O}_7$, obtained from the oxidation products of extract IV is now proved to be a trihydroxyadipic acid

with a normal carbon chain, since it yields *n*-adipic acid on reduction with hydriodic acid and red phosphorus.

With the object of further characterising meta- and para-saccharin, the following compounds have been prepared.

Metasaccharin phenylhydrazide, $C_{12}H_{18}O_5N_2$, obtained by mixing the finely powdered lactone with three times its weight of 95% alcohol and rather less than its own weight of phenylhydrazine, crystallises from a mixture of methyl alcohol and ether in nodular aggregates, m. p. 145° .

Parasaccharin phenylhydrazide separates from water in an amorphous condition, which shows that it is not identical with Nef's parasaccharin, which gives a phenylhydrazide, m. p. 125° .

Metasaccharin when heated over a water-bath with water and brucine yields a salt, $C_{29}H_{38}O_{10}N_2 \cdot 3H_2O$, which separates from a mixture of aqueous alcohol and ether in colourless, glistening cubes or hexagonal plates, m. p. 136° , $[\alpha]_D - 12^\circ$.

Parasaccharin under similar conditions yields a brucine salt, $C_{29}H_{38}O_{10}N_2 \cdot H_2O$, which forms nodular aggregates, m. p. 137° , with loss of water; it has $[\alpha]_D - 27^\circ$. The brucine salt of Nef's parasaccharin forms glistening needles, m. p. $193-194^\circ$.

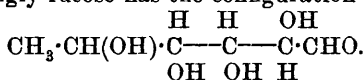
Although the melting points of the brucine salts of meta- and parasaccharin lie so close together, the two substances were proved to be different by showing that the melting point of a mixture of the two lay considerably below the melting point of either alone. P. H.

Inversion of Sucrose by Invertase. III. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1909, 31, 655—664. Compare Abstr., 1908, i, 605, 856).—Since α -dextrose, liberated from sucrose by invertase, changes to β -dextrose at 30° at a rate identical with that of the mutarotation of dextrose, it is to be expected that the freshly liberated l  vulose will change similarly with a velocity equal to that of the mutarotation of l  vulose. Since the latter proceeds rapidly at 30° , the experiments have been executed at 0° . In two experiments at 0° , with 1 litre of 5% sucrose and 100 c.c. of especially active invertase solution and with 1 litre of 8% sucrose and 500 c.c. of the invertase solution respectively, it is shown that the inversion of the sucrose proceeds almost instantaneously, the subsequent slow change of rotation with time being due to the change of the freshly liberated dextrose and l  vulose to their stable states. The results are expressed graphically. The first rapid decrease of the rotation is due to the change of the freshly formed l  vulose to its stable state, and the succeeding very slow change is due to the conversion of α -dextrose into β -dextrose. By extrapolation, the value 110° at 0° is obtained for the specific rotatory power of α -dextrose, which agrees with the value observed directly, 109° at $20-30^\circ$. From the values of the rotation in the first twenty-five minutes, the velocity coefficient of the change of the freshly formed l  vulose into its stable form is calculated from the equation for a unimolecular reaction and its value is almost identical with that of the mutarotation of l  vulose. The freshly formed l  vulose is therefore the suspected, but hitherto unknown, α -l  vulose; its specific rotatory power, calculated from the data of the preceding experiments, is 17° .

The cause of the discrepancy between this and the value, -77° , calculated by a different method (*loc. cit.*) is being investigated. The specific rotation of sucrose, 66° , is additively related to those of its component sugars, 109° for α -dextrose and 17° for α -lævulose. It is also shown that the rotation of raffinose, 124° , is equal to the sum of those of its constituents, α -melibiose, 171° , and α -lævulose, 17° . It appears to hold in general that the union of α -dextrose and α -lævulose carries with it an additive relation between the rotatory powers of the constituents and their compound. It is also a fact, and probably a closely related one, that α -dextrose and α -lævulose always combine to give a non-reducing, non-mutarotating sugar, such as sucrose, raffinose, or stachyose.

Experiments are described which indicate that brewers' yeast attacks α -dextrose slightly more rapidly than β -dextrose. C. S.

Fucose. BERNHARD TOLLENS and F. RORIVE (*Ber.*, 1909, 42, 2009—2012; *Zeitsch. Ver. Deut. Zuckerind.*, 1909, 579—585).—Fifty grams of fucose were obtained from 6000 grams of dried *Fucus* from Heligoland. Fucose does not form a crystalline hydrate. It shows mutarotation having $[\alpha]_D -124.1^\circ$ ten minutes after solution, and a final value of -75.6° . The initial value is calculated as -150° . The final value for the rotation of the fucohexonic acid prepared by means of the addition of hydrogen cyanide, etc. (compare Mayer and Tollens, *Abstr.*, 1907, i, 588) is $[\alpha]_D +37.6^\circ$. The oxidation of fucose (*loc. cit.*) and of rhamnose with dilute nitric acid has been carried out under identical conditions. The trihydroxyglutaric acid from fucose has $[\alpha]_D +27.6^\circ$, and its potassium salt, $[\alpha]_D -8.2^\circ$ and -8.7° ; that from rhamnose has $[\alpha]_D -24.9^\circ$, and its potassium salt, $+8.5^\circ$. The acids are optical antipodes, accordingly fucose has the configuration:



E. F. A.

Molecular and Solution Volumes of Colloidal Carbohydrates. CHARLES F. CROSS and EDWARD J. BEVAN (*Ber.*, 1909, 42, 2198—2204).—The gram-molecular volume of solid anhydrous starch is 98.5, and the molecular solution volume for soluble starch is 92.6—93.3, whereas the value calculated from the formula $\text{C}_6\text{H}_{10}\text{O}_5$, using Traube's numbers, is 102.6. This difference is much greater than that observed by Traube in the case of various mono- and disaccharoses, but is comparable with the differences met with in the case of certain cyclic carbohydrates, for example, quercitol and inositol. The authors put forward the suggestion that ring formation may be the cause of the differences between the experimental and calculated values in the case of soluble starch.

In the case of the nitrate esters of cellulose it is found that the introduction of each NO_2 -group has the same effect on the molecular volume, namely, an increment of 26.8 cm. In the case of the nitrates of other aliphatic alcohols, for example, glycerol, the effect of the nitro-groups on the molecular volume diminishes from the first to the third.

ISIDOR TRAUBE (*ibid.*, 2204), in a short, critical note, supports the authors' views. J. J. S.

Soluble Starch. CHARLES TANRET (*Compt. rend.*, 1909, 148, 1775—1776).—When soluble starch is prepared by Wolff's method (Abstr., 1905, i, 510) a sparingly soluble product is also formed, having $[\alpha]_D$ 208—210°, and resembling the amylocellulose of Maquenne and Roux (Abstr., 1905, i, 511). The soluble portion is not a single substance, since fractional precipitation of its aqueous solution by alcohol resolves it into two substances having $[\alpha]_D$ 180.5° and 173°, and giving with iodine reddish-violet and red colorations respectively. The alcoholic mother liquor contains a mixture of erythrodextrins having $[\alpha]_D$ + 154.5°.

The author also describes substances obtained by varying the conditions under which starch is rendered soluble, and shows in each case that the product is not homogeneous. W. O. W.

Organic Tungstates. JOHN B. EKELEY (*J. Amer. Chem. Soc.*, 1909, 31, 664—666).—Freshly prepared tungstic acid dissolves in aqueous solutions of most aliphatic amines, forming substituted ammonium tungstates, which generally crystallise out on evaporation. When heated, the amine is driven off, and the tungstic acid is partially reduced to the blue oxide. The following are described: *Methylammonium tungstate*, $(NMeH_3)_6W_7O_{24} \cdot 6H_2O$; *dimethylammonium tungstate*, $(NMe_2H_2)_{10}W_{12}O_{41} \cdot 13H_2O$; *trimethylammonium tungstate*, $(NMe_3H)_2W_4O_{13} \cdot H_2O$; *ethylammonium tungstate*, $(NEtH_3)_6W_7O_{24} \cdot 5H_2O$;

diethylammonium tungstate, $(NEt_2H_2)_2W_4O_{13} \cdot 3H_2O$; *propylammonium tungstate*, $(NPrH_3)_{10}W_{12}O_{41} \cdot 6H_2O$; *dipropylammonium tungstate*, $(NPr_2H_2)_2W_4O_{13} \cdot H_2O$;

diamylammonium tungstate, $[N(C_5H_{11})_2H_2]_2W_5O_{16}$; and *ethylenediammonium tungstate*, $C_2H_{10}N_2W_2O_7$. C. S.

Acid Haloid Salts. II. FELIX KAUFLE and E. KUNZ (*Ber.*, 1909, 42, 2482—2487. Compare this vol., i, 136).—Various bases have been examined with respect to the capacity of forming perhydrobromides and iodides. As a rule, the per-iodides are least, and the corresponding chlorides most, stable.

The following compounds are described: *Trimethylamine trihydrochloride*, $NMe_3 \cdot 3HCl$, pale yellow liquid, not solid at -28° . *Tetraethylammonium chloride trihydrochloride*, $NEt_4Cl \cdot 3HCl$, solidifies at -6° to -7° . *Trimethylamine dihydrobromide*, $NMe_3 \cdot 2HBr$. *Tetramethylammonium bromide hydrobromide*, $NMe_4Br \cdot HBr$. *Tetraethylammonium bromide dihydrobromide*, $NEt_4Br \cdot 2HBr$. *Dimethylaniline dihydrobromide*, $NPhMe_2 \cdot 2HBr$, brown liquid. *Diethylaniline dihydrobromide*, $NPhEt_2 \cdot 2HBr$, colourless, hygroscopic crystals, m. p. 37.3° . *Dimethyl-o-toluidine dihydrobromide*, $C_6H_4Me \cdot NMe_2 \cdot 2HBr$, m. p. 29.6° . *Tetramethyldiaminodiphenylmethane trihydrobromide*, $CH_2(C_6H_4 \cdot NMe_2)_2 \cdot 3HBr$.

Dimethylamine hydriodide, $NHMe_2 \cdot HI$, m. p. 147° . *Tetraethylammonium iodide trihydriodide*, $NEt_4I \cdot 3HI$. *Quinoline dihydriodide*, $C_9H_7N \cdot 2HI$.

Dimethylaniline dihydriodide, $\text{NPhMe}_2 \cdot 2\text{HI}$, reddish-brown oil. The introduction of alkyl groups into the amine molecules tends to render the salts more stable. Negative radicles, on the other hand, tend to inhibit the formation of perhaloid salts. J. J. S.

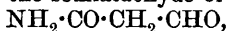
Behaviour of α -Amino-acids towards Sodium Hypochlorite.

KURT LANGHELD (*Ber.*, 1909, 42, 2360—2374).—In cold aqueous solution, neutral sodium hypochlorite, free from chlorate, reacts with α -amino-acids containing primary or secondary amino-groups to form the sodium salt of the chlorinated amino-acid. The solution of the sodium salt liberates iodine from potassium iodide, and by acidification with dilute acetic acid a solution of the chlorinated amino-acid is obtained; only in the cases of chloroleucine and dichloroleucine have the substances been isolated. The aqueous solutions of the sodium salts decompose in a simple way by heating, yielding sodium chloride, carbon dioxide, ammonia or an amine, and an aldehyde or ketone. The formation and decomposition of the salts can be represented thus:

$$\text{NHR} \cdot \text{CR}'\text{R}'' \cdot \text{CO}_2\text{H} \xrightarrow{\text{NaOCl}} \text{NRCl} \cdot \text{CR}'\text{R}'' \cdot \text{CO}_2\text{Na} \rightarrow \text{NaCl} + \text{CO}_2 + \text{NR} \cdot \text{CR}'\text{R}'' \xrightarrow{\text{H}_2\text{O}} \text{NH}_2\text{R} + \text{R}'\text{COR}''.$$

In order that the decomposition may occur without complications, it is necessary that the hypochlorite, the amino-acid, and the products of decomposition should be in contact for as brief a period as possible; an apparatus is described which satisfies this condition. Since substituted acid amides, amino-acids containing a tertiary amino-group, and certain proteins, such as egg-albumin, gelatin, and casein, do not react, or only slightly, with sodium hypochlorite, the reaction may serve to separate polypeptides which do not contain the group $\text{:C}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ from amino-acids and peptones with this reactive complex.

The following substances have been decomposed by sodium hypochlorite: glycine, sarcosine, alanine, α -aminoisobutyric acid, *i*-valine, *i*-leucine, phenylalanine, aspartic acid, asparagine, glutamic acid, tyrosine, serine, *i*-proline, and histidine, and the following new compounds have been obtained: β -iminazoleacetaldehyde from histidine, isolated as the *hydrochloride*, $\text{C}_5\text{H}_5\text{ON}_3 \cdot \text{HCl}$; a *pyrroline* from proline, isolated as the *hydrochloride*, $\text{C}_4\text{H}_8\text{N} \cdot \text{HCl}$; *p*-hydroxyphenylacetaldehyde from tyrosine, isolated as the *p*-nitrophenylhydrazone, $\text{C}_{14}\text{H}_{13}\text{O}_3\text{N}_3$, which separates from alcohol in crystals containing 1 mol. EtOH , m. p. 158° ; the amide of the semialdehyde of malonic acid,



from asparagine, isolated as the *phenylhydrazone*, $\text{C}_9\text{H}_{11}\text{ON}_3$, m. p. 239 — 240° . C. S.

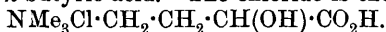
Constituents of Meat Extract. R. ENGELAND (*Ber.*, 1909, 42, 2457—2462. Compare this vol., ii, 71).—Carnitine (*Abstr.*, 1905, i, 726; 1907, i, 264; 1908, i, 41, 842) contains a carboxylic group as the hydrochloride, and when heated with an ethyl alcoholic solution of hydrogen chloride yields the *ester*, which can be isolated as the *platinichloride*. This salt, unlike the platinichloride of carnitine, is sparingly soluble in water. The ester, when treated with gold chloride solution, is hydrolysed, and yields carnitine aurichloride.

Novaine (Abstr., 1907, i, 18, 114) behaves in exactly the same manner as carnitine, and is probably identical with it. Novaine contains an impurity, probably homobetaine, which remains in the mother liquor when carnitine ester platinichloride crystallises from the solution obtained by esterifying novaine and subsequently treating with platinichloride. The compound described by Krimberg as oblitine (Abstr., 1908, i, 842) is in all probability carnitine ethyl ester.

Carnitine also contains an alcoholic hydroxyl group, as the dry chloride of the ester reacts with acetyl chloride, yielding a *monoacetyl* derivative of carnitine, $\text{OAc} \cdot \text{C}_6\text{H}_4\text{NCl} \cdot \text{CO}_2\text{H}$, the *platinichloride* of which, $(\text{C}_8\text{H}_{14}\text{O}_4\text{N})_2\text{PtCl}_6$, forms pale yellow crystals, m. p. 199° .

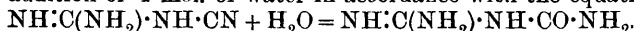
When an aqueous solution of carnitine chloride is made alkaline with sodium carbonate and oxidised with calcium permanganate, β -homobetaine is obtained. The ethyl ester of homobetaine forms a *platinichloride*, $2\text{C}_8\text{H}_{18}\text{O}_2\text{N}_2\text{PtCl}_6$, which crystallises from water in orange-red needles, m. p. 210 — 211° (decomp.).

These reactions point to the conclusion that carnitine is an α -hydroxy- γ -trimethylamino-*n*-butyric acid. The chloride is therefore



J. J. S.

The Chemical Nature of Dicyanodiamide. N. CARO and HERMANN GROSSMANN (*Chem. Zeit.*, 1909, 33, 734. Compare *ibid.*, 1907, 31, 1195, and *Zeitsch. angew. Chem.*, 1909, 22, 1182).—Radlberger having described salts of dicyanodiamide with certain acid dyes (Abstr., 1908, i, 1001), the neutral character of this substance required further establishment. It is found, on careful repetition of Radlberger's work that salts of dicyanodiamide do not exist, those described by him being salts of dicyanodiamidine, which is produced from dicyanodiamide by the addition of 1 mol. of water in accordance with the equation:



Most probably some quantity of this substance accompanied the dicyanodiamide used by Radlberger.

Conductivity measurements, the activity towards various indicators (Abstr., 1907, ii, 389), and the effect on the optical rotation of tartaric acid solutions (*Chem. Zeit.*, 1907, 31, 1195), all give additional evidence of the neutrality of dicyanodiamide.

J. V. E.

Hexathiocyano-salts of Molybdenum. ARTHUR ROSENHEIM (*Ber.*, 1909, 42, 2295—2296).—Crystallographic measurements have been made of the series of salts $\text{M}_3\text{X}(\text{SCN})_6 \cdot 4\text{H}_2\text{O}$, in which $\text{M} = \text{K}, \text{NH}_4$, or Na , and $\text{X} = \text{Mo}$ or Cr . It is found that the molybdenum or chromium salts are not isomorphous amongst themselves, but that each molybdenum salt is isomorphous with the corresponding chromium salt, the potassium salts being pseudo-hexagonal, the ammonium salts rhombic, and the sodium salts asymmetric.

The results support the view that the potassium molybdenum salt is $\text{K}_3[\text{Mo}(\text{SCN})_6] \cdot 4\text{H}_2\text{O}$, and not, as supposed by Maas and Sand (Abstr., 1908, i, 961), $\text{K}_3[\text{Mo}(\text{SCN})_6\text{H}_2\text{O}] \cdot 4\text{H}_2\text{O}$.

C. H. D.

Nitroacetonitrile. V. Nitroacetic Acid. WILHELM STEINKOPF (*Ber.*, 1909, 42, 2026—2031. Compare this vol., i, 216).—Adopting the constitution of fulminic acid as nitrocyanoacetamide, it appeared possible to hydrolyse the amide group to nitrocyanoacetic acid. When concentrated potassium hydroxide is used to effect hydrolysis, the reaction goes further, the cyano-group being also hydrolysed, so that potassium nitromalonate, $\text{OK} \cdot \text{NO} \cdot \text{C}(\text{CO}_2\text{K})_2$, is first formed, and, losing potassium carbonate, is converted into potassium nitroacetate, $\text{OK} \cdot \text{NO} \cdot \text{CH} \cdot \text{CO}_2\text{K}$. This crystallises well, gives an intense red coloration with ferric chloride, and forms a colourless salt with lead acetate, and yellow salts with mercuric chloride or silver nitrate. These all explode in the flame. Potassium nitroacetate was obtained from ammonium fulminate, from nitroacetonitrile, from nitroacetamide, and from methazonic acid—the last substance giving a pure product in good quantity. This behaviour affords proof of the presence of the $-\text{C}-\text{C}-$ group in methazonic acid. E. F. A.

Application of the Theory of Complex Ions to the Reactions of Mercury Cyanide with Silver Salts and Alkali Hydroxides. KARL A. HOFMANN and H. WAGNER (*Zeitsch. Elektrochem.*, 1909, 15, 441—447).—Mercuric cyanide combines with anions to complex anions of the form $\text{Hg}(\text{CN})_2\text{X}'$. By measuring the solubility of mercury cyanide in different salts, the values of $k = [\text{Hg}(\text{CN})_2\text{X}'] / [\text{Hg}(\text{CN})_2][\text{X}']$ are found to be for NO_3' , 0.43; for OH' , 1.68, and for CN' , about 40. It appears that the greater the tendency of a group of atoms to assume an electric charge, the less tendency it has to combine with mercury cyanide. The complex ions split up also, thus: $\text{Hg}(\text{CN})_2\text{X}' \rightleftharpoons \text{Hg}(\text{CN})\text{X} + \text{CN}'$, and this decomposition proceeds much further when X is a weak ion, such as $\text{CH}_3 \cdot \text{COO}'$, than in the case of a strong one, like NO_3' . For this reason, a precipitate of silver cyanide is formed when mercuric cyanide is treated with silver acetate or nitrite, but not when silver nitrate is used. T. E.

Results of Cooling certain Hydrated Platinocyanides in Liquid Air. J. EMERSON REYNOLDS (*Proc. Roy. Soc.*, 1909, 82, A, 380—383).—It was observed that when a specimen labelled lithium platinocyanide was cooled in liquid air, the original white compound became red and regained its original colour on warming, but after repeated cooling and warming, it assumed a yellow colour in liquid air, which was retained at the ordinary temperature. It was found that the salt was a very impure lithium platinicyanide, $\text{Li}_2\text{Pt}(\text{CN})_5$, and the explanation of this behaviour has been found in the properties of this salt, which is white when anhydrous, whilst the monohydrate is yellow, the dihydrate orange-red, and the trihydrate colourless.

The trihydrate is obtained in needles by evaporating the aqueous solution at 40—50° and suddenly cooling to 15°; on heating cautiously, or on cooling in liquid air, it gives the red dihydrate. The monohydrate is best obtained by evaporating a solution of the trihydrate to which a hydrated salt, for example, sodium sulphate, has been added, and then cautiously heating the residue, or by repeated cooling in liquid air of the trihydrate, mixed with a salt having affinity for water.

Lithium platincyanide, $\text{Li}_2\text{Pt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$, grass-green crystals, is scarcely affected by cooling in liquid air. G. S.

Hydrazo- and Azo-methane. JOHANNES THIELE (*Ber.*, 1909, 42, 2575—2580).—*s*-Diformyldimethylhydrazine, $\text{CHO} \cdot \text{NMe} \cdot \text{NMe} \cdot \text{CHO}$, prepared from diformylhydrazine and methyl sulphate in alkaline solution, extraction with ether, and crystallisation of the oil by addition of a little ethyl acetate, forms glistening crystals, m. p. 52° .

By acidifying the alkaline solution without isolating the dimethyl derivative, evaporating, distilling with sodium hydroxide, and absorbing the distillate in hydrochloric acid, *s*-dimethylhydrazine dihydrochloride is obtained. It does not yield yellow products with aldehydes. When a concentrated solution of the hydrochloride is dropped into potassium chromate, azomethane is formed, and is pumped off and condensed by means of carbon dioxide and ether.

Azomethane, $\text{CH}_3 \cdot \text{N} : \text{N} \cdot \text{CH}_3$, is a colourless gas, b. p. $1.8^\circ/756$ mm. (corr.), D_4^{25} 0.744, vapour density 32. For analysis, it is largely diluted with carbon dioxide or nitrogen, and passed into the combustion tube. It is very soluble in water to a neutral solution. The liquefied compound is faintly yellow; it solidifies not far below -78° to colourless leaflets. It explodes on heating or sparking, forming nitrogen, methane, ethylene, hydrogen, and a little ethane. If diluted with inert gas and heated, it forms ethane and nitrogen.

Acids decompose its solution into formaldehyde and methylhydrazine. Zinc dust and sodium hydroxide reduce it to *s*-dimethylhydrazine.

C. H. D.

Action of Cacodylic and Methylarsinic Acids on Antimony Trichloride. LÉONCE BARTHE and ADOLPHE MINET (*Compt. rend.*, 1909, 148, 1609—1611).—A syrupy solution of cacodylic acid reacts with deliquesced antimony trichloride, forming *dichloroantimony cacodylate*, $\text{O} : \text{AsMe}_2(\text{OSbCl}_2)$. This is a stable compound, crystallising in long, lustrous, acicular prisms, sparingly soluble in hot water and alcohol.

When a solution of methylarsinic acid is saturated with sodium hydrogen carbonate, heated to boiling, and treated with antimony trichloride, a precipitate appears which becomes crystalline on digestion. This consists of *antimonyl methylarsinate*, $\text{MeAsO}(\text{OSbO})_2$.

Details are given of a method for the analysis of compounds of this type. W. O. W.

Molecular Rearrangements in the Camphor Series. II. Laurolene. WILLIAM A. NOYES and C. G. DERICK (*J. Amer. Chem. Soc.*, 1909, 31, 669—673. Compare this vol., i, 133).—Laurolene, obtained from aminolauronic acid hydrochloride and sodium nitrite (Tiemann, *Abstr.*, 1901, i, 5), and having $[\alpha]_D^{25}$ 22.8° and D_4^{15} 0.8030, yields by oxidation with cold dilute alkaline potassium permanganate a product which appears to be a diketone that has partly condensed to an unsaturated cyclic monoketone. Since the pure ketone could not be obtained, the experiment has been repeated on laurolene obtained

by boiling the nitroso-compound of aminolauroic anhydride with 10% sodium hydroxide, and having $[\alpha]_D^{20} - 14.5^\circ$ and $D_4^{15} 0.8043$. The hydrocarbon is oxidised at 0° by 2% potassium permanganate. The oxidation product and unchanged lauroleone are extracted by ether and separated by distillation under diminished pressure. The oxidation product distils as an oil, but the last portions solidify to a substance, m. p. 68° (corr.), of the same composition, $C_8H_{14}O_2$, as the oil. The substance has $D_{15}^{15} 0.9888$ and $[\alpha]_D^{25} - 8.5^\circ$ in 32.5% ethereal solution, and forms an oily oxime and hydrazone and an impure semicarbazone. Its constitution is briefly discussed, and the deduction drawn that Eykmann's formula (Abstr., 1907, i, 378) most probably represents correctly the constitution of lauroleone. C. S.

A Peculiar Method of Formation of Nitrobenzene from *m*-Dinitrobenzene. MORITZ KOHN (*Monatsh.*, 1909, 30, 397—399. Compare Schultze, Abstr., 1897, i, 40; Meisenheimer and Patzig, Abstr., 1906, i, 642, 652).—Nitrobenzene is formed by boiling *m*-dinitrobenzene with an aqueous alkaline solution of hydroxylamine for about thirty minutes. W. H. G.

The Preparation of Benzenesulphonyl Chloride. RUDOLF PUMMERER (*Ber.*, 1909, 42, 2274—2275. Compare this vol., i, 465; Ullmann and Korselt, Abstr., 1907, i, 306).—In the action of chlorosulphonic acid on benzene, a temperature of 25° gives a better yield of benzenesulphonyl chloride than one of 5° . C. H. D.

Action of Nitric Acid on Triphenylmethane. ROBERT SCHWARZ (*J. Amer. Chem. Soc.*, 1909, 31, 848—850).—It has been shown by E. and O. Fischer (Abstr., 1879, 384) that trinitrotriphenylmethane can be prepared readily by the action of nitric acid ($D 1.5$) on triphenylmethane. Smith (Abstr., 1897, i, 573), in attempting to prepare this nitro-compound, obtained triphenylcarbinol, but on repeating the experiment was unable to get the same result.

Experiments have now been carried out in order to ascertain the conditions under which the carbinol and trinitro-compound respectively are produced. It has been found that, under varying conditions, the action of nitric acid on triphenylmethane results in the formation of trinitrotriphenylmethane, triphenylcarbinol, and a red oil of unknown composition. When the hydrocarbon is added to strong fuming nitric acid at 0° , trinitrotriphenylmethane is produced. If small quantities of red, fuming acid of about $D 1.48$ are added to triphenylmethane and the reaction takes place at a moderate temperature, triphenylcarbinol is obtained, but trinitrotriphenylmethane is not produced. If, however, stronger acid is used under the latter conditions and the temperature is allowed to rise to the boiling point, the red oil is formed. The best yield of triphenylcarbinol obtained amounted to about 45% of the theoretical. E. G.

The Dinaphthylmethane Series. JULIUS SCHMIDLIN and PAUL MASSINI (*Ber.*, 1909, 42, 2377—2392).—The paper describes deriv-

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atives of *aa*-dinaphthylmethane; attempts to prepare from them the parent hydrocarbon have been unsuccessful.

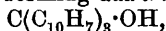
aa-*Dinaphthylcarbinol*, $\text{CH}(\text{C}_{10}\text{H}_7)_2\cdot\text{OH}$, m. p. 146—147° (corr.), obtained from magnesium *a*-naphthyl bromide and ethyl formate in ethereal solution, forms colourless needles, develops a greenish-blue coloration with sulphuric acid, and is readily converted by alcohol and hydrochloric acid into the *ethyl ether*, $\text{CH}(\text{C}_{10}\text{H}_7)_2\cdot\text{OEt}$, m. p. 136° (corr.). *aa*-*Dinaphthylmethyl chloride*, $\text{CH}(\text{C}_{10}\text{H}_7)_2\text{Cl}$, m. p. 188—189° (corr.), obtained from hydrogen chloride and the carbinol in benzene solution, forms colourless needles, develops a faint green coloration with sulphuric acid, and is reconverted into the carbinol by boiling water. By shaking its benzene solution with dry "molecular" silver, *tetranaphthylethane*, $\text{CH}(\text{C}_{10}\text{H}_7)_2\cdot\text{CH}(\text{C}_{10}\text{H}_7)_2$, m. p. 285—286° (corr.), is obtained, which is also produced by the action of magnesium phenyl iodide or magnesium naphthyl bromide on dinaphthylmethyl chloride. The reaction between carbon dioxide and ethereal magnesium *aa*-dinaphthylmethyl chloride leads to the formation of *aa*-*dinaphthyl acetic acid*, $\text{CH}(\text{C}_{10}\text{H}_7)_2\cdot\text{CO}_2\text{H}$, m. p. 228·5° (corr.), which forms a *silver salt*, m. p. 205° (decomp.), *copper salt*, m. p. 205° (decomp.), and, by heating with phosphoric chloride and acetyl chloride, a *chloride*, $\text{CH}(\text{C}_{10}\text{H}_7)_2\cdot\text{COCl}$, which loses carbon monoxide at its m. p., 167—169° (corr.), and does not readily lose its halogen by treatment with water, alkalis, or silver.

aa-*Dinaphthylfluorene*, $\text{CH}_2<\begin{matrix} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{matrix}$, m. p. 242·5° (corr.), is obtained when *aa*-dinaphthylcarbinol is heated with zinc, glacial acetic acid, and a little concentrated hydrochloric acid; it forms a strongly violet-red fluorescent solution in benzene. Cold fuming nitric acid converts *aa*-dinaphthylcarbinol into a *tetranitro*-derivative, m. p. 190—193° (decomp., corr.). *aa*-*Dinaphthyl ketone*, $\text{CO}(\text{C}_{10}\text{H}_7)_2$, m. p. 104° (corr.), is the final product of the reaction between magnesium *a*-naphthyl bromide and naphthoyl chloride in ethereal solution. *a*-*Naphthylmethyl bromide*, $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{Br}$, b. p. 183°/18 mm., obtained from *a*-methylnaphthalene and bromine at 200°, does not react with ethereal magnesium *a*-naphthyl bromide, but by distillation the mixture yields *aa*-dinaphthyl.

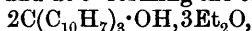
In boiling glacial acetic acid *aa*-dinaphthylcarbinol condenses with phenol to form the *ether*, $\text{CH}(\text{C}_{10}\text{H}_7)_2\cdot\text{OPh}$, m. p. 217—219° (corr.); with *a*-naphthol, with aniline hydrochloride, and with *a*-naphthylamine to form *substances* of undetermined constitution, m. p. 278·5—279·5°, 233—238°, and 215° (all corr.) respectively. C. S.

a-*Dinaphthyl Ketone*. HUGO BAUER (*Ber.*, 1909, 42, 2588—2589). —By oxidising *a*-dinaphthylcarbinol with chromic acid, the author in conjunction with Reichardt some years ago prepared the *a*-dinaphthyl ketone recently described by Schmidlin and Massini (preceding abstract); at the same time phenyl- β -methoxynaphthylcarbinol, colourless needles, m. p. 237°, was prepared by the interaction of benzaldehyde and the magnesium compound of *a*-iodo- β -methoxynaphthalene; *phenylbenzyl-a-naphthylcarbinol*, colourless crystals, m. p. 149—150°, was similarly obtained by acting on benzyl magnesium chloride with phenyl *a*-naphthyl ketone. P. H.

The Trinaphthylmethane Series. JULIUS SCHMIDLIN and PAUL MASSINI (*Ber.*, 1909, 42, 2392—2404).—The interaction of α -naphthoyl chloride and an excess of magnesium α -naphthyl bromide in ether yields a compound, $2C(C_{10}H_7)_3 \cdot OMgBr \cdot 3Et_2O$, which is decomposed by water, at the b. p. of ether forming *aaa-trinaphthylcarbinol*,



m. p. 168—169° (corr.), and at 0° forming the compound,



m. p. 103—104° (decomp., corr.). The latter loses its ether exceedingly slowly even in a vacuum, and by crystallisation from cold benzene is changed into the compound, $3C(C_{10}H_7)_3 \cdot OH, C_6H_6$, m. p. 123° (decomp., corr.). At 160° both substances lose ether or benzene, and are changed into a substance which in its properties is identical with *aaa-trinaphthylcarbinol*, although its m. p. cannot be raised above 131° by repeated crystallisation. Tri- α -naphthylcarbinol does not retain, when once formed, the property of uniting with ether or benzene, develops an orange-red colour with sulphuric acid, forms a yellow *hexanitro*-compound, $C[C_{10}H_5(NO_2)_2]_3 \cdot OH$, m. p. 236—241° (decomp., corr.), by nitration with fuming nitric acid, and contains a very immobile hydroxyl group. Mild reducing agents, thionyl chloride, or a molecular quantity of phosphorus pentachloride have no action. Hydriodic acid and amorphous phosphorus at 95° convert the carbinol into a *dihydro-aaa-trinaphthylcarbinol*, $C_{31}H_{23} \cdot OH$, m. p. 160—161° (corr.), whilst an excess of phosphorus pentachloride in acetyl chloride produces a *dichloro*-additive compound, $C_{31}H_{21}Cl_2 \cdot OH$, m. p. 238—239° (decomp., corr.). The carbinol, however, when heated in acetyl chloride with moist phosphoryl chloride, yields

naphthylidinaphthylmethane, $C_{10}H_7 \cdot CCl \begin{matrix} \nearrow C_{10}H_6 \\ \searrow C_{10}H_6 \end{matrix}$, m. p. 233—234°

(decomp., corr.), which crystallises in citron-yellow leaflets, develops an intense blue coloration with sulphuric acid, and is converted by "molecular" silver into *dinaphthylididnapthylene-ethane* (annexed formula), m. p. 180° (decomp.), a dark green, crystalline powder, which is stable in the air and gives a carmine-red colour with sulphuric acid.

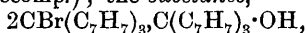
aa β -Trinaphthylcarbinol, $C(C_{10}H_7)_3 \cdot OH$, m. p. 263—264° (corr.), obtained from β -naphthoyl chloride, forms colourless needles, and gives an orange-yellow colour with sulphuric acid. C. S.

2-Methylantracene from Ditolylmethane or Ditolylethane. OTTO FISCHER (*J. pr. Chem.*, 1909, ii, 79, 555—562).—Pure 2-methylantracene is obtained from ditolylethane, that from ditolylmethane being mixed with anthracene (*Abstr.*, 1875, 151). Bromine in carbon disulphide forms 9:10-*dibromo-2-methylantracene*, m. p. 142—143°, the positions of the halogen atoms being determined by the oxidation of the substance to 2-methylanthraquinone. The latter and bromine at 130—140° yield a colourless *dibromomethylantracene*, m. p. 219—220°. C. S.

Hexabenzylethane and Its Derivatives. FRITZ SCHMERDA (*Monatsh.*, 1909, 30, 387—395).—The object of this investigation was to prepare tribenzylmethane from tribenzylcarbinol, and to pass from

this to the homologue of rosaniline, $\text{CH}(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2)_3$, but the only substance obtained by the reduction of the carbinol was hexabenzylethane.

Tribenzylmethyl bromide, $\text{CBr}(\text{C}_7\text{H}_7)_3$, prepared by the action of phosphorus pentabromide on tribenzylcarbinol, is a white, crystalline powder, m. p. 157° (decomp.); the substance,



has m. p. 145° . The *chloride*, $\text{CCl}(\text{C}_7\text{H}_7)_3$, formed by the action of an alcoholic solution of hydrogen chloride on the carbinol, crystallises in needles, m. p. 145° (decomp.).

Hexabenzylethane, $\text{C}_2(\text{C}_7\text{H}_7)_6$, is formed together with dibenzyl by heating tribenzylcarbinol with hydriodic acid under pressure at 200° ; it crystallises in large, transparent prisms, m. p. 81° , b. p. $353\text{--}358^\circ/746\text{ mm.}$; the *hexanitro-derivative*, $\text{C}_{44}\text{H}_{36}\text{O}_{12}\text{N}_6$, is a yellow substance, which softens at 75° and decomposes at about 115° ; the *hexa-amino-derivative*, $\text{C}_{44}\text{H}_{48}\text{N}_6$, is a pale, yellowish-red powder, which sinters at 61° and decomposes at 105° ; the *platinichloride*,



is a somewhat unstable, yellow, crystalline substance. W. H. G.

Electrochemical Reduction of *p*-Nitroacetanilide. KURT BRAND and EDUARD STOHR (*Ber.*, 1909, 42, 2478—2482. Compare Abstr., 1907, i, 100, 206).—When *p*-nitroacetanilide is subjected to electrolytic reduction, using a solution of the anilide and sodium acetate in a mixture of alcohol, glacial acetic acid, and ethyl acetate as the cathode liquid, the chief product is *p*-hydroxylaminoacetanilide. This could not be isolated as such, but was oxidised to *p*-nitrosoacetanilide (Cain, *Trans.*, 1908, 93, 681), and was also obtained as

benzylidene-p-hydroxylaminoacetanilide, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{CHPh} \end{smallmatrix}$, which

crystallises from alcohol in pale yellow plates, m. p. 215° . When hydrolysed with alcoholic potassium hydroxide or hydrogen chloride, the benzylidene derivative yields azoaniline and *p*-phenylenediamine.

When further reduced in acetic acid solution, the chief product is *p*-aminoacetanilide, the *benzylidene* derivative of which, $\text{C}_{15}\text{H}_{14}\text{ON}_2$, has m. p. $165\text{--}166^\circ$. When the nitro-compound is reduced in acid solution, the chief product is *p*-phenylenediamine. J. J. S.

Coloured Isomeric Picrylamines. MAX BUSCH and ERNST PUNGS (*J. pr. Chem.*, 1909, ii, 79, 546—554).—When alcoholic solutions of picryl chloride and the following amines are mixed, the picrylamine, $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{NHR}$, is deposited frequently in two differently coloured forms. *p*-Toluidine gives a mixture of labile, yellow prisms, m. p. 163° , and stable, blood-red needles, m. p. 165° ; the former alone are obtained by treating the alkaline alcoholic solution of the mixture with hydrochloric acid, whilst the red form separates when the mixture is crystallised from alcohol and benzene. *m*-Toluidine gives a mixture of yellow prisms, m. p. 130° , and orange-red needles, m. p. $129\cdot5^\circ$. *p*-Xylidine gives only blood-red needles, m. p. 163° , but the labile, yellow form is obtained by acidifying the cold alkaline alcoholic solution. 1 : 3 : 4-Xylidine gives orange-red, monoclinic needles, m. p.

158°, which change at 190° to the orange-brown, triclinic needles, m. p. 159°. 1:3:2-Xylidine yields only citron-yellow leaflets, m. p. 212°. ψ -Cumidine gives a product which separates from acetone in blood-red, dichroic needles, m. p. 160°, and from alcohol containing hydrochloric acid in dichroic needles, m. p. 160°, of a lighter colour. *o*- and *p*-Anisidines form only orange-red, rhombic needles, m. p. 142° and 138° respectively, whilst *o*- and *p*-phenetidines give scarlet needles, m. p. 136—137°, and red needles, m. p. 123—124°, respectively. Methylaniline gives Turpin's reddish-brown leaflets, m. p. 108°, which, by slow heating, change to Sudborough and Picton's garnet-red prisms, m. p. 128—129°. C. S.

Fission of Quaternary Ammonium Salts by Nascent Hydrogen. HERMANN EMDE (*Ber.*, 1909, 42, 2590—2594).—The observation recorded previously (*Abstr.*, 1906, i, 945) that cinnamyltrimethylammonium chloride is resolved by sodium amalgam into phenylpropylene and trimethylamine, whereas the corresponding chlorohydrin is not affected by this reagent, has led the author to study the action of nascent hydrogen on a number of quaternary ammonium salts with the object of determining what influence the olefinic grouping has on the stability of the carbon nitrogen linking in such compounds, but the investigation is not as yet sufficiently advanced to admit of any generalisations. The decomposition of dibenzyl dimethylammonium chloride and of phenylcinnamyl dimethylammonium chloride can be employed for the preparation of benzyl dimethylamine and of phenylpropylene.

Benzyl dimethylamine is obtained in 80% yield by heating together benzyl chloride and dimethylamine and treating the resulting product with water and an excess of 5% sodium amalgam; after the reaction, the oily layer, consisting of toluene and benzyl dimethylamine, is separated, washed, dried, and distilled.

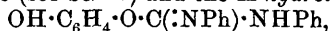
Phenylpropylene is obtained in almost theoretical yield by the action of sodium amalgam on phenylcinnamyl dimethylammonium chloride prepared by condensing cinnamyl chloride with dimethylaniline; the *platinichloride* of this quaternary salt, $C_{34}H_{40}N_2Cl_6Pt$, melts at 177°; a double salt with *cadmium chloride*, $C_{34}H_{40}N_2Cl_4Cd$, melts at 141°.

P. H.

Carbodi-imides. MAX BUSCH, GUSTAV BLUME, and ERNST PUNGS [and, in part, MARTIN FLEISCHMANN] (*J. pr. Chem.*, 1909, ii, 79, 513—546).—The paper deals with the additive compounds obtained from carbodiphenylimide and aromatic phenols or aminocarboxylic acids.

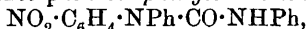
When carbodiphenylimide is heated at 150—160° with an equal molecular quantity of phenol, *p*-cresol, or α - or β -naphthol, an *O*-ether of diphenyl- ψ -carbamide, $NPh:C(OR) \cdot NHPh$, is obtained. The *phenyl ether*, $NPh:C(OPh) \cdot NHPh$, m. p. 104°, possesses basic properties [*oxalate*, m. p. 149° (decomp.); *picrate*, m. p. 204°], and is decomposed by warm dilute acids or alkalis, yielding phenol and diphenylcarbamide. The *p*-tolyl ether, $NPh:C(O \cdot C_6H_4) \cdot NHPh$, has m. p. 111°, and the α - and β -naphthyl ethers, $NPh:C(O \cdot C_{10}H_7) \cdot NHPh$, have m. p. 205° and

201° respectively. Resorcinol and carbodiphenylimide at 120° form γ -carbodiphenylimide (see below) and the *m*-hydroxyphenyl ether,

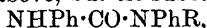


m. p. 147°. Phenyl mercaptan and carbodiphenylimide form in boiling benzene the *thiophenyl ether*, $\text{NPh}\cdot\text{C}(\text{SPh})\cdot\text{NHPh}$, m. p. 82°, which is decomposed by acids into carbanilide and phenyl mercaptan.

The mononitrophenols react with carbodiphenylimide only with difficulty. *p*-Nitrophenol in boiling benzene forms a substance, m. p. 100°, which is probably the *O*-ether, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}(\text{NPh})\cdot\text{NHPh}$, and changes at 160° into *p*-nitrotriphenylcarbamide,



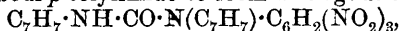
m. p. 152°, which is obtained directly when carbodiphenylimide and *p*-nitrophenol are heated at 140°, and also from *p*-nitrodiphenylamine and phenylcarbimide on the water-bath. 2:4-Dinitrophenol and picric acid react easily with carbodiphenylimide in boiling benzene, yielding, not *O*-ethers as above, but tri-substituted carbamides,



the evidence for this constitution being the lack of basic properties and the ready decomposition into phenylcarbimide and diarylamine,



2:4-Dinitrotriphenylcarbamide, $\text{NHPh}\cdot\text{CO}\cdot\text{NPh}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, forms yellow needles, and decomposes into phenylcarbimide and 2:4-dinitrodiphenylamine at its m. p., 134—135°, whilst 2:4:6-trinitrotriphenylcarbamide, $\text{NHPh}\cdot\text{CO}\cdot\text{NPh}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, m. p. 213—214°, decomposes in a similar manner. Picric acid unites with carbodi-*o*-tolylimide or carbodi-*p*-tolylimide to form analogous compounds,



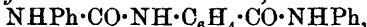
m. p. 210° and 210—211° respectively, which decompose in a similar manner.

The action of di- and tri-nitrophenols on carbodiphenylimide serves to explain the behaviour of the latter with carboxylic acids. Dains claims (Abstr., 1899, i, 592) that acetic acid and carbodiphenylimide yield acetic anhydride and carbanilide. Acetanilide and carbon dioxide are also produced, however, and the formation of the four substances is indicated in the reactions: (I) $\text{C}(\text{NPh})_2 + \text{Ac}\cdot\text{OH} = \text{NHPh}\cdot\text{CO}\cdot\text{NPhAc} \rightarrow \text{NPhCO} + \text{PhNHAc}$; (II) $2\text{NPhCO} + 2\text{Ac}\cdot\text{OH} = \text{CO}(\text{NHPh})_2 + \text{Ac}_2\text{O} + \text{CO}_2$. These reactions have been verified experimentally, and the acetyldiphenylcarbamide has been isolated by the interaction of acetic acid and carbodiphenylimide in petroleum ether. Since it readily decomposes into phenylcarbimide and acetanilide, its formation at 150° by Creath (Abstr., 1875, 885) and Kühn (Abstr., 1885, 260) is doubtful, but it can be obtained in 15% yield from phenylcarbimide and acetanilide on the water-bath.

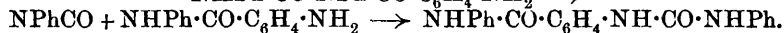
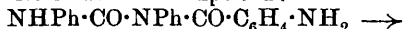
Equal molecular quantities of carbodiphenylimide and *o*-amino-phenol in boiling benzene react to form an additive compound, the point of attack being the nitrogen and not the oxygen atom; in consequence of its amphoteric character and the absence of an amino-group, the compound is regarded as *o*-hydroxytriphenylguanidine, $\text{NHPh}\cdot\text{C}(\text{NPh})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m. p. 132—133°. In a similar way carbodiphenylimide and phenylhydroxylamine yield *triphenylhydroxy-*

guanidine, $\text{NPh}\cdot\text{C}(\text{:NPh})\cdot\text{NPh}\cdot\text{OH}$, m. p. 154° , which forms tri-phenylguanidine by reduction.

Carbodiphenylimide attacks aminocarboxylic acids at the carboxyl group. With *m*- and *p*-aminobenzoic acids in boiling benzene the corresponding *phenylcarbamidobenzanilides*,

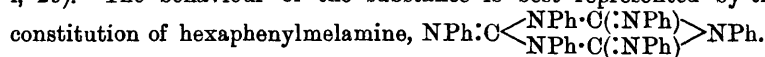


m. p. 250 — 254° and $>300^\circ$ respectively, are formed by the decomposition of the initial additive compound:



In the case of anthranilic acid, the *o*-phenylcarbamidobenzanilide suffers ring closure with loss of aniline, phenyldiketotetrahydroquinazoline being produced.

When carbodiphenylimide is heated with different phenols, a crystalline by-product is obtained in larger or smaller quantity; it is best obtained by saturating a cold benzene solution of phenol and α -carbodiphenylimide with hydrogen chloride. It has m. p. 196° , and its molecular weight in acetone corresponds to the formula $\{\text{C}(\text{NPh})_2\}_3$. The substance, which is called *γ -carbodiphenylimide*, does not revert to the unimolecular α -carbodiphenylimide by heating, forms a *hydrochloride*, $\text{C}_{39}\text{H}_{30}\text{N}_6\cdot\text{HCl}$, m. p. 207° , *picrate*, m. p. 157° , and *aurichloride*, $\text{C}_{39}\text{H}_{30}\text{N}_6\cdot\text{HAuCl}_4$, decomposing at 125° , and by careful heating with alcohol and hydrochloric acid yields carbon dioxide, aniline, and Marckwald's pentaphenyldiguanide (Abstr., 1896, i, 29). The behaviour of the substance is best represented by the



C. S.

Behaviour of Tribromophenol Towards Benzene in the Presence of Aluminium Chloride. MORITZ KOHN and NOE L. MÜLLER (*Monatsh.*, 1909, 30, 407—409).—Bromobenzene and phenol are formed by the action of aluminium chloride on a solution of tribromophenol in benzene. Trichlorophenol under similar conditions remains unattacked.

W. H. G.

Derivatives of 3:5-Dinitrophenol. GUSTAV HELLER [with MAX KAMMANN] (*Ber.*, 1909, 42, 2191—2198).—3:5-Dinitrophenol is prepared by converting *s*-trinitrobenzene into dinitroanisole and hydrolysing this with concentrated sulphuric acid at 140° (Hantzsch, Abstr., 1907, i, 207). 3:5-Dinitrophenyl acetate, $\text{C}_8\text{H}_6\text{O}_6\text{N}_2$, crystallises from a mixture of benzene and light petroleum, and has m. p. 126 — 127° ; the corresponding benzoate, $\text{C}_{13}\text{H}_8\text{O}_6\text{N}_2$, crystallises from alcohol in needles, m. p. 130 — 131° . 3-Nitro-5-acetylaminophenol, $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NHAc}$, obtained by reducing an acetic acid solution of the dinitrophenol with stannous chloride and hydrochloric acid, crystallises from ethyl acetate in yellow, microscopic prisms; it changes colour at 240° , decomposes at 260° , and is completely molten at 270° . When hydrolysed with hydrochloric acid, it yields Blanksma's 5-nitro-3-aminophenol (*Rec. trav. chim.*, 1892, 21, 254). An acetic acid solution of bromine reacts with the acetyl-amino-derivative, yielding

2-bromo-5-nitro-3-acetylaminophenol, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Br}(\text{OH}) \cdot \text{NHAc}$, which crystallises from ethyl acetate in yellow, pointed prisms, m. p. 242—243°. When hydrolysed with hydrochloric acid, *2-bromo-5-nitro-3-aminophenol*, $\text{C}_6\text{H}_5\text{O}_3\text{N}_2\text{Br}$, is obtained, and separates from hot water or glacial acetic acid in reddish-brown crystals, m. p. 205°. The same compound can be obtained somewhat more readily by brominating nitroaminophenol with an acetic acid solution of bromine, but *tribromo-5-nitro-2-aminophenol*, $\text{C}_6\text{H}_3\text{O}_3\text{N}_2\text{Br}_3$, is also formed. The latter crystallises from light petroleum in yellow plates, m. p. 147°. The constitution of the 2-bromo-5-nitro-3-aminophenol follows from the fact that by the elimination of the amino-group a bromonitrophenol is obtained, which is identical with the *2-bromo-5-nitrophenol*, $\text{C}_6\text{H}_4\text{O}_3\text{NBr}$, formed by the replacement of the amino-group in Friedlander and Zeitlin's 5-nitro-2-aminophenol (Abstr., 1894, i, 185). 2-Bromo-5-nitrophenol crystallises from light petroleum in colourless rods, m. p. 118—119°, and yields a *benzoate*, $\text{C}_{13}\text{H}_8\text{O}_4\text{NBr}$, which crystallises from alcohol in colourless needles, m. p. 127—128°.

3-Bromo-5-nitrophenol (Blanksma, *loc. cit.*) can be obtained by replacing the amino-group in 5-nitro-3-aminophenol by bromine. Its *benzoate*, $\text{C}_{13}\text{H}_8\text{O}_4\text{NBr}$, has m. p. 93—95°. *2-Bromo-5-acetylaminophenol*, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{NHAc}$, obtained by reducing the 2-bromo-5-nitrophenol with stannous chloride and then treating with acetic anhydride, crystallises from aqueous acetic acid in colourless needles, m. p. 209—211°. When hydrolysed, it yields *2-bromo-5-aminophenol*, $\text{C}_6\text{H}_6\text{ONBr}$, in the form of plates, m. p. 150° (decomp.). It has not been found possible to eliminate the amino-group from this compound.

4-Bromo-3-nitrophenol can be obtained by replacing the amino-group in Friedlander and Zeitlin's 3-nitro-4-aminophenol (Abstr., 1894, i, 185) by bromine (compare Lindner, Abstr., 1885, 774).

J. J. S.

A New Method for the Alkylation of Phenols. ALFRED EINHORN (*Ber.*, 1909, 42, 2237—2238).—The mixed carbonic esters of phenols lose carbon dioxide on heating, and pass into alkyl ethers of phenols: $\text{Ar} \cdot \text{O} \cdot \text{CO} \cdot \text{OR} = \text{CO}_2 + \text{Ar} \cdot \text{O} \cdot \text{R}$. The reaction is a general one, but does not proceed with equal readiness in all cases. The esters containing basic alkyl groups, such as guaiacol diethylaminoethyl carbonate, are completely converted after distilling once, or at most twice, in a vacuum, whilst β -naphthyl methyl carbonate requires thirty-six hours' boiling under atmospheric pressure. Secondary products are sometimes formed at the same time.

Guaiacol ethyl carbonate, when heated for seven days under atmospheric pressure, yields both guaiacol carbonate and guaiacol ethyl ether. The latter has b. p. 207—209° (Tiemann and Hoppe, Abstr., 1882, 54, give 213°).

C. H. D.

A New Formation of Esters by the Action of Chloro-carbonates on Acids. JOHANNES HERZOG (*Ber.*, 1909, 42, 2557—2559. Compare Einhorn, preceding abstract).—Chloro-carbonic esters react with acids, eliminating carbon dioxide:

$R \cdot CO \cdot OH + Cl \cdot CO \cdot OR' = R \cdot CO \cdot OR' + HCl + CO_2$, although the yield is only small. Unlike the chlorocarbonates of phenols obtained by Einhorn, the intermediate products in this case, the anhydrides, $R \cdot CO \cdot O \cdot CO \cdot OR'$, decompose at once.

The preparation of methyl benzoate and methyl cinnamate is described. C. H. D.

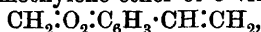
Preparation of the Salts of *p*-Ethoxyphenylaminomethyl Sulphurous Acid. ROBERTO LEPETIT (D.R.-P. 209695. Compare Knoevenagel, Abstr., 1904, i, 981; Bucherer and Schwalbe, Abstr., 1906, i, 828).—*p*-Ethoxyphenylaminomethyl sodium sulphite, $OEt \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot SO_3Na, H_2O$,

lustrous, white leaflets, is obtained by adding successively solutions of formaldehyde and sodium hydrogen sulphite to an alcoholic solution of *p*-phenetidine.

p-Ethoxyphenylaminomethyl hydrogen sulphite separates in white needles on acidifying the solution of the sodium salt. Its barium salt is sparingly soluble; its potassium and ammonium salts closely resemble the sodium derivative. The acid has interesting physiological properties, comparing favourably in this respect with phenacetin and lactophenin. F. M. G. M.

Preparation of α -3:4-Trihydroxyphenylethylamines. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 209609 and 209610).—Bases having the physiological properties of adrenaline may be produced by the following series of reactions.

β -Chloro- α -hydroxy- α -3:4-methylenedioxyphenylethane, m. p. 95—96° (Barger, Trans., 1908, 93, 2083, gives 95°), is produced by adding chlorine to the methylene ether of 3-vinylcatechol,



and removing the α -chlorine atom from the resulting dichloride with moist acetone. The chlorohydrin is then treated with phosphorus pentachloride; this replaces the methylene hydrogen by chlorine, yielding an unstable product, which when boiled with moist acetone gives rise to β -chloro- α -3:4-trihydroxy- α -phenylethane. This rather

unstable substance when treated with ammonia or primary amines yields the required bases, which have the annexed general formula, where R is hydrogen or an alkyl group. The conversion of methylenedioxyphenylethylene dichloride, $CH_2 : O_2 : C_6H_3 \cdot CHCl \cdot CH_2Cl$, into (1)- β -chloro- α -3:4-trihydroxyphenylethane can be effected in one operation by treating the former successively with phosphorus pentachloride and then with water. F. M. G. M.

Naphthan- β -diols. HENRI LEROUX (Compt. rend., 1909, 148, 1614—1616. Compare Abstr., 1904, i, 986; 1905, i, 278; this vol., i, 299).—The naphthan- β -diols (decahydronaphthyl β -glycols) are obtained from dibromo-octahydronaphthalene under the same conditions as are required for the preparation of the tetrahydronaphthyl glycols (*cis*- and *trans*-). *cis*-Naphthan- β -diol, $C_{10}H_{18}O_2$, crystallises in

slender needles or polygonal tablets, m. p. 160° ; the *diacetate* forms large prisms, m. p. 85° ; the *diphenylurethane* occurs in needles, m. p. 195° . *trans-Naphthan- β -diol* forms needles or prisms, m. p. 140° ; its *diacetate* has not been obtained crystalline; its *diphenylurethane* forms fine needles, m. p. 121° . As in the case of the tetrahydronaphthyl glycols, a third isomeride exists, consisting of a *compound* of the *cis*- and *trans*-modifications; this is much more soluble than either of its generators, and has m. p. 125° . A similar *cis* + *trans*-*compound*, m. p. about 145° , exists in the case of the terpane diols. Bredt's compound, m. p. 96° , isomeric with *cis*- and *trans*-camphyl glycol, is probably of the same type (this vol., i, 498).
W. O. W.

Phenyl Sulphide. ALFRED HIMMELBAUER (*Centr. Min.*, 1909, 396).—The refractive index of phenyl sulphide was found to be 1.635 for sodium light; by dissolving sulphur in the liquid the refractive index may be increased to 1.641. These values are considerably lower than that given in some text-books for this substance.
L. J. S.

Aromatic Homologues of *s*-Dichlorodimethyl Ether. ALFRED KIEGL and KARL HAAS (*Ber.*, 1909, 42, 2581—2588).—The first aromatic homologue of *s*-dichlorodimethyl ether was obtained from *o*-nitrobenzaldehyde (Kiegl, *Abstr.*, 1908, i, 82). Similar compounds are obtained by the action of phosphorus pentachloride on nitrobenzaldehydes without the presence of a solvent. Their reactions resemble those of the aliphatic homologues. When heated above the melting point they decompose into the nitrobenzaldehyde and nitrobenzylidene chloride.

aa-Dichloro-2 : 2'-dinitrobenzyl ether (*loc. cit.*) crystallises from xylene in colourless needles. Acetic anhydride and sodium acetate convert it into the *diacetoxy*-compound, $[\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OAc})]_2\text{O}$, leaflets, m. p. 171° .

aa-Dibromo-2 : 2'-dinitrobenzyl ether forms colourless, prismatic needles, decomp. 137 — 147° .

aa-Dichloro-3 : 3'-dinitrobenzyl ether, from *m*-nitrobenzaldehyde, crystallises from benzene in radiating bundles of prisms, m. p. 144° .

aa-Dichloro-4 : 4'-dinitrobenzyl ether, from *p*-nitrobenzaldehyde, separates from acetone in colourless rhombohedra, and from toluene in aggregates, m. p. about 170° .

aa-Dibromo-4 : 4'-dinitrobenzyl ether has m. p. about 175° .

Hydrogen chloride in presence of phosphoryl chloride containing phosphoric acid converts *m*-nitrobenzaldehyde into *m*-nitrobenzylidene chloride.
C. H. D.

A Method of Applying the Grignard Reaction to Hydroxyaldehydes and Alkyl Hydroxycarboxylates. PAUL HOERING and FRITZ BAUM (D.R.-P. 208886).—Hydroxyaldehydes and alkyl hydroxycarboxylates cannot be treated with the Grignard reagent, because the latter is decomposed by the free hydroxyl group. This result may be avoided by alkylating or acylating the hydroxyl group, but the former process has the disadvantage of yielding

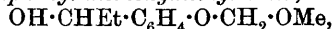
products which are only hydrolysed with difficulty, and the latter is rendered ineffectual because certain acyl residues, such as carbonyl or sulphonyl groups, inhibit the condensation. These difficulties have been overcome by employing the alkyl oxyalkyl ethers of the hydroxy-compounds. These groups are inert towards the Grignard reagent and are easily hydrolysed away from the product of the condensation, and in this way a series of secondary and tertiary aromatic alcohols has been obtained, which on account of their relatively slight toxicity and remarkably antiseptic properties have a distinct therapeutic value.

o-*Hydroxyethylphenyl methoxymethyl ether*,

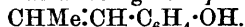


colourless, odourless liquid, b. p. $141\text{--}143^\circ/12\text{ mm.}$, $D^{19}_D 1\cdot065$, is produced by adding an ethereal solution of *o*-methoxymethoxybenzaldehyde to a solution of methyl iodide and magnesium in dry ether. This compound, which is stable to alkali, is hydrolysed by alcoholic H_2SO_4 with the formation of *o*-vinylphenol, $\text{CH}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$.

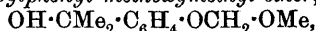
p-*Hydroxypropylphenyl methoxymethyl ether*,



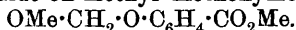
b. p. $133\text{--}142^\circ/16\text{ mm.}$, is similarly prepared from *p*-methoxymethoxybenzaldehyde, $\text{OMe}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{COH}$, and magnesium ethiodide. When hydrolysed with acid it gives *p*-anol,



o-*Hydroxyisopropylphenyl methoxymethyl ether*,

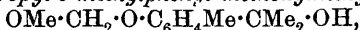


colourless liquid, b. p. $143^\circ/15\text{ mm.}$, $D^{17}_D 1\cdot083$, results from the action of magnesium methiodide on methyl methoxymethoxybenzoate,

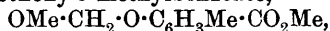


Hydrolysis of this product and distillation under ordinary pressure lead to the formation of *o*-propylenesphenol, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CMe}\cdot\text{CH}_2$, a liquid with the odour of thymol, b. p. $83^\circ/15\text{ mm.}$, $D^{18}_D 1\cdot028$.

2-*Hydroxyisopropyl-5-methylphenyl methoxymethyl ether*,

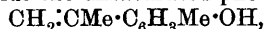


b. p. $153\text{--}154\cdot5^\circ/18\text{ mm.}$, $D^{18}_D 1\cdot053$, is produced by condensing methyl 2-methoxymethoxy-5-methylbenzoate,



with magnesium methiodide.

6-*Hydroxyisopropyl-m-cresol*, $\text{OH}\cdot\text{CMe}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$, odourless, rhombic plates, m. p. $62\text{--}63^\circ$, is also formed in this reaction, and this, when distilled, yields the unsaturated phenol,



colourless liquid with odour of thymol, b. p. $221\text{--}222^\circ/76\text{ mm.}$, $D^{20}_D 1\cdot0065$.

F. M. G. M.

Preparation of Tertiary Aromatic Alcohols. PAUL HOERING and FRITZ BAUM (D.R.-P. 208962).—Tertiary alcohols can be produced from the aromatic alkyl hydroxy-carboxylates or their alkali derivatives by treating these with excess (2—3 mols.) of magnesium alkyl halide.

An ethereal solution of magnesium ethyl bromide when added to the sodium derivative of methyl salicylate suspended in toluene and

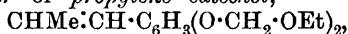
the mixture acidified with dilute acetic acid gives rise to *o*-*α*-hydroxy-isoamylphenol, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CEt}_2\cdot\text{OH}$, colourless needles, m. p. 55.5—56°, b. p. 151—152°/16 mm.

4-α-Hydroxyisopropyl-m-cresol, $\text{OH}\cdot\text{CMe}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$, colourless, odourless, rhombic plates, m. p. 63°, is produced similarly by the interaction of methyl *m*-cresotate and magnesium methyl iodide. When magnesium ethyl iodide is employed in the foregoing condensation, then *4-α-hydroxyisoamyl-m-cresol*, colourless needles, m. p. 74—74.5°, is obtained. F. M. G. M.

Preparation of Alkoxyethyl Ethers of Aromatic Hydroxy-compounds. PAUL HOERING and FRITZ BAUM (D.R.-P. 209608).—The alkoxyethyl ethers of the aromatic hydroxy-compounds can be obtained by condensing the alkali derivatives of these substances with halogenated methyl alkyl ethers having the general formula $\text{X}\cdot\text{CH}_2\cdot\text{O}\cdot\text{Alk}$, where X is a halogen atom.

Phenyl methoxymethyl ether, $\text{OPh}\cdot\text{CH}_2\cdot\text{OMe}$, colourless liquid with fruity odour, b. p. 188—189°/760 mm., and D²² 1.0270, is prepared by adding chloromethyl ether to an alcoholic solution of sodium phenoxide. The alkoxyethyl ethers of the cresols are similarly prepared. *p*-Nitrophenyl methoxymethyl ether, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{OMe}$, crystals with sweet taste and pleasant odour, m. p. 24—25°, is prepared by adding chloromethyl ether to an alcoholic solution of sodium *p*-nitrophenoxide.

*iso*Eugenyl ethoxymethyl ether, $\text{OEt}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}:\text{CHMe}$, when condensed with chloromethylethyl ether gives rise to the bisethoxymethyl ether of propylene catechol,



b. p. 187—191°/760 mm.

o-Methoxymethoxybenzaldehyde, $\text{COH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{OMe}$, b. p. 139—140°/11 mm. and 255—265°/760 mm., D¹⁸ 1.1450, is prepared by adding successively to finely divided sodium in toluene, alcohol and salicylaldehyde; the alcohol is then removed by distillation and chloromethyl ether is introduced.

Methyl o-methoxymethoxybenzoate, b. p. 154—155°/12 mm. and 270—273°/760 mm., is prepared by substituting methyl salicylate for salicylaldehyde in the preceding condensation; *o*-methoxymethoxybenzoic acid, needles, m. p. 64—65°, is obtained by alkaline hydrolysis.

F. M. G. M.

Cotton-seed Oil, Especially the Unsaponifiable Constituents. HERMANN MATTHES and W. HEINTZ (*Arch. Pharm.*, 1909, 247, 161—175).—Previous work on the unsaponifiable matter of cotton-seed oil has been confined to the solid portion, and this has been generally regarded as consisting of a single phytosterol (Bömer, *Abstr.*, 1899, ii, 191, 192, 259; Bömer and Winter, *Abstr.*, 1902, i, 30; ii, 184; and Heiduschka and Gloth, *Abstr.*, 1908, i, 883). In the present paper it is shown that the unsaponifiable matter consists of liquid oxygenated substances and a mixture of three solid phytosterols.

On saponification of the oil and extraction of the aqueous solution

with ether, 0.71% of unsaponifiable matter was obtained, in the form of a yellowish-brown mass, containing some crystals and having a pleasant odour. It was free from chlorine and sulphur (compare Wagner and Clement, *Zeit. Nahr-Genussm.*, 1909, 17, 266). On washing with light petroleum, the liquid portion passes into solution, leaving a residue, which on recrystallisation from alcohol yields first a minute quantity of a slightly yellow, flocculent substance, m. p. 81—82°, which does not absorb iodine, but gives characteristic colorations with the usual phytosterol reagents. The alcoholic mother liquor, on concentration, deposits a phytosterol, $C_{27}H_{46}O, H_2O$, m. p. 139°, $[\alpha]_D - 23.14^\circ$ in alcohol and ether, which is apparently identical with that described by Bömer and others; the acetate has $[\alpha]_D - 21.42^\circ$ in alcohol and ether.

The solution in light petroleum, referred to above, was concentrated and cooled in a freezing mixture. This caused the separation of a colourless substance, $C_{10}H_{16}O$, m. p. 172—180°, $[\alpha]_D + 36.7^\circ$ in alcohol, which crystallises best from acetone. It gives characteristic colorations with the usual phytosterol reagents, and absorbs iodine.

The liquid portion of the unsaponifiable matter remains in the light petroleum mother liquor, and, after removal of the solvent, was separated into five portions by fractional distillation. None of these boiled constantly. All the fractions contained oxygenated substances, but were free from nitrogen. The fractions gave characteristic colorations with the usual phytosterol reagents, and absorbed iodine.

T. A. H.

Reduction of *o*-Nitrobenzoic Acid and its Esters. EUGEN BAMBERGER and FRANK LEE PYMAN (*Ber.*, 1909, 42, 2297—2330).—Pure *o*-hydroxylaminobenzoic acid, $OH \cdot NH \cdot C_6H_4 \cdot CO_2H$, m. p. 142.5° (decomp.) (119°: Kalle & Co., D.R.-P. 89978), is obtained by adding ammonium chloride to an aqueous solution of barium *o*-nitrobenzoate at 10°, and then gradually zinc dust, the temperature being kept below 20° and air excluded; the mixture is filtered, and the filtrate treated with 25% hydrochloric acid at 0°; the precipitate, which is almost white in the absence of light, is dried and purified by precipitating its warm alcoholic solution with warm chloroform in the dark, and finally crystallising from ether to free it from *o*:*o'*-azoxybenzoic acid. *o*-Hydroxylaminobenzoic acid separates from ether in white needles, and has the general properties of the β -aryl-hydroxylamines. It is amphoteric, and is oxidised by alkalis in the air. Nitrous acid at -10° converts it into nitroso-*o*-carboxyphenyl-hydroxylamine, or, in excess, into a diazonium salt. It is oxidised by alcoholic ferric chloride to *o*-nitrosobenzoic acid, and condenses with the latter in alcohol to form *o*:*o'*-azoxybenzoic acid. At the ordinary temperature air-free 10% alcoholic potassium hydroxide converts it into *o*:*o'*-azoxybenzoic acid, *o*-nitrobenzoic acid, and anthranilic acid. Boiling water, free from oxygen, converts it into *o*:*o'*-azoxybenzoic acid and 6-amino-3-hydroxybenzoic acid. Boiling 2*N*-sulphuric acid also forms the aminohydroxybenzoic acid, but acts mainly as a dehydrating agent, giving the anhydride, $C_7H_5O_2N$, which

is also produced by 50% sulphuric acid at the ordinary temperature, and is shown in the sequel to be benzisooxazolone.

Ethyl o-hydroxylaminobenzoate, $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{OH}$, m. p. $78\cdot5^\circ$, softening at $75\cdot5^\circ$, is obtained by shaking ethereal ethyl *o*-nitrobenzoate and aqueous ammonium chloride with zinc dust for two hours at the ordinary temperature; by-products of the reduction are benzisooxazolone, ethyl anthranilate, and ethyl *o*:*o'*-azoxybenzoate. Ethyl *o*-hydroxylaminobenzoate is precipitated from its chloroform solution by light petroleum in long needles, is soluble in mineral acids, reduces copper acetate and silver nitrate, is oxidised to ethyl *o*-nitrosobenzoate by ferric chloride, and to ethyl *o*-nitrobenzoate by potassium dichromate and sulphuric acid, and yields the nitrosoamine and a diazonium salt by treatment with nitrous acid. It differs from other β -arylhydroxylamines in not reducing Fehling's solution and in its behaviour with alkalis. Whilst solutions of β -arylhydroxylamines are rendered turbid by alkalis owing to more rapid atmospheric oxidation, ethyl *o*-hydroxylaminobenzoate forms a clear, orange-yellow solution in dilute sodium hydroxide, which quickly turns yellow, and by acidification yields a white, crystalline precipitate of benzisooxazolone.

Methyl o-hydroxylaminobenzoate has been obtained in a similar manner as a brownish-yellow oil, possessing properties similar to those of the ethyl ester.

Benzisooxazolone, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{NH} \\ \text{CO}\end{smallmatrix}\rangle\text{O}$, m. p. 112° (decomp.), crystallises in colourless needles, forms solutions which quickly turn red, and is not more soluble in acids than in water. It reddens litmus and dissolves in alkalis, ammonium hydroxide, and sodium carbonate. It does not reduce boiling Fehling's solution, can be reduced to anthranilic acid, is oxidised by aqueous alcoholic ferric chloride, giving an indigo-blue solution, becoming green and then turbid, and when heated, alone or in boiling water, is converted into *o*:*o'*-azobenzoic acid. When treated with acetyl chloride, it forms 2-acetylbenzisooxazolone, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{NAc} \\ \text{CO}\end{smallmatrix}\rangle\text{O}$, m. p. $117\cdot5$ — $118\cdot5^\circ$, identical with the by-product obtained by Ciamician and Silber (Abstr., 1901, i, 548; 1902, i, 378) during the interaction of paraldehyde and *o*-nitrobenzaldehyde; the same substance is produced by heating *o*-nitrosobenzoic acid with paraldehyde. The last reaction, in view of the interaction of nitrosobenzene and formaldehyde to yield the compound $\text{OH}\cdot\text{NPh}\cdot\text{CHO}$ (Abstr., 1902, i, 279), leaves little doubt as to the constitution of 2-acetylbenzisooxazolone; the constitution is supported by the reduction of the substance to *N*-acetyl anthranilic acid by aluminium foil and water. 2-Benzoylbenzisooxazolone, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{NBz} \\ \text{CO}\end{smallmatrix}\rangle\text{O}$, m. p. 153 — 154° , is obtained by the Schotten-Baumann method.

2-Ethylbenzisooxazolone, obtained by heating alcoholic benzisooxazolone with ethyl iodide and sodium ethoxide, is an oil, D^{22}_4 1.164, which is volatile with steam, is reduced to *N*-ethylanthranilic acid by zinc and sulphuric acid, and is insoluble in acids. Its solution in sodium hydroxide yields by acidification *N*-ethyl-*o*-hydroxylaminobenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NEt}\cdot\text{OH}$, m. p. $100\cdot5^\circ$, which reduces

Fehling's solution, is oxidised to *o*-nitrosobenzoic acid by alkaline potassium permanganate, and is soluble in acids, the solution, however, depositing shortly the original 2-ethylbenzisooxazolone. 2-Methylbenzisooxazolone, D²⁴ 1.398, behaves like the ethyl ether, and is obtained in a similar manner.

Benzisooxazolone itself may be either $C_6H_4 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} O$ or $C_6H_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \end{smallmatrix} O$. The alkali salts are probably of the latter type; benzisooxazolone has the former constitution, which is supported by the great similarity in the method of formation and the behaviour of the substance to Claisen's monocyclic isooxazolones. C. S.

Acylation of Amines. HARTWIG FRANZEN (*Ber.*, 1909, 42, 2465—2468).—A convenient method of acylating amino-derivatives of benzene consists in suspending the hydrochloride of the base in benzene, adding rather more than the theoretical amount of benzoyl or other acid chloride, and heating on the water-bath in a reflux apparatus until hydrogen chloride is no longer evolved. The acyl derivative separates as the solution cools, or may be obtained after removal of the benzene. Benzoyl derivatives of aniline, dibenzylamine, glycine ester, phenylhydrazine, phenylbenzylhydrazine, and hydroxylamine; *m*-nitrobenzoyl derivatives of aniline, glycine ester, and phenylbenzylhydrazine, and *p*-methoxybenzoyl derivatives of glycine ester and phenylbenzylhydrazine have been prepared by this method.

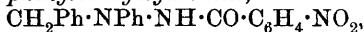
When aniline hydrochloride and acetic anhydride are heated at 130—140° for an hour, acetanilide is obtained.

Benzoyldibenzylamine, $COPh \cdot N(CH_2Ph)_2$, crystallises from alcohol in small, colourless needles, m. p. 112—113°.

Ethyl m-nitrobenzoylglycine, $NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$, crystallises from water in colourless needles, m. p. 75°.

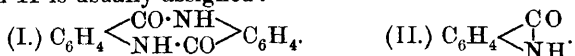
Ethyl p-methoxybenzoylglycine, $OMe \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$, crystallises from alcohol in slender, colourless needles, m. p. 98—99°.

m-Nitrobenzoyl- α -phenylbenzylhydrazine,



crystallises from alcohol in pale yellow needles, m. p. 137°. *p-Methoxybenzoyl- α -phenylbenzylhydrazine*, $C_{21}H_{20}O_2N_2$, crystallises from alcohol in slender needles, m. p. 177°. J. J. S.

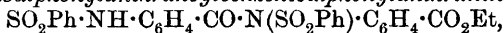
Bimolecular Anhydrides of Anthranilic Acid. GEORG SCHROETER and O. EISLEB (*Annalen*, 1909, 367, 101—168. Compare *Abstr.*, 1907, i, 529, 620).—The object of this investigation was to obtain information on the behaviour of *o*-aminocarboxylic acids of the aromatic series in the formation of cyclic amides; further, to prepare a bimolecular anhydride of anthranilic acid having the formula I in order to compare it with anthranil, to which the constitution II is usually assigned:



I. Preparation of *s*-Dianthranilides with a Negative Substituent

attached to the Nitrogen.—Derivatives of anthranilic acid of the type $\text{NHX} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ yield the corresponding chlorides on treatment with phosphorus pentachloride when X is a negative substituent such as arylsulphonyl, dinitrophenyl, or trinitrophenyl. The chlorides are converted into the corresponding dianthranilides by treating their solutions in pyridine with alcohol, water, or dilute acid.

Benzenesulphonylanthranilic chloride (Abstr., 1907, i, 529) is converted by methyl alcohol into *methyl benzenesulphonylanthranilate*, $\text{C}_{14}\text{H}_{13}\text{O}_4\text{NS}$, m. p. 107° . Dibenzenesulphonyldianthranilide (*loc. cit.*) is obtained in quantitative yield from the chloride by the method just described; it is decomposed (1) by hot, aqueous sodium hydroxide into benzenesulphonylanthranilic acid; (2) by alcoholic ammonia into benzenesulphonylanthranilamide; (3) by sodium ethoxide in alcohol into *ethyl benzenesulphonylanthranoylbenzenesulphonylanthranilate*,

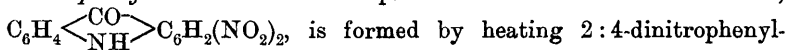


a crystalline substance, m. p. $201-202^\circ$.

p-Toluenesulphonylanthranilic chloride, $\text{C}_{14}\text{H}_{12}\text{O}_3\text{NSCl}$, forms compact crystals, m. p. $128-129^\circ$, and is converted by ethyl alcohol into *ethyl p-toluenesulphonylanthranilate*, $\text{C}_{16}\text{H}_{17}\text{O}_4\text{NS}$, m. p. 112° . *Di-p-toluenesulphonyldianthranilide*, $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{N}(\text{SO}_2 \cdot \text{C}_6\text{H}_4\text{Me}) \cdot \text{CO} \\ \text{CO} \cdot \text{N}(\text{SO}_2 \cdot \text{C}_6\text{H}_4\text{Me}) \end{smallmatrix} \right\rangle \text{C}_6\text{H}_4$, has m. p. 240° , and crystallises with chloroform of crystallisation.

β -Naphthalenesulphonylanthranilic acid, $\text{C}_{17}\text{H}_{13}\text{O}_4\text{NS}$, formed by the interaction of anthranilic acid and β -naphthalenesulphonyl chloride in benzene, has m. p. 223° ; the *chloride*, $\text{C}_{17}\text{H}_{12}\text{O}_3\text{NSCl}$, has m. p. 132° ; the *ethyl ester* crystallises in white needles, m. p. 131.5° . *Di- β -naphthalenesulphonyldianthranilide*, $\text{C}_{34}\text{H}_{22}\text{O}_6\text{N}_2\text{S}_2$, has m. p. $254-255^\circ$, and crystallises with 1CHCl_3 .

2:4-Dinitrophenylanthranilic chloride, $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$, forms compact, orange crystals, m. p. 179° (decomp.). *Ethyl 2:4-dinitrophenylanthranilate* has m. p. $164-166^\circ$. *1:3-Dinitroacridone*,



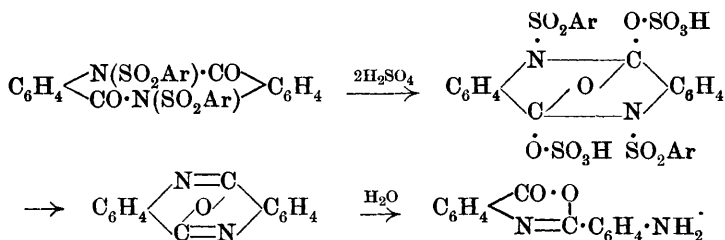
is formed by heating 2:4-dinitrophenylanthranilic acid in phosphorus oxychloride with phosphorus pentachloride; it crystallises in yellowish-brown leaflets, m. p. above 300° . *Bis-2:4-dinitrophenyldianthranilide*, $\text{C}_{26}\text{H}_{14}\text{O}_{10}\text{N}_2$, is a pale yellow powder which decomposes without melting when heated; it is converted by alcoholic ammonia under pressure at 100° into 2:4-dinitrophenylanthranilamide, $\text{C}_{13}\text{H}_{10}\text{O}_5\text{N}_4$, orange-yellow needles, m. p. 248° .

Picrylanthranilic chloride, $\text{C}_{13}\text{H}_7\text{O}_7\text{N}_4\text{Cl}$, crystallises in yellow needles, m. p. $224-225^\circ$ (decomp.), and is converted by boiling with nitrobenzene into 1:3-dinitroacridone; the *amide*, $\text{C}_{13}\text{H}_9\text{O}_7\text{N}_5$, forms deep red crystals, and decomposes before melting; the *ethyl ester*, $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$, crystallises in yellow needles, m. p. 169° . *Dipicryldianthranilide*, $\text{C}_{26}\text{H}_{12}\text{O}_{14}\text{N}_8$, crystallises in lemon-yellow needles, m. p. above 200° (decomp.).

II. *Anthranoylanthranilic Acids and their O-Anhydrides. Structure of the So-called Acylanthranils*.—Anthranoylanthranilic acid when treated with thionyl chloride yields an anhydride (compare Schroeter, Abstr., 1907, i, 529), which is also formed by the action of concentrated sulphuric acid on dibenzenesulphonyldianthranilide. It is shown that this substance is not dianthranilide, but an *o*-amino-derivative of the

so-called benzoylanthranil. Two formulæ have been suggested for the latter substance, namely: (I) $C_6H_4 \begin{smallmatrix} \text{NBz} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}$ and (II) $C_6H_4 \begin{smallmatrix} \text{N}=\text{CPh} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{O} \end{smallmatrix}$; the second must, however, be the correct one for the following reason.

All *N*-carbacylanthranilic acids capable of reacting as iminohydrins, $CO_2H\cdot C_6H_4\cdot N\cdot CR\cdot OH$, readily pass into unimolecular anhydrides, which must consequently have constitutions analogous to II; on the other hand, *N*-anthranilic acid derivatives with negative substituents, such as arylsulphonyl and polynitrophenyl, which do not exist in the enolic form, yield bimolecular anhydrides, namely, the dianthranilides. The yellow anhydride obtained from anthranoylanthranilic acid has therefore the formula $C_6H_4 \begin{smallmatrix} \text{CO}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{N}=\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 \end{smallmatrix}$, or more probably $C_6H_4 \begin{smallmatrix} \text{CO}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{NH}\cdot\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NH} \end{smallmatrix}$, since the salts are colourless. The formation of the anhydride from diarylsulphonyldianthranilides by the action of sulphuric acid, for reasons given in III, is represented as follows:



o-Nitrobenzoylanthranilic-*O* anhydride, $C_6H_4 \begin{smallmatrix} \text{CO}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{N}=\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 \end{smallmatrix}$, prepared by the action of thionyl chloride on *o*-nitrobenzoylanthranilic acid, crystallises in colourless needles, m. p. 197°; attempts to reduce it to anthranoylanthranilic-*O*-anhydride were successful.

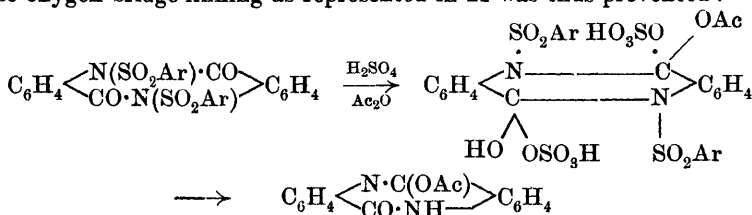
The presence of the amino-group in anthranoylanthranilic-*O*-anhydride was shown (1) by conversion into the *hydroxyazo*-derivative, $C_6H_4 \begin{smallmatrix} \text{CO}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{N}=\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH} \end{smallmatrix}$, crystallising in red needles; (2) by combination with 1:2-naphthaquinone-4-sulphonic acid, yielding the substance, $C_6H_6 \begin{smallmatrix} \text{CO}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{N}=\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{O} \end{smallmatrix}$, a dark red, crystalline powder.

Benzenesulphonylanthranoylanthranilic - *O* - anhydride (compare Schroeter, Abstr., 1907, i, 620) may be prepared (1) by the action of thionyl chloride on benzenesulphonylanthranilic acid; (2) by treating anthranoylanthranilic-*O*-anhydride with benzenesulphonyl chloride; (3) by acting on anthranil with benzenesulphonyl chloride; (4) by the interaction of anthranil and benzenesulphonylanthranilic chloride; (5) when benzenesulphonylanthranilic acid is heated with phosphorus pentachloride at 140–160°.

III. *Dianthranilide and its Derivatives* — Attempts to prepare simple derivatives of dianthranilide by the following methods were

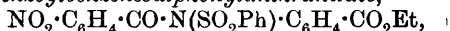
unsuccessful: (1) hydrolysis and reduction of ethyl *o*-nitrobenzoylbenzenesulphonylanthranilate; (2) reduction of *o*-nitrobenzoylmethylanthranilic acid; (3) elimination of water from anthranoylphenylanthranilic acid.

An acetate of dianthranilide was finally obtained by treating an arylsulphonyldianthranilide with sulphuric acid in the presence of acetic anhydride; the formation of the intermediate compound with the oxygen-bridge-linking as represented in II was thus prevented:



The acetyl derivative is readily converted by alkalis into dianthranilide.

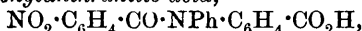
Ethyl o-nitrobenzoylbenzenesulphonylanthranilate,



prepared by the action of *o*-nitrobenzoyl chloride on ethyl sodiobenzene-sulphonylanthranilate, has m. p. 137°.

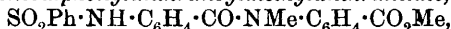
Methyl methylanthranilate is a liquid, b. p. 256°/760 mm., 128°/13 mm.; it reacts with *o*-nitrobenzoyl chloride, forming *methyl o*-nitrobenzoylmethylanthranilate, colourless prisms, m. p. 117°, which when hydrolysed yields the *acid*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, m. p. 216°.

o-Nitrobenzoylphenylanthranilic acid,

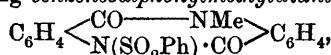


prepared from phenylanthranilic acid and *o*-nitrobenzoyl chloride, crystallises with 1Me·OH or 1Et·OH in yellow needles, m. p. 178—179°. The *methyl ester*, $\text{C}_{21}\text{H}_{16}\text{O}_5\text{N}_2$, can only be prepared by the action of methyl iodide on the *silver salt*; it has m. p. 174°. The *acid* is reduced by titanous chloride to *anthranoylphenylanthranilic acid*, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, crystallising in pale yellow needles, m. p. 227° (decomp.).

Methyl benzenesulphonylanthranoylmethylanthranilate,



is formed by the interaction of benzenesulphonylanthranilic chloride and methyl methylanthranilate; it has m. p. 125°. The *ethyl ester*, prepared similarly, has m. p. 133°. The *acid*, $\text{C}_{22}\text{H}_{18}\text{O}_5\text{N}_2\text{S}$, has m. p. 207°, and is converted by cold concentrated sulphuric acid into *anthranoylmethylanthranilic acid*, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, compact, yellow crystals, m. p. 170° (when heated quickly); the *copper salt* forms olive-green needles. Benzenesulphonylanthranoylmethylanthranilic acid is converted by thionyl chloride into the *chloride*, $\text{C}_{21}\text{H}_{17}\text{O}_4\text{N}_2\text{S}\text{Cl}_2$, a colourless powder, which is acted on by pyridine, yielding *benzenesulphonylmethyldianthranilide*,



obtained as a white, crystalline powder, m. p. 212°. The latter substance when treated with cold concentrated sulphuric acid yields

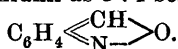
methyl-dianthranilide, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{NMe} \\ \text{NH} - \text{CO} \end{smallmatrix} C_6H_4$, crystallising in white needles, m. p. 259° , which with methyl sulphate and aqueous sodium hydroxide yields *dimethyl-dianthranilide*, $C_6H_4 \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \text{CO} \cdot \text{NMe} \end{smallmatrix} C_6H_4$, crystallising in large, transparent, colourless prisms.

Acetyldianthranilide, $C_6H_4 \begin{smallmatrix} \text{CO} - \text{NH} \\ \text{N} : \text{C}(\text{OAc}) \end{smallmatrix} C_6H_4$ (?), crystallises in small, colourless needles, and decomposes above 280° ; it is converted by acetyl chloride in quinoline or acetic anhydride in pyridine into a substance, m. p. about 200° .

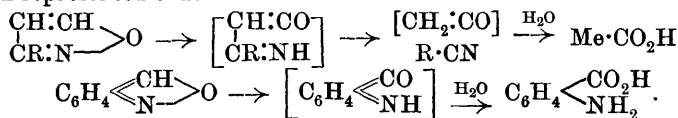
Dianthranilide, $C_6H_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} C_6H_4$, crystallises in colourless needles, m. p. 330° (decomp.); the *silver* salt is a white powder; the *sodium* salt, $C_{14}H_8O_2N_2Na_2$, crystallises with $2Et \cdot OH$, and is converted (1) by methyl sulphate into methyl-dianthranilide, (2) by benzenesulphonyl chloride into dibenzenesulphonyldianthranilide, (3) by β -naphthalenesulphonyl chloride into di- β -naphthalenesulphonyldianthranilide.

IV. *Conclusions*—(a) *Fission of Arylsulphonylanilides by Sulphuric Acid*.—The method adopted in this investigation for the elimination of arylsulphonyl groups, namely, by the action of cold concentrated sulphuric acid, is shown to be generally applicable. Thus, ethyl benzenesulphonylanthranilate is converted into ethyl anthranilate, similarly with the corresponding acid; benzenesulphonanilide yields sulphanilic acid.

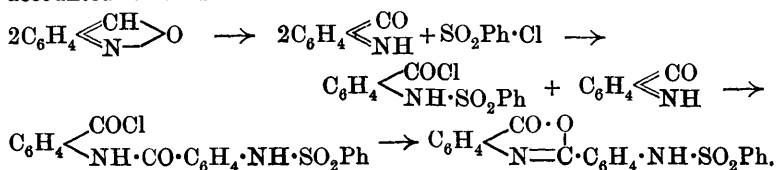
(b) *Relationship between the Formulae of Dianthranilide, Anthranil, and Derivatives of Anthranilic Acid*.—Arguments are advanced in favour of representing anthranil as 3:4-benzisooxazole,



Claisen has shown (Abstr., 1904, i, 14) that 3:5-dialkylisooxazoles are far more stable than 3- or 5-alkylisooxazoles, in agreement with which, methylantranil, corresponding with the former class of compounds, is far more stable towards alkali than anthranil (compare Bamberger, Abstr., 1904, i, 422). The analogy between the decomposition of 3-alkylisooxazolones and anthranil by alkalis is striking when represented thus:

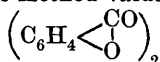


The formation of benzenesulphonylanthranoylanthranilic-*O*-anhydride by the action of benzenesulphonyl chloride on anthranil is readily accounted for thus:



In agreement with this assumption is the fact that an 80% yield of the anhydride is obtained by the action of benzenesulphonylanthranilic chloride on anthranil (1 mol.).

(c) *Comparison of Dianthranilide with the Di- and Poly-salicylides.*—Mol. wt. determinations of Anschütz's chloroform-salicylide (Abstr., 1893, i, 165) in phenol and nitrobenzene by the cryoscopic method give values corresponding with $(C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix})_4$, whilst in nitrobenzene by the ebullioscopic method values agreeing with



are obtained.

It is considered probable that this salicylide, obtained by the action of phosphoryl chloride on salicylic acid, is a polymericide of $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix}$,

existing as $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix} C \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix} C \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown O \end{smallmatrix}$, $(C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix})_3$, etc., according to the nature of solvent, temperature, etc. The disalicylide of Einhorn and Pfeiffer (Abstr., 1901, i, 712), on the contrary, is probably structurally analogous to dianthranilide, $C_6H_4 \begin{smallmatrix} \diagup CO \cdot O \\ \diagdown O \cdot CO \end{smallmatrix} C_6H_4$.

W. H. G.

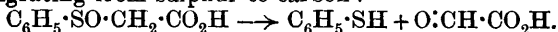
Bromides of Arylthioglycolic [Arylthiolacetic] Acids. RUDOLF PUMMERER (*Ber.*, 1909, 42, 2275—2282).—Arylthiolacetic acids are capable of taking up two atoms of bromine in carbon disulphide to form crystalline dibromides.

Phenylthiolacetic acid dibromide, $C_6H_5 \cdot SBr_2 \cdot CH_2 \cdot CO_2H$, crystallises from carbon disulphide in groups of golden-yellow prisms. It turns moist potassium iodide-starch paper blue. Alcohol converts it into ethyl phenylthiolacetate and brominated esters. The dibromide changes, especially on heating, into the *p*-bromo-acid, which may be converted by the action of chlorosulphonic acid, followed by the removal of bromine by alkali and zinc dust, into thioindigotin.

p-Tolylthiolacetic acid monobromide, which is the chief product of the action of bromine on the acid, behaves as a double compound of the dibromide with the acid, $C_7H_7 \cdot SBr_2 \cdot CH_2 \cdot CO_2H, C_7H_7 \cdot S \cdot CH_2 \cdot CO_2H$. It crystallises in thick plates or prisms, m. p. 82°, which are yellow by transmitted, but scarlet by reflected, light, with a bluish-red reflex. The *dibromide*, obtained from the mother liquor, forms thin, yellow plates, decomp. 70°. It is capable of taking up more bromine, but a definite compound could not be isolated.

C. H. D.

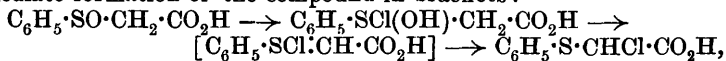
Phenylsulphoxyacetic Acid. RUDOLF PUMMERER (*Ber.*, 1909, 42, 2282—2291).—*Phenylsulphoxyacetic acid* is obtained either by hydrolysing phenylthiolacetic acid dibromide (preceding abstract), or by oxidising phenylthiolacetic acid with hydrogen peroxide. It crystallises from ethyl acetate in prisms, m. p. 116°. Even traces of mineral acids decompose it into thiophenol and glyoxylic acid, the oxygen migrating from sulphur to carbon:



This reaction takes place even in presence of hydriodic acid, or on heating alone. Dilute aqueous solutions are stable.

Concentrated hydrobromic acid forms the bromophenyl acid. Hydrogen chloride, on the other hand, forms *α-chloro-α-phenylthiol-acetic acid*, $C_6H_5 \cdot S \cdot CHCl \cdot CO_2H$, m. p. 69—72°, which decomposes readily, forming thiophenol. The *ethyl* ester is an oil, b. p. 158—160°/14.5 mm., which readily loses chlorine. Phenyl and benzyl sulfoxides also absorb hydrogen chloride, forming oils, which appear to be labile hydrochlorides. These sulfoxides, like phenylsulphoxyacetic acid, give intense blue colorations with fuming sulphuric acid.

The reaction with hydrogen chloride may occur through the intermediate formation of the compound in brackets:

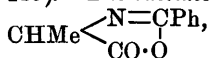


and a similar reaction may be assumed for the formation of thiophenol by acids.

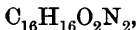
The dynamic isomerism of the sulfoxides assumed by Smythe (Trans., 1909, 95, 349) is unlikely, since the tendency of quadrivalent sulphur to become bivalent is not likely to be reversible.

C. H. D.

Lactimones of Benzoylalanine and of Benzoylphenylalanine. ERNST MOHR and FRITZ STROSCHER (Ber., 1909, 42, 2521—2523. Compare Abstr., 1907, i, 415).—The *lactimone* of benzoylalanine,



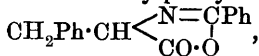
m. p. 39°, is obtained by heating benzoylalanine with acetic anhydride and fractionally distilling at 0.2 to 0.5 mm. With water, ammonia, and alcohol, it yields benzoylalanine and its amide and ethyl ester respectively, whilst with aniline it forms benzoylalanineanilide,



m. p. 175°. In ethereal solution the lactimone adds on hydrogen chloride to form *benzoylalanyl chloride*, $COPh \cdot NH \cdot CHMe \cdot COCl$, a white powder, which decomposes at 125°, and reacts with *α-aminoisobutyric acid* in aqueous, faintly alkaline solution to form *benzoylalanyl-α-aminoisobutyric acid*, $COPh \cdot NH \cdot CHMe \cdot CO \cdot NH \cdot CMe_2 \cdot CO_2H$, m. p. 199°, which, when warmed with acetic anhydride, yields the

lactimone, $COPh \cdot NH \cdot CHMe \cdot C \begin{array}{l} \diagup N \cdot CMe_2 \\ \diagdown O \cdot CO \end{array}$, b. p. 138°/0.2—0.5 mm.,

m. p. 116°. The *lactimone* of benzoylphenylalanine,



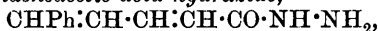
obtained from hippuric acid, has m. p. 71°, and reacts with water, alcohol, ammonia, aniline, and hydrogen chloride in a similar manner to the lactimone of benzoylalanine.

C. S.

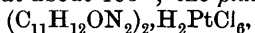
Additive Capacity of Unsaturated Organic Acids and their Esters. ADOLF RIEDEL and ERNST SCHULZ (Annalen, 1909, 367, 14—39. Compare Posner and Oppermann, Abstr., 1907, i, 55; Posner, *ibid.*, 212; Riedel, Abstr., 1908, i, 536).—An investigation on the

behaviour of acids with conjugated ethylene linkings towards hydrazine, phenylhydrazine, and hydroxylamine. It is found that the tendency of these acids to form additive compounds with the reagents mentioned varies largely with the nature of the acid and the addendum; rules of general applicability cannot be deduced. Attempts to combine toluenesulphonic acid, sulphur dioxide, potassium sulphite, and hydrogen chloride with cinnamylideneacetic acid and sorbic acid were unsuccessful.

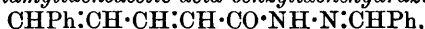
Cinnamylideneacetic acid yields with hydrazine hydrate the *hydrazine* salt, $C_{11}H_{14}O_2N_2$, crystallising in glistening, white leaflets, m. p. 140° (decomp.). The ethyl ester, however, reacts with hydrazine hydrate, yielding *cinnamylideneacetic acid hydrazide*,



which crystallises in long, slender, white needles, m. p. 155° ; the *sodium* salt, $C_{11}H_{11}ON_2Na$, is a reddish-yellow powder, which crepitates when heated; the *hydrochloride*, $C_{11}H_{12}ON_2 \cdot HCl$, crystallises in colourless leaflets and decomposes at about 195° ; the *platinichloride*,

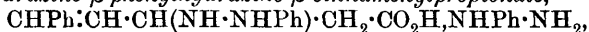


is a yellowish-brown powder; the *oxalate*, $C_{24}H_{26}O_6N_4 \cdot 4H_2O$, forms white, glistening leaflets, m. p. 270° ; the *picrate*, $C_{17}H_{15}O_8N_5$, crystallises in prismatic, coppery-red, glistening leaflets, m. p. $98-103^\circ$ (decomp.). The parent substance is converted by bromine in chloroform into $\alpha\beta\gamma\delta$ -*tetrabromo- δ -phenylvaleric acid hydrazide*, $C_{11}H_{12}ON_2Br_4$, obtained as small, white crystals, m. p. 170° (decomp.). The following compounds are prepared by treating the hydrazide with the necessary aldehyde. *Cinnamylideneacetic acid benzylidenehydrazide*,



stellate groups of sulphur-yellow needles, m. p. 207° ; *isopentylidene* derivative, $C_{11}H_9O \cdot NH \cdot N:CH \cdot C_4H_9$, slender, white needles, m. p. 158° ; *p-tolylidene* derivative, $C_{11}H_9O \cdot NH \cdot N:CH \cdot C_6H_4Me$, slender, sulphur-yellow needles, m. p. 204° ; *o-hydroxybenzylidene* derivative, $C_{18}H_{16}O_2N_2$, felted, slender, yellow needles, m. p. 232° ; *p-methoxybenzylidene* derivative, slender, yellow needles, m. p. 203° ; *m-nitrobenzylidene* derivative, $C_{18}H_{15}O_3N_3$, golden-yellow needles, m. p. 204° ; *4-hydroxy-3-methoxybenzylidene* derivative, $C_{19}H_{18}O_3N_2$, golden-yellow needles, m. p. 225° ; *cinnamylidene* derivative, $C_{20}H_{18}ON_2$, slender, golden-yellow needles, m. p. 236° . *Cinnamylideneacetic acid acethydrazide*, $C_{10}H_9 \cdot CO \cdot NH \cdot NHAc$, prepared by the action of acetic anhydride on the parent substance, forms small, yellowish-white crystals, m. p. 214° (decomp.). The corresponding *benzhydrazide*, $C_{10}H_9 \cdot CO \cdot NH \cdot NHBz$, crystallises in silvery, white, prismatic leaflets, m. p. 212° . The *semicarbazide*, $C_{10}H_9 \cdot CO \cdot NH \cdot NH \cdot CO \cdot NH_2$, crystallises in faintly yellow leaflets, m. p. 164° (decomp.).

Cinnamylideneacetic acid reacts with phenylhydrazine, yielding *phenylhydrazine β -phenylhydrazino- β -cinnamenylpropionate*,



which forms small, yellow, crystalline nodules, m. p. 160° (decomp.); the *dibromide*, $C_{23}H_{26}O_2N_4Br_2$, forms small, granular crystals, m. p. about 150° (decomp.).

Hydroxylamine cinnamylideneacetate, $C_{10}H_9 \cdot CO_2H \cdot NH_2 \cdot OH$, is obtained by the action of hydroxylamine on the acid as compact,

colourless crystals, decomposing at 135°. When the methyl ester is treated with hydroxylamine it yields *hydroxylamine β-hydroxylamino-β-cinnamenylpropionylhydroxamate*,

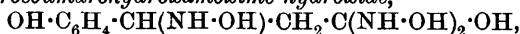
$\text{CHPh} \cdot \text{CH} \cdot \text{CH}(\text{NH} \cdot \text{OH}) \cdot \text{CH}_2 \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{OH} \cdot \text{NH}_2 \cdot \text{OH}$, obtained as yellow crystals which decompose at 120—130°. The acid, $\text{C}_{11}\text{H}_{14}\text{O}_3\text{N}_2$, prepared by heating a solution of the hydroxylamine salt in methyl alcohol, forms small, granular, white crystals, and decomposes at 131—133°; the *tetrabenzoyl* derivative, $\text{C}_{39}\text{H}_{30}\text{O}_7\text{N}_2$, crystallises in glistening, long, white, prismatic needles, m. p. 167—168°. The hydroxamic acid is converted by ammoniacal silver nitrate into *γ-cinnamenylisooxazolone*, $\text{C}_{11}\text{H}_9\text{O}_2\text{N}$, obtained as a reddish-brown, sandy powder, decomposing at 90°.

Sorbyl chloride reacts with phenylhydrazine in ethereal solution, yielding *sorbic acid phenylhydrazide*, $\text{CH}_3 \cdot [\text{CH}]_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPh}$, pearly leaflets, m. p. 162—163°, and with *o*-toluidine, yielding the *o*-toluidide, $\text{CH}_3 \cdot [\text{CH}]_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, colourless crystals, m. p. 173°.

Sorbyl cyanide is obtained by treating an ethereal solution of sorbyl chloride with hydrogen cyanide and pyridine; it is a yellow oil with a pleasant odour.

W. H. G.

Action of Hydroxylamine on Coumarins. THEODOR POSNER (*Ber.*, 1909, 42, 2523—2532).—A claim of priority over Francesconi and Cusmano (this vol., i, 233). The compound described as dihydroxylaminohydrocoumarin by these investigators is a mixture. Free hydroxylamine and coumarin in cold methyl-alcoholic solution react with rupture of the lactone ring, yielding unstable *β-hydroxyl-aminodihydrocoumarohydroxamoxime hydroxide*,



a white, crystalline powder, which decomposes at 123°, regenerates coumarin when heated with hydrochloric acid, and yields *β*-aminodihydrocoumaric acid, m. p. 214° (208°: Francesconi and Cusmano), when treated with warm solvents. The same acid is obtained by heating coumaric acid or its acetyl derivative with an excess of alcoholic hydroxylamine, although in these two cases the steric influence of the ortho OH-group retards the reactions. *Diacetyl-β*-amino-

dihydrocoumarin, $\text{NAC}_2 \cdot \text{CH} \begin{matrix} \text{C}_6\text{H}_4 \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CO} \end{matrix}$, m. p. 116—117°, obtained

from *β*-aminodihydrocoumaric acid and acetic anhydride, is insoluble in sodium carbonate, whilst *benzoyl-β*-aminodihydrocoumaric acid, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{NHBz}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, m. p. 168—169°, is readily soluble in this alkali carbonate. These facts and also the exactly analogous behaviour of *β*-aminodihydrocoumaric acid to that of *β*-aminodihydrocinnamic acid (*Abstr.*, 1906, i, 955; 1907, i, 212) are in favour of the constitution $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, as against the cyclic formula advocated by Francesconi and Cusmano for *β*-aminodihydrocoumaric acid.

C. S.

Some Amino- and Nitroamino-derivatives of Benzoic, *m*-Toluic, and *iso*Phthalic Acids. MARSTON T. BOGERT and ALFRED H. KROPFF (*J. Amer. Chem. Soc.*, 1909, 31, 841—848).—In earlier papers (Bogert and Dox, *Abstr.*, 1905, i, 841, 949; Bogert and

Nelson, Abstr., 1907 i, 660), several derivatives of 2:5-diaminoterephthalic acid have been described. The present work deals chiefly with 4:6-diaminoisophthalic acid and its derivatives.

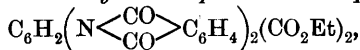
Errera and Maltese (Abstr., 1904, i, 307) attempted to prepare 4:6-diaminoisophthalic acid, but without success, and on repeating their experiments, the present authors also failed to obtain it. The acid has been prepared, however, by converting diacetyl-amino-*m*-xylene into 4:6-diacetylaminoisophthalic acid by oxidation with potassium permanganate and boiling this compound with strong hydrochloric acid.

Diacetyl-amino-*m*-xylene melts at 295.2° (corr.). 4:6-Diacetylaminoisophthalic acid, $C_6H_2(NHAc)_2(CO_2H)_2$, m. p. 276.2° (decomp., corr.), forms long, colourless needles; its *methyl* and *ethyl* esters melt at 256° (corr.) and 230.4° (corr.) respectively. 4:6-Diaminoisophthalic acid, $C_6H_2(NH_2)_2(CO_2H)_2$, m. p. 235° (corr.), is obtained as a pink powder, and dissolves in alkali hydroxide to form a fluorescent solution; its *hydrochloride* melts at $229-230^{\circ}$ (corr.). The *diethyl* ester, m. p. 171.5° (corr.), crystallises in long, yellow needles; its *hydrochloride* melts at 245.4° (corr.). The *monoethyl* ester, m. p. 211.6° (corr.), forms reddish-yellow prisms. The *dimethyl* ester, m. p. 204.6° (corr.), crystallises in red needles; its *hydrochloride* melts at 235.5° (decomp.).

The *dilactam* of 4:6-diacetylaminoisophthalic acid (*m-bisacetanthranil*), $\begin{array}{c} NAc \\ | \\ CO \end{array} > C_6H_4 < \begin{array}{c} NAc \\ | \\ CO \end{array}$, m. p. 282.3° (corr.), forms colourless needles; it generally condenses with ammonia and primary amines to produce 1:3:7:9-naphthatetrazines, but with *isoamylamine* it yields the intermediate 4:6-diacetylaminoisophthalisoamylamide,

$C_6H_2(NHAc)_2(CO \cdot NH \cdot C_5H_{11})_2$, m. p. 189.6° (corr.), which crystallises in long, silky needles, and can also be obtained by the action of *isoamylamine* on ethyl 4:6-diacetylaminoisophthalate.

4:6-Diformylaminoisophthalic acid, $C_6H_2(NH \cdot CHO)_2(CO_2H)_2$, m. p. above 360° , forms minute needles. *Ethyl* 4:6-diphenylcarbaminoisophthalate, $C_6H_2(NH \cdot CO \cdot NHPh)_2(CO_2Et)_2$, m. p. 256.8° (corr.), obtained by heating ethyl 4:6-diaminoisophthalate with phenylcarbamide, crystallises in needles. *Ethyl* 4:6-diphthaliminoisophthalate,



m. p. 251.8° (corr.), obtained by fusing ethyl 4:6-diaminoisophthalate with phthalic anhydride, forms cream-coloured crystals.

4:6-Diacetyl-amino-*m*-toluic acid, $C_6H_2Me(NHAc)_2 \cdot CO_2H$, m. p. 272.4° (corr.), obtained as a by-product in the oxidation of diacetyl-amino-*m*-xylene, crystallises in colourless needles, and when boiled with acetic anhydride is converted into 4-acetyl-amino-5-methylacetyl-anthranil, $NHAc \cdot C_6H_2Me < \begin{array}{c} CO \\ | \\ NAc \end{array}$, m. p. 166.2° (corr.). 4-Nitroacetyl-

anthranil-5-carboxylic acid, $CO_2H \cdot C_6H_2(NO_2) < \begin{array}{c} CO \\ | \\ NAc \end{array}$, m. p. 274.4° (corr.), obtained by boiling 6-nitro-4-aminoisophthalic acid (Errera and Maltese, *loc. cit.*) with acetic anhydride, forms yellow crystals.

When 6-nitro-4-aminoisophthalic acid is heated with 50% sulphuric acid, it loses carbon dioxide and yields a mixture of 2-nitro-4-amino- and 4-nitro-2-amino-benzoic acids. 2-Nitro-4-acetotoluidide melts at 148.5° (corr.), and on oxidation with potassium permanganate yields 2-nitro-4-acetylaminobenzoic acid, m. p. 219° (corr.). The latter compound, on hydrolysis, is converted into 2-nitro-4-aminobenzoic acid, m. p. 239.5° (corr.), which has recently been prepared by Lucius and Brüning (D.R.-P. 204884) by the partial reduction of 2:4-dinitrobenzoic acid.

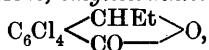
The mother liquors obtained in the preparation of ethyl 4:6-diaminoisophthalate yielded a dark red substance, m. p. about 102°, which, when boiled with acetic anhydride, furnished a compound, m. p. 189.4° (corr.), which was probably ethyl 2:4-diacetylaminobenzoate.

E. G.

Action of Organo-magnesium Compounds on Anhydrides of Dicarboxylic Acids. HUGO BAUER (*Arch. Pharm.*, 1909, 247, 220—225).—The author has shown previously (*Abstr.*, 1904, i, 417; 1905, i, 210) that the normal reaction between magnesium alkyl haloids and phthalic anhydride results in the formation of dialkylphthalides. Houben and Hahn have observed, however, that in the case of camphoric anhydride some monoalkylcampholide is also formed, and have also noted other variations of the normal reaction (*Abstr.*, 1908, i, 539). The author has therefore examined several other condensations of this type.

Propyl chloride reacts with magnesium powder and phthalic anhydride to form *dipropylphthalide*, $C_6H_4 \begin{smallmatrix} \text{CPr}^a \\ \text{CO} \end{smallmatrix} O$, m. p. 76°, which crystallises in flat prisms and is readily soluble in most organic solvents. *Diisopropylphthalide*, m. p. 83—84°, similarly obtained, forms long crystals, and is easily soluble in hot alcohol and difficultly so in cold alcohol.

Magnesium methyl iodide reacts with tetrachlorophthalic anhydride to form *dimethyltetrachlorophthalide*, m. p. 165—166°, which crystallises in slender, colourless needles. With magnesium ethyl bromide and tetrachlorophthalic anhydride, *ethyltetrachlorophthalide*,

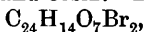


m. p. 132—133°, is formed. It crystallises from alcohol in almost colourless needles, and is remarkably stable towards nitric acid, being precipitated unchanged from solution in the acid by water. With magnesium *p*-tolyl bromide, phthalic anhydride reacts to form *o*-*dip-toluoylbenzene*, $C_6H_4(CO \cdot C_6H_4Me)_2$, m. p. 190—191°, which crystallises from alcohol. Magnesium phenyl bromide gives with tetrachlorophthalic anhydride a mixture of mono- and di-phenyltetrachlorophthalides, which it has so far proved impossible to separate into its components.

T. A. H.

Asymmetric Dibromofluorescein. GUSTAV HELLER and HEINRICH L. MEYER (*Ber.*, 1909, 42, 2188—2190).—Baeyer's *as*-dibromofluorescein (this *Journ.*, 1877, i, 200) is best prepared by heating a mixture of dibromodihydroxybenzoylbenzoic acid and resorcinol in

molecular proportions with zinc chloride (20%) at 170° for two hours. It crystallises from alcohol in dark red prisms, $C_{20}H_{10}O_6Br_2 \cdot C_2H_6O$, m. p. about 300°. The fluorescence of its alkaline solutions is midway between those of fluorescein and eosin. The *diacetyl* derivative,



crystallises from toluene in colourless, flat plates containing a molecule of toluene, m. p. 173° (decomp.). When heated with 50% sodium hydroxide solution at 130—135°, the dibromofluorescein yields dibromodihydroxybenzoylbenzoic acid, but not dihydroxybenzoylbenzoic acid.

J. J. S.

Cholic Acids. MAURICE PIETTRE (*Compt. rend.*, 1909, 148, 1779—1782).—It is shown that the cholic acids of bile differ between themselves, and not only in the fact that they exist in combination with different amino-acids. Cholic acid, prepared by the hydrolysis of pure sodium glycocholate (Abstr., 1908, i, 959), is a yellow, resinous mass, which, on distillation under ordinary pressure, loses water and forms a pitch-like mass having the properties of an acid, and agreeing with the formula $C_{25}H_{38}O_3$. The acid obtained on hydrolysing sodium taurocholate differs from the foregoing in that it cannot be distilled, and undergoes reduction by sodium and amyl alcohol, giving a colourless, tasteless, crystalline compound, $C_{24}H_{42}O_5$, m. p. 180°, $[\alpha]_D + 54.46'$.

W. O. W.

Energetic Oxidation of Cholic Acid by Nitric Acid. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1909, 60, 376—407).—Cholecamphoric (choloidanic) acid, obtained by oxidising cholic acid by concentrated nitric acid, is destroyed by the prolonged action of the mineral acid. To examine the complex mixture of oxidation products, the following process is used. Cholic acid, freed from fatty acids, is heated with nitric acid, D 1.4, for three days, repeatedly evaporated with water to remove nitrous acid, dissolved in hot water, and the cold solution treated with lead acetate, whereby a voluminous precipitate is obtained. The filtrate contains succinic acid, a glutaric acid, α -methylglutaric acid, and a saturated, dibasic acid, $C_8H_{12}O_5$, which is probably 1-hydroxycyclohexane-1:4-dicarboxylic acid, since *p*-hydroxybenzaldehyde has been prepared from it.

From the lead acetate precipitate an individual, crystalline substance has not been isolated, but, after removal of the lead, a number of fractions, all oils of acid character, has been obtained by the use of different solvents and precipitants. Of these fractions, the following appear to be individual substances: a saturated, dibasic acid, $C_9H_{14}O_6$, which is oxidised by hydrogen peroxide to a saturated, dibasic acid, $C_9H_{12}O_5$; an unsaturated acid, oxidised by hydrogen peroxide to a saturated, tribasic acid, $C_{12}H_{18}O_6$; and a saturated, dibasic acid, $C_8H_{12}O_5$, which is oxidised by hydrogen peroxide to an unsaturated, monobasic acid, $C_7H_{10}O_4$, possibly a dihydroxycyclohexenecarboxylic acid.

The chief result of the investigation is the probability that cholic

confirms the constitution of ellagic acid proposed by Graebe (Abstr., 1903, i, 262) and supported by Perkin and Nierenstein (Trans., 1905, 87, 1412), and also that of gallotannic acid, from which it is obtained by oxidation. The author agrees with Nierenstein (this vol., i, 174) that gallotannic acid is not a glucoside, and shows by converting it into gallic acid that it is a digallic acid. E. H.

Distribution of Chlorogenic Acid in Nature. K. GORTER (*Arch. Pharm.*, 1909, 247, 184—196).—The paper is prefaced by a short description of the chief properties and characters of the acid as already published (Abstr., 1908, i, 186, 345). For the detection of the acid in plants, the following colour reaction is used. Ten grams of leaves are boiled with 50 c.c. of dilute hydrochloric acid during one hour in a reflux apparatus. The filtrate from this is shaken with 15 c.c. of ether. The latter is washed with a dilute solution of sodium hydrogen carbonate and then twice with water, and to it is added a small quantity of a very dilute solution of ferric chloride, when, if chlorogenic acid is present in the leaves, a violet coloration is produced in the aqueous layer on shaking, whilst the ethereal layer develops a yellow tint. Out of 230 species of plants examined in this way, 98 gave a positive result. The acid appears to occur in many plants of the orders: *Araliaceae*, *Convulvulaceae*, *Boraginaceae*, *Gesneraceae*, *Acanthaceae*, and *Compositae*. T. A. H.

Igasuric Acid. K. GORTER (*Arch. Pharm.*, 1909, 247, 197—200).—This name was first given by Pelletier and Caventou to a crystalline acid isolated from nux-vomica seeds. Later investigators have always obtained it in an amorphous state, and Sander (Abstr., 1897, i, 383) regarded it as identical with caffetannic acid. The author finds that it is identical with the chlorogenic acid obtained by him from coffee berries (Abstr., 1908, i, 186, 345, and preceding abstract). Pelletier and Caventou's acid, he suggests, may have been impure quinic acid, since the latter is produced by the action of alkalis on chlorogenic acid. T. A. H.

Action of Ammonia on Benzaldehyde and the Preparation of Benzaldehyde-ammonia. FRANCIS FRANCIS (*Ber.*, 1909, 42, 2216—2218).—Hydrobenzamide is most readily prepared by shaking a concentrated solution of ammonia with an emulsion of benzaldehyde containing a little soap solution.

Benzaldehyde-ammonia, $2C_6H_5 \cdot CHO, NH_3$, probably $NH(CHPh \cdot OH)_2$,

is readily obtained by adding concentrated aqueous ammonia and alcohol to a mixture of benzaldehyde and a little alcohol at 0° and then cooling to -20° , when the additive compound separates in the form of well developed plates, m. p. 45° . The formation of the compound is favoured by the presence of alkalis, whereas ammonium chloride tends to produce hydrobenzamide. When kept for some time, the additive compound yields hydrobenzamide, benzaldehyde, and water. With benzoyl chloride and potassium carbonate, it yields

a small amount of benzylidenedibenzamide (Hoffmann and V. Meyer, Abstr., 1892, 604).

The additive compound is undoubtedly an intermediate product in the preparation of hydrobenzamide. *p*-Tolualdehyde-ammonia, $2\text{C}_6\text{H}_4\text{Me}\cdot\text{CHO}\cdot\text{NH}_3$, melts at $43\text{--}44^\circ$, and is less stable than the benzaldehyde compound. It readily yields *p*-trimethylhydrobenzamide, $(\text{C}_6\text{H}_4\text{Me}\cdot\text{CH})_3\text{N}_2$, m. p. 95° .

An additive compound could not be obtained from anisaldehyde and ammonia. J. J. S.

***o*-Nitrosobenzaldehyde.** EUGEN BAMBERGER and ANDOR FODOR (*Ber.*, 1909, 42, 2573—2574. Compare this vol., i, 509).—*o*-Nitrosobenzaldehyde is obtained by the decomposition of *o*-aldehydonitrosophenylhydroxylamine with acids as white, glistening needles, m. p. $109\text{--}110^\circ$.

[With O. BAUDISCH].—Zinc dust and amyl nitrite convert *o*-nitrobenzaldehyde into *o*-aldehydonitrosophenylhydroxylamine.

C. H. D.

Optically Active Benzaldehydecyanohydrin. KARL FEIST (*Arch. Pharm.*, 1909, 247, 226—232. Compare Abstr., 1908, i, 437, 903; Rosenthaler, *ibid.*, i, 817; Auld, *Trans.*, 1909, 95, 927).—Since Rosenthaler has shown that *d*-benzaldehydecyanohydrin is formed by the action of emulsin on a mixture of benzaldehyde and hydrocyanic acid, it ought to be possible to prepare *l*-benzaldehydecyanohydrin by the action of emulsin on *dl*-benzaldehydecyanohydrin, since it is also known that only the *d*-form is destroyed by the enzyme. This proves to be the case, and a slightly *laevo*-product can be obtained by allowing emulsin to react with the *dl*-form in presence of much water and a little alcohol during forty-eight hours, the hydrogen cyanide formed being carried away by a stream of air passed through the mixture. This *l*-product, on hydrolysis, yields *d*-mandelic acid.

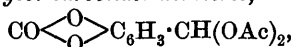
Further evidence is brought forward in favour of the view that *d*-benzaldehydecyanohydrin ($[\alpha]_D = 14^\circ$) is the first product of the action of emulsin on amygdalin (*loc. cit.*), and it is shown that auto-racemisation of the *d*-form does not occur at ordinary temperatures, but that, in presence of water, racemisation occurs slowly, although no hydrogen cyanide is split off. T. A. H.

A Synthesis of Aldehydes and Indole. III. R. A. WEERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 42—44. Compare Abstr., 1908, i, 22).—Methyl styrylcarbamate on hydrolysis with acid yields phenylacetaldehyde, the *oxime*, $\text{C}_8\text{H}_9\text{ON}$, of which has m. p. $99\text{--}100^\circ$.

o-Nitrophenylacetaldehyde, $\text{C}_8\text{H}_7\text{O}_3\text{N}$, obtained similarly from methyl *o*-nitrostyrylcarbamate, has b. p. $133\text{--}135^\circ/5\text{ mm.}$, m. p. $22\text{--}23^\circ$; its alkaline solution turns red. The *oxime*, $\text{C}_8\text{H}_8\text{O}_3\text{N}_2$, crystallises from water in long needles, m. p. 110° . The *m*- and *p*-nitrophenylacetaldehydes can also be obtained from the corresponding carbamates. It is thus rendered possible to synthesise an aldehyde containing one carbon atom less from a cinnamide.

Indole is obtained when *o*-nitrophenylacetaldehyde is reduced with iron in hydrogen sulphite solution, or, better, by the reduction of the methyl *o*-nitrostyrylcarbamate. W. R.

"Dichloropiperonal." HERMANN PAULY and THOMAS J. R. ALEXANDER (*Ber.*, 1909, 42, 2350—2354. Compare Abstr., 1907, i, 709; this vol., i, 165).—"Dichloropiperonal," the structure of which is established as the carbonate of 3:4-dihydroxybenzylidene chloride, cannot be hydrolysed to the corresponding phenol; instead, protocatechualdehyde is formed. When the theoretical quantity of water and dry pyridine are used to effect hydrolysis, an orange-brown *chloro*-compound was obtained; using methyl alcohol and pyridine, or, better, sodium acetate, *methylprotocatechualdehyde-m-carbonate* is obtained; this is a syrup solidifying to minute needles, m. p. 93°. On boiling dichloropiperonal with sodium acetate and acetic anhydride, *dihydroxybenzylideneglycol carbonate diacetate*,



is formed, m. p. 84·5—85°. By the partial reduction of dichloropiperonal in absolutely anhydrous acetic acid with zinc dust, the *carbonate of dihydroxybenzyl chloride*, $\text{CO} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{CH}_2\text{Cl}$, is obtained; this crystallises in very long, lustrous needles, m. p. 53·5—54°, and interacts with silver acetate, forming the *carbonate acetate* of 3:4-dihydroxybenzyl alcohol, $\text{CO} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{OAc}$, separating in microscopic needles, m. p. 59·5°. The monochloride is hydrolysed by the theoretical quantity of water in presence of pyridine, but the product immediately combines with pyridine to form 3:4-dihydroxybenzylpyridinium chloride, $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_5\text{Cl}$, crystallising in prismatic plates, m. p. 170—171° (corr.). E. F. A.

Preparation of Hydroxyuvitaldehyde from *p*-Cresol. FRITZ ULLMANN and KARL BRITTNER (*Ber.*, 1909, 42, 2539—2548).—*p*-Cresol, 35% formaldehyde, and concentrated sodium hydroxide react in four days to form the sodium salt of 3:5-dimethylol-*p*-cresol (Auwers, Abstr., 1907, i, 610). The alcohol, liberated by acetic acid, yields 3:5-dinitro-*p*-cresol by treatment with 30% nitric acid, and is converted by alkali and methyl sulphate into *methoxyuvityl alcohol*, $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Me}(\text{CH}_2 \cdot \text{OH})_2$ [$= 4:1:3:5$], m. p. 106·5° (corr.), which is oxidised by cold alkaline potassium permanganate to 4-*methoxyuvitic acid*, $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Me}(\text{CO}_2\text{H})_2$, m. p. 180° (corr.), which, by gentle warming with hydriodic acid, D 1·7, is converted into hydroxyuvitic acid. Methoxyuvitic acid is oxidised by hot potassium permanganate to *methoxytrimesic acid*, $\text{OMe} \cdot \text{C}_6\text{H}_2(\text{CO}_2\text{H})_3$, m. p. 248°, which yields anisole above its m. p., forms a trimethyl ester, m. p. 86° (corr.), with methyl sulphate and sodium carbonate, and is converted by hydriodic acid into hydroxytrimesic acid.

Methoxyuvityl alcohol is oxidised by sodium dichromate and hot dilute sulphuric acid to *methoxyuvitaldehyde*, $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Me}(\text{CHO})_2$, m. p. 96° (corr.), which forms a *bisphenylhydrazone*, m. p. 185.5° (decomp.), and a *dioxime*, m. p. 193° (corr.). The conversion of the methoxy-derivative into 4-hydroxyuvitaldehyde can be effected by heating with aluminium chloride in benzene, but the aldehyde is more readily obtained as follows. By shaking a mixture of aqueous 3 : 5-dimethylol-*p*-cresol and sodium hydroxide with toluenesulphonyl chloride in benzene, the *ester*, $\text{C}_6\text{H}_2\text{Me}(\text{CH}_2 \cdot \text{OH})_2 \cdot \text{O} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7$, m. p. 132.5° (corr.), is obtained, which is oxidised by sodium dichromate and glacial acetic acid to the *compound*, $\text{C}_6\text{H}_2\text{Me}(\text{CHO})_2 \cdot \text{O} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7$, m. p. 146.5° , which is quantitatively hydrolysed by concentrated sulphuric acid, yielding 4-hydroxyuvitaldehyde, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Me}(\text{CHO})_2$, m. p. 133.5° , which begins to sublime at 100° , gives a yellowish-green, fluorescent solution in water (due to alkali in the glass vessel), and forms a *bisphenylhydrazone*, m. p. 185° (decomp.), and a *dioxime*, m. p. 199° (corr.).

Methoxyuvitaldehyde condenses with dimethylaniline in the presence of zinc chloride to form a colourless leuco-compound, which oxidises to a green dye, 4-methoxy-1-methyl-3 : 5-bistetramethyldiaminobenzhydrylbenzene, $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Me}[\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2]_2$, m. p. 252° .

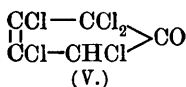
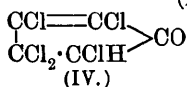
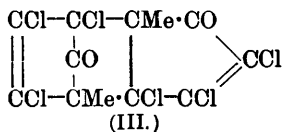
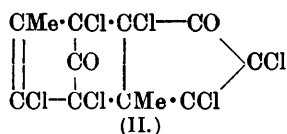
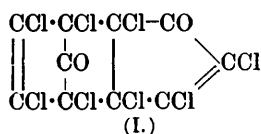
C. S.

Transformation of cyclopentene Derivatives into Indene Derivatives. THEODOR ZINCKE and KURT H. MEYER (*Annalen*, 1909, 367, 1—13).—It has been shown by Zincke and Küster (Abstr., 1890, 1255) that hexachloro-1-hydroxy- Δ^2 -cyclopentene-1-carboxylic acid and the corresponding Δ^3 -cyclopentene compound when boiled with water yield hexachloroindone. On the other hand, derivatives of these acids containing one or two chlorine atoms replaced by methyl, when similarly treated, do not yield indene derivatives, but substances having the formulæ $\text{C}_{10}\text{Me}_2\text{O}_2\text{Cl}_6$ and $\text{C}_{10}\text{Me}_4\text{O}_2\text{Cl}_4$ (compare Zincke, Bergmann, and Franke, Abstr., 1897, i, 507; Zincke and Prenzel, Abstr., 1897, i, 509). This subject has been re-investigated, and a substance, $\text{C}_{10}\text{O}_2\text{Cl}_8$, obtained as an intermediate product in the conversion of hexachlorohydroxycyclopentenecarboxylic acid, m. p. 186° , into hexachloroindone. The isomeric acid, m. p. 111° , is decomposed so slowly by water that the substance $\text{C}_{10}\text{O}_2\text{Cl}_8$ could not be isolated; it is probable, however, that the acid at first decomposes, thus: $\text{C}_6\text{H}_2\text{O}_3\text{Cl}_6 = \text{C}_6\text{HOCl}_5 + \text{CO}_2 + \text{HCl}$; the substance C_5HOCl_5 has not been obtained in this manner, but by the reduction of the hexachlorocyclopentenone, m. p. 28° ; it passes into the substance $\text{C}_{10}\text{O}_2\text{Cl}_8$ with elimination of hydrogen chloride. The substance $\text{C}_{10}\text{O}_2\text{Cl}_8$ probably has the constitution (I), whilst the homologues may be represented by (II) and (III).

The stability of the homologues is undoubtedly due to the presence of the methyl groups in place of the labile chlorine atoms.

The substance C_5HOCl_5 has the formula (IV) or (V), since it does not form an acetyl derivative with acetic anhydride, and yields with

phosphorus pentachloride a substance C_5Cl_8 , which may also be prepared from the hexachlorocyclopentenones.



Pentachlorocyclopentenone, $\begin{array}{c} \text{CCl} = \text{CCl} \\ \diagdown \quad \diagup \\ \text{CCl}_2 \cdot \text{CHCl} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{CO}$, prepared by the action of stannous chloride in glacial acetic acid on hexachlorocyclopentenone, m. p. 28° , crystallises in colourless needles, m. p. $81-82^\circ$. When warmed with glacial acetic acid and sodium acetate, it is converted into the substance $C_{10}O_2Cl_8$, which has already been described (Zincke, Abstr., 1897, i, 507).

Decachlorohydrindene, $C_6Cl_4 \begin{array}{c} \text{CCl}_2 \\ \diagdown \quad \diagup \\ \text{CCl}_2 \end{array} \text{CCl}_2$, is prepared by heating the substance $C_{10}O_2Cl_8$ with phosphorus pentachloride under pressure at 280° ; it crystallises in small, glistening prisms, m. p. 135° .

Pentachloroaminoindone, $C_6Cl_4 \begin{array}{c} \text{CO} \\ \diagdown \quad \diagup \\ \text{C}(\text{NH}_2) \end{array} \text{CCl}$, is formed by the action of ammonia on the substance $C_{10}O_2Cl_8$, or pentachlorocyclopentenone; it crystallises in orange needles, m. p. 205° . W. H. G.

Dichlorocyclohexenones and cycloHexadienes from o-Cresol. KARL AUWERS and FRIEDRICH VON DER HEYDEN (*Ber.*, 1909, 42, 2404—2423. Compare Abstr., 1908, i, 550—551).—A number of hydroaromatic ketones and hydrocarbons were synthesised with the object of determining the effect of the position of the double linking on the optical and other physical properties of cyclic compounds, and it is found that in the case of the ketones the shifting of a double linking into the conjugated position to the double linking of the carbonyl group produces an exaltation of molecular refraction and dispersion as well as a rise in boiling point and density; similarly, in the case of the hydrocarbons it is found that conjugated ethylene linkings produce exaltation in optical properties in accordance with Brühl's laws, and the authors are, accordingly, of opinion that a careful determination of the physical constants of compounds of this kind is a more trustworthy criterion of their purity than any chemical reactions, such as oxidation, etc., which are not of a quantitative nature.

1-Methyl-1-dichloromethylcyclohexadienone and the corresponding 4-methyl derivative were prepared as previously described (Abstr.,

1908, i, 550); they have b. p. 115—115.5°/13 mm. and 140—142°/13 mm. respectively.

1-Methyl-1-dichloromethyl-4-ethyl- Δ^2 -cyclohexen-6-one, best prepared by previously activating the magnesium by means of methyl iodide, should have D_4^{180} 1.1671 or D_4^{184} 1.1683, instead of the higher value previously quoted.

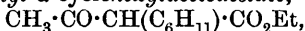
1-Methyl-1-dichloromethyl-4-isopropyl- Δ^2 -cyclohexen-6-one, $C_{11}H_{16}OCl_2$, obtained in 80—90% yield by the action of magnesium isopropyl iodide on the chloroketone, is a colourless oil, b. p. 135.4—136.4°/8 mm., D_4^{168} 1.1421, n_D^{168} 1.50142. When poured into ice-cold concentrated sulphuric acid, the double linking is shifted from the 2 to the 3 position and there results.

1-Methyl-1-dichloromethyl-4-isopropyl- Δ^3 -cyclohexen-2-one, $C_{11}H_{16}OCl_2$, b. p. 149.4—150.4°/7 mm., D_4^{158} 1.1654, n_D^{158} 1.51769. The following substances were also prepared by a similar shifting of the double bond: 1-methyl-1-dichloromethyl-4-ethyl- Δ^3 -cyclohexen-2-one, $C_{10}H_{14}OCl_2$, b. p. 150.8—151.2°/10 mm., D_4^{156} 1.1953, n_D^{17} 1.52331, and 1:4-dimethyl-1-dichloromethyl- Δ^3 -cyclohexen-2-one, which has been previously described, but for which some new physical data are given.

1-Methyl-4-isopropyl- $\Delta^{1:3}$ -cyclohexadiene or $\Delta^{1:3}$ -dihydrocymene, obtained by the action of boiling alcoholic potash on the corresponding ketone, appears to be identical with the substance described by Wallach as α -terpinene, since it behaved like this substance on oxidation, giving rise to α -dihydroxy- α -methyl- δ -isopropyladipic acid (compare Abstr., 1908, i, 813). P. H.

Hexahydropropio-phenone, Hexahydrobenzyl Methyl Ketone, Ethyl cycloHexylacetoacetate, and a Compound, $C_{10}H_{12}O_4$, Obtained in the Preparation of the Acetoacetate CARL HELL and OSCAR SCHAAL (*Ber.*, 1909, 42, 2230—2236).—Hexahydropropio-phenone (V. Meyer and Scharvin, Abstr., 1897, i, 613) can be prepared by oxidising cyclohexylethylcarbinol with chromic acid. The semicarbazone, $C_{10}H_{19}ON_3$, crystallises from dilute alcohol in plates, m. p. 149—150°. The carbinol, $C_6H_{11}\cdot CHEt\cdot OH$, obtained from magnesium cyclohexyl iodide and propaldehyde, is an oil with a penetrating odour, and has b. p. 199—201°.

A small yield of ethyl α -cyclohexylacetoacetate,



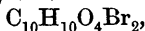
is obtained by the action of cyclohexyl iodide on sodioethylacetoacetate. It is a colourless liquid, b. p. 126—127°/14 mm. The semicarbazone, $C_{13}H_{23}O_3N$, crystallises from aqueous acetone in cubes, m. p. 114°. The free acid, $CH_3\cdot CO\cdot CH(C_6H_{11})\cdot CO_2H$, has m. p. 67—68°, and decomposes readily into carbon dioxide and hexahydrobenzyl methyl ketone.

Other products obtained in the preparation of ethyl cyclohexylacetoacetate are: cyclohexene, hexahydrobenzyl methyl ketone, ethyl dicyclohexylacetoacetate, and a compound, $C_{10}H_{12}O_4$.

Hexahydrobenzyl methyl ketone, $C_6H_{11}\cdot CH_2\cdot CO\cdot CH_3$, obtained by the ketonic hydrolysis of the acetoacetate, is a colourless liquid, b. p. 195—196°; its semicarbazone, $C_{10}H_{19}ON_3$, has been analysed.

The compound, $C_{10}H_{12}O_4$, crystallises from dilute alcohol in long

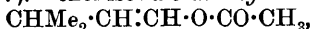
needles, m. p. 61°. It combines with bromine, but at the same time loses hydrogen bromide and yields the *dibromo*-derivative,



which crystallises from light petroleum in prisms, m. p. 118—119°.

J. J. S.

Components of Ethereal Oils. *enol-iso*Valeraldehyde Acetate and *enol*-Citronellal Acetate, and the Conversion of the Latter into *iso*Pulegol Acetate. FRIEDRICH W. SEMMLER (*Ber.*, 1909, 42, 2014—2017).—*enol-iso*Valeraldehyde acetate,



prepared by heating *isovaleraldehyde* with acetic anhydride and sodium acetate in an autoclave, is an oil, b. p. 127—133°, D_{20}^{20} 0.8818, n_D 1.41655. A small quantity of diacetate is formed at the same time, which decomposes during distillation into monoacetate.

enol-Citronellal acetate, $\text{C}_{10}\text{H}_{17}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$, is an oil, b. p. 110—115°/10 mm., D_{20}^{20} 0.902, n_D 1.45762, $[\alpha]_D^{20}$ -1°. A fraction b. p. 125—150°/10 mm. consisted mainly of diacetate. On boiling the monoacetate with acetic anhydride and acetic acid for twenty hours, *isopulegol acetate*, b. p. 100—105°/10 mm., D_{20}^{20} 0.925, n_D 1.459, is formed (compare Tiemann and Schmidt, *Abstr.*, 1897, i, 198).

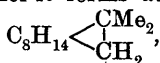
E. F. A.

[Combinations of Camphor with Phenols.] E. CAILLE (*Compt. rend.*, 1909, 148, 1458—1461).—The author has examined the freezing-point curves of mixtures of β -bromocamphor with salol (phenyl salicylate) and of camphor with salol, α - and β -naphthols, and resorcinol. In each case the curves show minima corresponding with the existence of eutectic mixtures. No evidence has been obtained of the existence of definite compounds, such as have been described by Léger (*Abstr.*, 1890, 1427). The formation of a compound containing resorcinol and camphor in molecular proportions is indicated, however, by a maximum in the curve.

W. O. W.

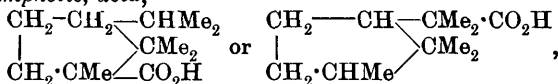
Dimethylcamphor and Dimethylcampholic Acid. ALBIN HALLER and ED. BAUER (*Compt. rend.*, 1909, 148, 1643—1648).—When camphor is treated successively with sodamide and a magnesium alkyl halide, a mixture of mono- and di-alkylcamphors results. The separation of these compounds is affected by treatment with hydroxylamine zinc hydrochloride, when the mono-alkyl derivative alone undergoes oximation. *Dimethylcamphor*, $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CMe}_2 \\ | \\ \text{CO} \end{smallmatrix}$, is a mobile

liquid with a camphoraceous odour, b. p. 106°/11 mm., D_4^{25} 0.94708, M_D 53.21, $[\alpha]_D^{24}$ 92.7°. It does not form a semicarbazone. When reduced by sodium and alcohol it forms *dimethylborneol*,



a crystalline mass, m. p. 18—20° (probably consisting of a mixture of isomerides, since crystals were obtained with m. p. 28—30°), b. p. 109—111°/13 mm., $[\alpha]_D^{23}$ 32.4°. The *phenylurethane* occurs as needles, m. p.

111.5—112°, $[\alpha]_D$ 29.5°. Dimethylcamphor resembles fenchone (Semmler, Abstr., 1906, i, 681) and the trialkylacetophenones already studied (this vol., i, 131) in its behaviour with sodamide, this reagent converting it into *dimethylcampholamide*, $C_{12}H_{28}O$, m. p. 72—73°, $[\alpha]_D$ 70.8°. Sulphuric acid and sodium nitrite convert this into *dimethylcampholic acid*,



m. p. 73—74°, $[\alpha]_D$ +47.4°. A substance corresponding with the first formula should give camphoric acid on oxidation. The acid actually obtained, however, by oxidising dimethylcampholic acid with potassium permanganate loses carbon dioxide when heated, and has not yet been identified.

W. O. W.

Preparation of *o*-, *m*-, and *p*-Hydroxy-, *p*-Dimethylamino-, and *p*-Diethylamino-benzylidenecamphors, and of *p*- and *m*-Tolylidenecamphors. ALBIN HALLER and ED. BAUER (*Compt. rend.*, 1909, 148, 1490—1496. Compare Abstr., 1891, 1498).—New derivatives of benzylidenecamphor have been prepared with the object of examining the influence of substituents in the benzene ring on the rotatory power of the compounds. The hydroxy-derivatives were obtained by acting on sodium camphor with the acetyl derivatives of *o*-, *m*-, and *p*-hydroxybenzaldehyde; the oily product was then hydrolysed to remove the acetyl group.

Salicylidenecamphor, $C_8H_{14} \begin{array}{l} \text{C}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH} \\ \text{CO} \end{array}$, occurs as highly refrac-

tive crystals, m. p. 209—210°, $[\alpha]_D$ 469°. *m*-Hydroxybenzylidenecamphor has m. p. 144—145°, $[\alpha]_D$ 423°, whilst the *p*-hydroxy-derivative has m. p. 207°, $[\alpha]_D$ 500°. These compounds are colourless, but dissolve in aqueous alkalis, giving yellow solutions which show considerably higher rotatory power.

p-Dimethylaminobenzylidenecamphor, $C_{10}H_{14}O:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, prepared by the general method, forms lamellæ, m. p. 139°, $[\alpha]_D$ 758°; the *p*-diethyl derivative, $C_{19}H_{25}ON$, forms tablets, m. p. 78—79°, $[\alpha]_D$ 740°, and like the dimethyl compound is yellow, but dissolves in hydrochloric acid, forming a colourless *hydrochloride* readily dissociated by water. The rotatory power of these two bases is considerably lower in acid solutions.

p-Tolylidenecamphor, $C_{10}H_{14}O:\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$, crystallises in colourless needles or prisms, m. p. 98°, $[\alpha]_D$ 458°; it combines with hydrogen bromide. The *meta*-derivative forms colourless prisms, m. p. 77.5°, $[\alpha]_D$ 396°. The above specific rotations are those of the compounds in *N*/30-alcoholic solution.

W. O. W.

Synthesis of Derivatives of Racemic Fenchone LOUIS BOUVEAULT and LEVALLOIS (*Compt. rend.*, 1909, 148, 1524—1526. Compare this vol., i, 497).—The following observations render it probable that the low m. p. of synthetic *r*-dihydrofencholenamide is due to the presence of a geometrical isomeride. Hypobromites act on the racemic amide (prepared from the two active amides), giving two

isomeric *carbamides*, m. p. 175° and 161°. The synthetic amide gives two *carbamides*, m. p. 162—163° and 136°. Each active amide forms a carbamide, m. p. 168° (Abstr., 1908, i, 193).

The *r-carbamide*, prepared by mixing the two active forms, has m. p. 185° (175° after re-solidification). After heating for an hour at 200°, however, it can be separated into two isomeric carbamides, m. p. 162—163° and 148°.

The two products having m. p. 162—163° are identical. It follows, therefore, that the synthetic amide contains an isomeride capable of forming the racemic *diapofenchylcarbamide* when treated with hypobromite. The active amides do not undergo the above transformation when heated.

W. O. W.

Alcohols and Aromatic Hydrocarbons Derived from Fenchone. J. LEROIDE (*Compt. rend.*, 1909, 148, 1611—1613).—Fenchol forms additive compounds with phenyl- and tolyl-magnesium bromides; these are insoluble in ether and toluene, but on prolonged heating with these solvents are converted into the magnesium derivatives of the corresponding tertiary alcohol. *tert.-Phenylfenchol*, $C_{16}H_{22}O$, has m. p. 47°, b. p. 166—177°/13 mm., $[\alpha]_D^{18}$ 45·65° in alcohol. Pyruvic acid converts it into a compound, m. p. 151—153°. When treated with anhydrous formic or oxalic acid it forms a *hydrocarbon*, $C_{16}H_{20}$, b. p. 157—158°/13—14 mm., D_4^{15} 0·9795, $[\alpha]_D^{18} + 0·60°$, n_D^{12} 1·5536. When the dehydration is effected by potassium hydrogen sulphate, an isomeric *hydrocarbon* is produced, having m. p. 16—17°, b. p. 139—141°/16 mm., $[\alpha]_D^{18} + 22·60°$; hydrobromic acid converts this into a *bromo-derivative*, m. p. 115—116°.

tert.-o-Tolylfenchol, $C_{17}H_{24}O$, b. p. 175—177°/14 mm., D_4^{15} 1·0890, $[\alpha]_D^{18} + 23·23°$. *tert.-p-Tolylfenchol*, b. p. 180—181°/15 mm., D_4^{15} 1·0272, $[\alpha]_D^{18} + 16·30°$. *tert.-Benzylfenchol*, $C_{17}H_{24}O$, crystallises in needles, m. p. 65—66°, b. p. 181—182°/15 mm., $[\alpha]_D^{18} + 24·20°$ in alcohol. When treated with anhydrous formic or oxalic acid it forms a mixture of two compounds: (1) a *hydrocarbon*, $C_{10}H_{16}$ ·CHPh, b. p. 152—154°/14—15 mm., $[\alpha]_D^{18} + 71·89°$ in alcohol, n_D^{19} 1·5472; (2) a *hydrocarbon*, $C_{17}H_{22}$, b. p. 163—166°/13—14 mm., $[\alpha]_D^{18} - 35·33°$, n_D^{19} 1·5694°.

W. O. W.

The Terpinene Question. KARL AUWERS (*Ber.*, 1909, 42, 2424—2439).—The physical constants of terpinenes prepared from eighteen different sources have been tabulated and subjected to a critical examination. Of the samples under consideration, those prepared by means of terpin cannot be regarded as terpinenes in the sense of the word employed by Wallach to indicate the α -compound containing the conjugated ethylene linkings, since their optical properties exclude the possibility of their containing more than a trace of this substance. The author is of opinion that not even the carvenene described by Semmler (this vol., i, 110) or the one obtained by Harries and Majima (Abstr., 1908, i, 734) are pure α -terpinene, but considers that the sample which he prepared from *o*-cresol (compare this vol., i, 592) is very fairly pure.

P. H.

Constituents of Ethereal Oils. Carlina Oxide. FRIEDRICH W. SEMMLER and EDMUND ASCHER (*Ber.*, 1909, 42, 2355—2360).—Attempts to ascertain whether the chain of three carbon atoms uniting the benzene and the furan rings in carlina oxide (Abstr., 1906, i, 297) contains an acetylenic or a di-olefinic linking have been unsuccessful. When α -phenyl- γ -2-furyl- Δ^{β} -propene- α -one is reduced by sodium and alcohol, the main product, in addition to tetrahydrocarlina oxide, is α -phenyl- γ -2-furylpropane- α -ol, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_4\text{OH}_3$, b. p. 168—170°/12 mm., D_4^{20} 1.10, n_D 1.55, which is obtained alone when the reduction is effected by sodium amalgam and acetic acid; the phenylurethane, $\text{C}_{20}\text{H}_{19}\text{O}_3\text{N}$, has m. p. 95.5—96°, and the acetate, $\text{C}_{15}\text{H}_{16}\text{O}_3$, has b. p. 171—172°/11 mm., D_4^{20} 1.09, n_D 1.526. The chloride, $\text{CHPhCl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_4\text{OH}_3$, b. p. 154°/10 mm., D_4^{18} 1.13, n_D 1.552, obtained from the alcohol and phosphoric chloride in light petroleum, is converted by boiling alcoholic potassium hydroxide into the ethyl ether, $\text{OEt}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_4\text{OH}_3$, b. p. 145—147°/11 mm., D_4^{20} 1.055, n_D 1.545. Hydrogen chloride can be eliminated from the chloride, however, by three to five hours' heating with anhydrous sodium acetate and glacial acetic acid at 170—180°, whereby α -phenyl- γ -2-furyl- Δ^{α} -propene (dihydrocarlina oxide), $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{C}_4\text{OH}_3$, is obtained, which has b. p. 146.5—147°/13 mm., D_4^{20} 1.029, n_D 1.552, and in its physical properties lies intermediate between carlina oxide and tetrahydrocarlina oxide.

A second method for the synthesis of carlina oxide starts with α -phenyl- γ -2-furylpropane- α -y-dione, $\text{COPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_4\text{OH}_3$, m. p. 69°, b. p. 194—196°/11 mm., which is obtained by Claisen's method (Abstr., 1896, i, 557), gives a blood-red coloration with ferric chloride, and forms an oxime, $\text{C}_{13}\text{H}_{11}\text{O}_3\text{N}$, m. p. 137°, and a dioxime, $\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_2$, m. p. 168°. The reduction of the diketone by sodium amalgam and dilute acetic acid, however, does not yield the glycol, but a diacetate, $\text{C}_{13}\text{H}_{12}\text{O}_3\text{Ac}_2$, m. p. 149°. C. S.

Javanese Basilicum Oil and Methylchavicol. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 15—16. Compare Abstr., 1901, i, 220).—Distillation in steam and fractionation of this oil (D^{14} 0.962; $a_D + 1^\circ 20'/200$ mm.) gave a fraction boiling below 88°, which contains cineol and an oil, b. p. 60—70°/in vacuo, D^{15} 0.8208, which probably contains an olefinic terpene (ocimene?).

The methylchavicol obtained from this source is always optically active; this activity is destroyed by treatment with magnesium methyl iodide, but not by acetic anhydride, potassium permanganate, or sodium hydrogen sulphite. Methylchavicol, when heated in a sealed tube for forty-eight hours at 250°, gives two crystalline substances, m. p. 98° and 166°, which appear to be dimolecular isomerides of methylchavicol. The compound of m. p. 98° gives a dibromide, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{Br}_2$, m. p. 87°. W. R.

Essential Oil from the Fruit of Morinda citrifolia L. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 17—19).—This oil (D^{13} 0.927) is remarkable, as it contains 90% of free octoic and hexoic acids, the amount of the latter being approxi-

mately 12% of the free fatty acids present. The neutral volatile constituents consist of the ethyl esters of these acids together with traces of the methyl (?) esters. The crude oil also contains crystals of a saturated hydrocarbon, m. p. 60°, in suspension. W. R.

Turmeric Oil. HANS RUPE, E. LUKSCH, and A. STEINBACH (*Ber.*, 1909, 42, 2515—2520. Compare Abstr., 1908, i, 95).—From turmeric oil having D_{20}^{20} 0.9388 and $[\alpha]_D^{20}$ -24.76°, the authors have been unable to isolate Jackson and Menke's turmerol. By heating the oil with alcohol and 30% potassium hydroxide, a ketone, *curcumone*, $C_{13}H_{18}O$, has been obtained, which has b. p. 121°/10 mm., D_{20}^{20} 0.9566, n_D 1.50526, $[\alpha]_D$ 80.55°, forms a *semicarbazone*, m. p. 120—121°, an *oxime*, b. p. 159°/11 mm., a *phenylhydrazone*, m. p. 92°, a *p-bromophenylhydrazone*, m. p. 71°, and condenses with benzaldehyde to form the compound, $C_{13}H_{16}O:CHPh$, m. p. 106°, with piperonal to form the compound, $C_{13}H_{18}O:CH \cdot C_6H_5 \cdot O_2 \cdot CH_2$, m. p. 86°, and with anisaldehyde to form a similar compound, m. p. 77—78°. C. S.

Constitution of Bixin. J. F. B. VAN HASSELT (*Chem. Weekblad*, 1909, 6, 480—483. Compare Etti, Abstr., 1874, 907; 1878, 739; Zwick, Abstr., 1897, i, 630; Marchlewski, Abstr., 1906, i, 760).—A study has been made of the properties of bixin, the red colouring matter of *Bixa orellana*. Its empirical formula is $C_{29}H_{34}O_5$, containing one carbon atom more than that hitherto accepted. It has m. p. 189° (corr.). At 190° it yields *m*-xylene, but no other volatile product. When one gram-molecule is heated in a current of hydrogen at 200°, it loses one gram-molecule of *m*-xylene, but it is not probable that the *m*-xylene nucleus is present as such in the bixin molecule. Zwick's statement that heating for several hours in steam at 160° converts bixin into palmitic acid was not substantiated, no change taking place. The statement of Zwick that bixin contains two carbonyl groups, based on the formation of a condensation product with phenylhydrazine, is also regarded as of doubtful value.

Acids convert solutions of the di-potassium salt into a substance to which the name *norbixin* has been assigned. Unlike bixin, *norbixin* does not contain a methoxyl group. It is a light red mass of microscopic crystals, does not melt, but darkens and decomposes at 240°. It is readily oxidised. Its empirical formula is $C_{28}H_{32}O_5$.

Potassium bixinate and methyl sulphate yield diamond-shaped plates of *bixin methyl ether*, $R(OMe)_2$, m. p. 156°. On methylation, *norbixin* yields bixin, and then bixin methyl ether. From diethyl sulphate were prepared *bixin ethyl ether*, $R(OMe) \cdot OEt$, m. p. 138°; *norbixin monoethyl ether*, $OH \cdot R \cdot OEt$, m. p. 176°, and *norbixin diethyl ether*, $R(OEt)_2$, m. p. 121°. Methylation of *norbixin* monoethyl ether forms *norbixin methyl ethyl ether*, $OMe \cdot R \cdot OEt$, m. p. 149°, isomeric with bixin ethyl ether. *isoBixin*, $OH \cdot R \cdot OMe$, is obtained by partial saponification of methylbixin. It forms short, acicular crystals, m. p. 178°.

On reduction with zinc dust in isatin solution, bixin derivatives take up two hydrogen atoms, forming yellow, crystalline compounds. *Dihydrobixin* has m. p. 200°; *dihydrobixin methyl ether*, 174°, and

dihydroisobixin, 191°. *Dihydronorbixin* is infusible, and melts at 235°.

Bixin takes up ten bromine atoms, forming white, amorphous, very unstable bromo-derivatives. Its unsaturated character is also indicated by its reacting with iodine chloride. Both reagents point to the presence of five ethylene linkings.

A. J. W.

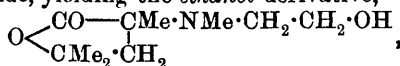
History of the Optical Activity of Tannin. OTTO ROSENHEIM (*Ber.*, 1909, 42, 2452—2453).—The optical activity of tannin was first observed by Ph. van Tieghem, who recorded the fact in *Ann. Sci. Nat.*, 1867, [v], 8, 210.

P. H.

The Lactones of α -Dihydroxy- α -dimethylvaleric Acid and α -Methylamino- γ -hydroxy- α -dimethylvaleric Acid. MORITZ KOHN (*Monatsh.*, 1909, 30, 401—406).—The lactone of α -dihydroxy- α -dimethylvaleric acid (4-hydroxy-5-keto-2:2:4-trimethyltetrahydrofuran) (compare Franke and Kohn, *Abstr.*, 1907, i, 816; Kohn, *Abstr.*, 1908, i, 819) may be prepared by hydrolysing the cyanohydrin of diacetone alcohol (β -methylpentane- β -ol- δ -one) with fuming hydrochloric acid; it has m. p. 66—68°, b. p. 230—232°/745 mm.; the b. p. given previously (*loc. cit.*) is incorrect.

Diacetone alcohol cyanohydrin cannot be prepared directly from diacetone alcohol, but is obtained as a viscid oil by the action of potassium cyanide on the sodium hydrogen sulphite compound of the keto-alcohol.

4-Methylamino-5-keto-2:2:4-trimethyltetrahydrofuran combines with ethylene oxide, yielding the *ethanol* derivative,



a viscid liquid which could not be crystallised; the *methiodide* is crystalline, and yields the crystalline *aurichloride*, $\text{C}_{11}\text{H}_{21}\text{O}_3\text{N} \cdot \text{HAuCl}_4$, when treated successively with silver chloride and auric chloride.

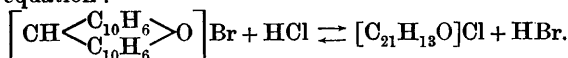
W. H. G.

Oxonium Compounds and Pyryl Salts. ROBERT FOSSE (*Bull. Soc. chim.*, 1909, [iv], 5, 692—698).—It is pointed out that the essential difference between oxonium compounds containing the elements of the halogen acids, and pyryl salts is that the former are produced by simple addition of the acid, and thus correspond with ammonium salts (compare Collie and Tickle, *Trans.*, 1899, 75, 710), whilst in the formation of pyryl salts, water is eliminated (Fosse, *Abstr.*, 1901, i, 604, 643; 1902, i, 171, and Werner, *Abstr.*, 1902, i, 50), so that the production of pyryl salts corresponds with the formation of ordinary metallic salts.

T. A. H.

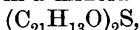
Metallic Character of an Organic Radicle. ROBERT FOSSE (*Compt. rend.*, 1909, 148, 1607—1609. Compare *Abstr.*, 1901, i, 604, 643; 1902, i, 51, 171).—The monohalogen derivatives of dinaphthaxanthone resemble certain metallic salts in their behaviour towards mineral acids and towards hydrogen sulphide. Thus the

monobromo-derivative reacts with hydrogen chloride in accordance with the equation :



A similar reversible reaction takes place when picric acid is added to a solution of the chloro-derivative in acetic acid. The *picrate*, $\text{C}_{27}\text{H}_{15}\text{O}_8\text{N}_3$, is deposited in reddish-violet crystals, m. p. above 220° (decomp.).

When hydrogen sulphide is passed into a solution of one of the salts of dinaphthaxanthone in a mineral acid, the *sulphide*,



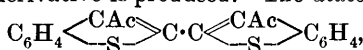
is precipitated. This is decomposed by boiling halogen acids into hydrogen sulphide and a halogen salt of dinaphthaxanthone.

W. O. W.

Reduction of the Thiophen Nucleus ; a Correction. VICTOR THOMAS (*Bull. Soc. chim.*, 1909, [iv], 5, 736).—The supposed reduction of thiophen by the Sabatier and Senderens method (this vol., i, 251) is erroneous. Pure thiophen is not reduced, and the benzene previously detected in the products of the reaction is to be attributed to impurities in the thiophen used.

E. H.

Derivatives of "Thioindigo." BÉCHAMP (*Compt. rend.*, 1909, 148, 1677—1679. Compare this vol., i, 425).—"Thioindigo" [2:2'-bisoxythionaphthen] undergoes reduction when treated with an organo-magnesium halide ; the product after treatment with water is a white substance, which rapidly reverts to "thioindigo" ; when the decomposition is effected by acetyl or benzoyl chloride, however, an acetyl or benzoyl derivative is produced. The *diacetyl* derivative,



forms colourless needles, m. p. 248° (decomp.) ; the *monobenzoyl* derivative, $\text{C}_{16}\text{H}_9\text{O}_2\text{S}_2 \cdot \text{COPh}$, forms slender needles, m. p. 225° (decomp.), which oxidise on exposure to air. These derivatives are identical with the substances obtained when "thioindigo" is reduced with tin and hydrochloric acid and then treated with acetic anhydride or benzoyl chloride.

W. O. W.

A New Alkaloid from the Bark of Pseudocinchona Africana (Rubiaceæ). ERNEST FOURNEAU (*Compt. rend.*, 1909, 148, 1770—1772).—The author describes the preparation and properties of a new monobasic alkaloid from *Pseudocinchona africana* (Perrot, *Compt. rend.*, 1909, 148, 1465). The compound is isomeric with quebrachine, and has the formula $\text{C}_{21}\text{H}_{26}\text{O}_3\text{N}_2$; it crystallises from absolute alcohol in anhydrous, hexagonal tablets, or from dilute alcohol in elongated spangles containing water of crystallisation. On the Maquenne block it melts below 200° , then solidifies, and again melts at 241 — 242° ; a 2% solution in alcohol has $[\alpha]_D^{23} - 125^\circ$. A solution in concentrated sulphuric acid rapidly becomes brown ; on the addition of a crystal of potassium dichromate a black film is formed and deep blue streaks are seen in the liquid. The *hydrochloride* crystallises from alcohol in

hexagonal leaflets, m. p. 285—290°, or from water in prismatic needles containing 2 to 3 H_2O ; $[\alpha]_{\text{D}} - 63^\circ$. The normal *sulphate* forms brilliant, acicular, hexagonal prisms very soluble in water. The *tartrate* crystallises in rectangular tablets; the *methiodide* in prismatic needles, m. p. above 300°.

W. O. W.

Alkaloids of *Dicentra pusilla*. Y. ASAHINA (*Arch. Pharm.*, 1909, 247, 201—212).—This Japanese plant has been found to contain protopine, a new alkaloid, dicentrine, and a yellow colouring matter, which appears to be identical with *isorhamnetin* (Perkin and Hummel, *Trans.*, 1896, 69, 1568).

The finely ground plant was extracted with alcohol containing acetic acid, and the concentrated extract poured into dilute acetic acid. On shaking the filtrate with ether, the latter extracted a substance crystallising in slender, yellow needles, and having the composition and properties of *isorhamnetin* and yielding a similar tetra-acetyl derivative (*loc. cit.*).

The acetic acid filtrate on addition of a slight excess of ammonia solution gave a dirty greenish-yellow precipitate, which was purified somewhat by re-precipitation several times and then dried and fractionally crystallised from ether. The first fraction consisted of protopine, which Gadamer had already found in *Dicentra spectabilis* (Abstr., 1902, i, 52) and Heyl in *D. formosa* (Abstr., 1903, i, 716). The later fractions consisted of *dicentrine*, $\text{C}_{20}\text{H}_{21}\text{O}_4\text{N}$, m. p. 168—169°, $[\alpha]_{\text{D}} + 62.1^\circ$ in chloroform, which forms prismatic crystals, $a:b:c = 0.7673:1.0000:0.4424$, from ether, alcohol, or ethyl acetate. The *hydrochloride*, *hydrobromide*, and *nitrate* are all crystalline, as is also the *platinichloride*, although the last-mentioned salt cannot be re-crystallised from water or alcohol. The *aurichloride* is very unstable. The *methiodide*, $\text{C}_{20}\text{H}_{21}\text{O}_4\text{N} \cdot \text{MeI} \cdot \text{H}_2\text{O}$, m. p. 224°, crystallises from dilute alcohol. Dicentrine contains two methoxyl groups, and yields a *monoacetyl* derivative, m. p. 202°, which forms colourless leaflets and is not hydrolysed by potassium hydroxide in alcohol even on boiling. Dicentrine resembles closely the alkaloid, m. p. 168.5—169°, previously obtained by Heyl (*loc. cit.*).

T. A. H.

ψ -Morphine. GABRIEL BERTRAND and V. I. MEYER (*Compt. rend.*, 1909, 148, 1681—1683. Compare Polstorff, Abstr., 1880, 408; Hesse, Abstr., 1884, 616).—Determinations of the molecular weight of ψ -morphine by the cryoscopic or ebullioscopic methods are valueless, owing to the tendency of the substance to molecular association; the hydrochloride, on the other hand, undergoes dissociation in aqueous solution, and gives values for the molecular weight which are in agreement with Hesse's formula for the base, $\text{C}_{34}\text{H}_{36}\text{O}_6\text{N}_2$. The molecular weight of the acetyl derivative also agrees with this formula. The author considers that ψ -morphine arises by elimination of two atoms of hydrogen from 2 mols. of morphine, followed by union of the two morphine residues through two carbon atoms. The optical properties of the substance suggest that the two morphine residues are not symmetrically arranged with respect to one another.

W. O. W.

Strychnos Alkaloids. IV. Reactions of Strychninonic Acid and Fission of the Strychnine Molecule. HERMANN LEUCHS and WILHELM SCHNEIDER (*Ber.*, 1909, 42, 2494—2499).—In its reactions strychninonic acid (*Abstr.*, 1908, i, 564) closely resembles brucinonic acid (this vol., i, 253). It yields a neutral monoethyl ester, and also an oxime and semicarbazone. The *ethyl* ester, $C_{23}H_{24}O_6N_2$, crystallises from hot alcohol in colourless prisms, m. p. 209—210° (corr.). The *oxime*, $C_{21}H_{21}O_6N_3 \cdot H_2O$, crystallises from hot water in rectangular prisms, loses its water of crystallisation at 135° under reduced pressure, and has m. p. 268—271° (decomp.). Its alkaline solution has $[\alpha]_D^{20} + 119^\circ$. The *semicarbazone*, $C_{22}H_{23}O_6N_3$, forms long, slender needles, m. p. 256—257° (corr.). When reduced with sodium amalgam, the acid yields *strychninolic acid*, $C_{21}H_{22}O_6N_2$, which crystallises from water in long prisms, m. p. 238°.

Acetylstrychninolic acid, $C_{23}H_{24}O_6N_2$, crystallises from 50% acetic acid in long needles, m. p. 281° (corr.). When a solution of the reduced acid in *N*-sodium hydroxide solution is kept for several hours, glycollic acid and *strychninolone*, $C_{19}H_{18}O_3N_2$, are formed. The latter crystallises from alcohol in glistening prisms, or from hot water in colourless, six-sided plates, m. p. 236° and $[\alpha]_D^{20} - 112.4^\circ$.

The conclusion is drawn that strychninonic acid contains the grouping $C_{17}H_{18}(:N \cdot CO)(:N)(CO_2H)_2(CO)$. J. J. S.

Pyrrole. EUGEN KHOTINSKY (*Ber.*, 1909, 42, 2506—2507).—By saturating a mixture of ammonium mucate and excess of glycerol with dry ammonia at 270°, and then distilling at 320—330°, and redistilling the distillate, the author has obtained a 41.6% yield of pyrrole.

C. S.

Equilibrium in the System: Silver Chloride and Pyridine. LOUIS KAHLENBERG and WALTER J. WITTICH (*J. Physical Chem.*, 1909, 13, 421—425).—The solubility of silver chloride in pyridine has been determined from the melting point of pyridine to 110°. The eutectic temperature lies at -56°; from -56° to -22° the solubility gradually increases, the solid in equilibrium with the solution being the compound $AgCl \cdot 2C_5H_5N$. From -22° to -1° the solubility continues to increase with the temperature, the solid in equilibrium with the solution being a second compound, $AgCl \cdot C_5H_5N$, occurring in small, needle-shaped crystals. From -1° to 110° the solution is in equilibrium with silver chloride, and the solubility steadily diminishes as the temperature rises, becoming almost zero at the higher temperature.

G. S.

Electrolysis of Quaternary Pyridinium and Quinolinium Salts. BRUNO EMMERT (*Ber.*, 1909, 42, 1997—1999. Compare this vol., i, 376).—By the electrolysis of benzylpyridinium chloride between platinum electrodes in sodium carbonate solution, dibenzylidihydrodipyridyl (compare Hofmann, *Abstr.*, 1881, 921) is formed. Seemingly, the unsaturated complex $C_5H_5N \cdot CH_2 \cdot C_6H_5$ is first formed;

in this the nitrogen tends to become tervalent, and in so doing frees a carbon valency in the pyridine nucleus with the result that two such nuclei unite. It is not yet established whether this takes place in the 2, 3, or 4-position.

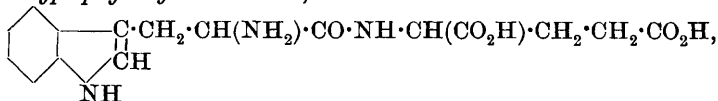
Similarly, methylquinolinium iodide forms *dimethyldihydrodiquinolyl*, and ethylquinolinium iodide gives *diethyldihydrodiquinolyl*. Both are microcrystalline, and reduce silver nitrate on warming. E. F. A.

Polypeptides containing *l*-Tryptophan. EMIL ABDERHALDEN (*Ber.*, 1909, 42, 2331—2336. Compare *Abstr.*, 1908, i, 932).—*l*-Leucyl-*l*-tryptophyl-*d*-glutamic acid has been synthesised for comparison with the polypeptide composed of leucine, tryptophan, and glutamic acid, obtained by the partial hydrolysis of edestin. The two peptides have many properties in common, but differ in that the synthetic product is not precipitated by tannin from aqueous solution, and is sparingly soluble in cold water, whereas the analytical product gives a dense precipitate with a tannin solution insoluble in excess, and is easily soluble in water. The synthetic peptide has $[\alpha]_D^{20} + 17.4^\circ$; the analytic compound, $[\alpha]_D^{20} + 8.2^\circ$.

A dipeptide composed of tryptophan and glutamic acid was also isolated from edestin, and is now compared with *l*-tryptophyl-*d*-glutamic acid. The two peptides are very similar; the synthetic product, however, has m. p. 173° , $[\alpha]_D^{20} + 34.35^\circ$; the analytic product, m. p. 162° , $[\alpha]_D^{20} + 19.8^\circ$. It is considered that the analytic product is possibly a mixture.

The tripeptide was synthesised both by converting *l*-leucyl-*l*-tryptophan into the chloride and coupling this with *d*-glutamic acid, whereby only small quantities of an amorphous product were obtained, and also by coupling *l*-tryptophyl chloride and *d*-glutamic acid to the dipeptide, *l*-tryptophyl-*d*-glutamic acid, coupling this further with *d*-bromoisohexoyl chloride, and converting the bromo-compound formed, by means of aqueous ammonia, into the tripeptide. The *d*-glutamic acid was prepared from gliadin; the *l*-tryptophan obtained from the digestion of casein with pancreatin; it is convenient to decompose the mercury sulphate precipitate with barium sulphide.

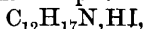
l-Tryptophyl-*d*-glutamic acid,



forms minute, colourless needles, which sinter at 170° , m. p. 173° (corr.), and have $[\alpha]_D^{20} + 34.35^\circ (\pm 0.2^\circ)$. It gives precipitates with phosphotungstic acid and tannin, soluble in excess of the reagents. *d*- α -Bromoisohexoyl-*l*-tryptophyl-*d*-glutamic acid was obtained as an oily product, which subsequently gave a hygroscopic solid. On hydrolysis with 25% aqueous ammonia at 37° , it was converted into *l*-leucyl-*l*-tryptophyl-*d*-glutamic acid, which crystallises in macroscopic plates aggregated in clusters; these sinter at 224° , m. p. 230° (corr.). It gives a precipitate with mercury sulphate, phosphotungstic acid, and ammonium sulphate, but none with tannin, and shows a violet-red biuret reaction. It has $[\alpha]_D^{20} + 17.4^\circ (\pm 0.2^\circ)$. E. F. A.

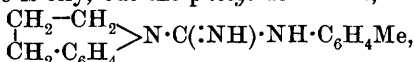
Relative Stabilities of the Piperidine and Tetrahydroquinoline Rings. JULIUS VON BRAUN (*Ber.*, 1909, 42, 2219—2227. Compare this vol., i, 507).—A study of the behaviour of cyanogen bromide towards ethylpiperidine and ethyl tetrahydroquinoline, propylpiperidine, and propyltetrahydroquinoline indicates that the piperidine ring is ruptured about twice as easily as the tetrahydroquinoline ring.

1-Propyltetrahydroquinoline, $C_6H_4 \begin{smallmatrix} CH_2 \cdot CH_2 \\ \diagup \quad \diagdown \\ N(C_3H_7) \end{smallmatrix} CH_2$, obtained from tetrahydroquinoline and propyl iodide, has b. p. $146^\circ/16$ mm. The *picrate*, $C_{12}H_{17}N, C_6H_3O_7N_3$, has m. p. 73° ; the *hydriodide*,



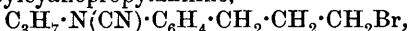
crystallises from water in brilliant needles, m. p. 178° ; the *hydrobromide* has m. p. 177° , and the *hydrochloride*, m. p. 162° . When heated on the water-bath with cyanogen bromide, the propyl derivative yields propyl bromide, cyanotetrahydroquinoline, and *o*- γ -bromopropylcyanopropylaniline.

1-Cyanotetrahydroquinoline, $C_6H_4 \begin{smallmatrix} CH_2 \cdot CH_2 \\ \diagup \quad \diagdown \\ N(CN) \end{smallmatrix} CH_2$, is a colourless oil, b. p. 185 — $188^\circ/17$ mm., and, when boiled with acid, yields tetrahydroquinoline, and with bases yields guanidine derivatives. The *phenyl* derivative is oily, but the *p-tolyl* derivative,



obtained by heating the cyano-compound with *p*-toluidine hydrochloride at 150° , crystallises from ether in brilliant, colourless needles, m. p. 180° .

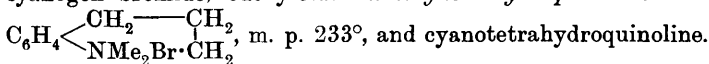
o- γ -Bromopropylcyanopropylaniline,



could not be isolated.

1-Ethyltetrahydroquinoline has b. p. 134 — $135^\circ/16$ mm., and the *picrate*, $C_{11}H_{15}N, C_6H_3O_7N_3$, has m. p. 122° .

1-Methyltetrahydroquinoline is not ruptured when heated with cyanogen bromide, but yields *dimethyltetrahydroquinolinium bromide*,



J. J. S.

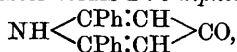
Rupture of Cyclic Bases by Hofmann's Method. JULIUS VON BRAUN (*Ber.*, 1909, 42, 2532—2538).—Having shown previously that cyanogen bromide breaks the ring in tertiary bases of the piperidine and tetrahydroquinoline series containing ethyl, propyl, butyl, or an aromatic group attached to the nitrogen, but not in those containing methyl or an unsaturated radicle (*Abstr.*, 1907, i, 960; this vol., i, 507; preceding abstract), the author has investigated the rupture of these bases by Hofmann's method of exhaustive methylation and distillation. It is known that 1-methyltetrahydroquinoline, by successive treatment with methyl iodide, silver oxide, and distillation, regenerates itself. Since 1-ethyltetrahydroquinoline methiodide and 1-propyltetrahydroquinoline methiodide, m. p. 135° , under these conditions yield a mixture of 1-methyltetrahydroquinoline and 1-ethyl-

tetrahydroquinoline or 1-propyltetrahydroquinoline, it appears that tertiary tetrahydroquinolines containing an alkyl group are not ruptured by Hofmann's method. In the piperidine series there seems to be a periodic relation between ease of rupture and the magnitude of the alkyl group attached to the nitrogen atom, for whereas 1-methylpiperidine is completely ruptured by the preceding treatment, the ethyl homologue is not, the propyl compound only very slightly (the main products being the original tertiary base and 1-methylpiperidine), the butyl compound is very largely ruptured, and the *iso*-amyl compound only partly. A plausible explanation of this behaviour cannot yet be found. C. S.

Synthesis of 6:7-Dimethoxyisoquinoline. LEOPOLD RÜGHEIMER and P. SCHÖN (*Ber.*, 1909, 42, 2374—2377. Compare Pictet and Kay, this vol., i, 513).—Veratrylaminoacetal (Abstr., 1908, i, 153) is added slowly to a mixture of concentrated sulphuric acid and arsenic acid cooled by ice and salt, and after one hour the mixture is heated on the water-bath. The resulting 6:7-dimethoxyisoquinoline is liberated by sodium hydroxide, removed by ether, and purified by means of the hydrochloride. It appears to be identical with the substance of the same composition obtained by Goldschmiedt by the oxidation of papaverine (Abstr., 1888, 302). C. S.

Condensation of Esters of Acetonedicarboxylic Acid with Aldehydes by means of Ammonia and Amines. PAVEL PETRENKO-KRITSCHENKO and S. SCHÖTTLE (*Ber.*, 1909, 42, 2020—2025. Compare Abstr., 1906, i, 452; 1907, i, 708; 1908, i, 564).—Ethyl 2:6-diphenylpiperidone-3:5-dicarboxylate (*loc. cit.*) possesses acid characters and forms a *potassium* salt, m. p. 300°.

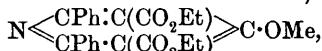
When kept for a time in alkaline solution, and then precipitated with acid, the ester is obtained in a form, m. p. 145—150°. On crystallisation, the melting point rises gradually to the normal (195°). The isomeride is probably the unstable enolic form. When hydrolysed and heated at 258°, the ester forms 2:6-diphenyl-4-pyridone,



m. p. 176—178°. This is still acidic, and forms a *potassium* salt, m. p. 114—140°; the *hydrochloride* has m. p. 249—253°; the *platinichloride*, m. p. 218—221°. The above dicarboxylic acid, when mixed with zinc dust and distilled, forms 2:6-diphenylpyridine, m. p. 81—82°, identical with that described by Scholtz (Abstr., 1895, i, 563).

4-Chloro-2:6-diphenylpyridine, $\text{N} \begin{array}{c} \diagup \text{CPh:CH} \\ \diagdown \text{CPh:CH} \end{array} \text{CCl}$, prepared by mixing diphenylpyridone with phosphorus pentachloride, moistening the mass with phosphoryl chloride, heating for two hours at 140—150°, and pouring into water, is obtained in needles, m. p. 72°. On repetition of the process, the *dichloride*, $\text{C}_{17}\text{H}_{13}\text{NCl}_2$, m. p. 120°, was alone obtained. 2:6-Diphenyl-1-methyl-4-pyridone, treated in a similar manner, forms a monochloride, m. p. 67°, or after treatment with ammonia, m. p. 72°. The last compound when dissolved in benzene and precipitated by hydrogen chloride has m. p. 67°.

Ethyl 2 : 6-diphenyl-1-methylpyridone-3 : 5-dicarboxylate, prepared by the action of methyl iodide, has m. p. 244° ; the corresponding *acid* has m. p. 270° . At the same time the isomeric *ester*, m. p. 189° ,



is formed. The corresponding *acid* has m. p. 125° , and when heated with alcoholic potassium hydroxide, it is readily converted into the isomeride, m. p. 270° . E. F. A.

Cyanodihydrocyclic Amines. I. Acridine Series. ADOLF KAUFMANN and ALBERTO ALBERTINI [and, in part, MAX HOLSBOER] (*Ber.*, 1909, 42, 1999—2008).—Analogous to the decomposition of quaternary tetramethylammonium cyanide into trimethylamine and acetonitrile, the cyclic ammonium cyanides should give cyanodihydrocyclic amines. The cyanoacridines studied are characterised by their marked crystallising power.

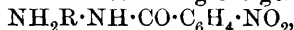
Acridine methochloride, $\text{C}_{13}\text{H}_9\text{N} \cdot \text{MeCl}$, crystallises in large, well-formed, yellow needles, m. p. 177° (decomp.); the *platinichloride* is a bright yellow, microcrystalline powder, which becomes brown at 230° , and then blackens, m. p. 278 — 280° ; the *mercurichloride* is a yellow, sparingly soluble powder, m. p. 242 — 244° .

5-Cyano-10-methyldihydroacridine, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}(\text{CN}) \\ \text{NMe} \end{array} \text{C}_6\text{H}_4$, prepared by the interaction of acridine methochloride with potassium cyanide, crystallises in colourless needles, m. p. 143° . It has basic properties and forms stable salts; the *platinichloride* separates as long, red needles, decomp. at 200° , which are not yet melted at 280° ; the *picrate* crystallises in red needles, m. p. 189° . It is very easily oxidised on warming the alcoholic solution with alkali, or in the cold with hydrogen peroxide, 10-methylacridone being formed.

5-Phenylacridine methochloride is a greenish-yellow powder, m. p. 225 — 226° ; the *platinichloride* forms golden-yellow, glistening plates, m. p. 230° to a red liquid; the *mercurichloride* separates as lustrous, yellow needles, m. p. 231° . 5-Cyano-5-phenyl-10-methyldihydroacridine (compare Hantzsch and Kalb, *Abstr.*, 1900, i, 113) has m. p. 182 — 183° , and crystallises in long, colourless needles or prisms. It has weak basic properties, forming a *platinichloride*, m. p. 242 — 243° , which, when heated with hydrochloric acid, is readily converted into the *platinichloride* of phenylacridine methochloride.

5-Phenylacridine ethiodide crystallises in well-formed, dark red needles, m. p. 220° . 5-Cyano-5-phenyl-10-ethyldihydroacridine is obtained in colourless needles, m. p. 140° . The cyano-10-methyldihydroacridines are remarkable stable towards mineral acids, and withstand prolonged heating with concentrated hydrochloric acid without changing. Heating with concentrated sulphuric acid eliminates hydrogen cyanide, and gives rise to the formation of the quaternary sulphate. E. F. A.

[Production of Aromatic Nitrobenzoyldiamines and their Azo-derivatives.] FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 208968).—The diamines having the general formula



where R is a bivalent aromatic radicle, are produced by treating with *m*- or *p*-nitrobenzoyl chloride the monoformyl derivative of the diamine, $R(NH_2)_2$. The formyl group is then readily removed by hydrolysis.

Nitrobenzoyl-p-phenylenediamine, $NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4 \cdot NH_2$, lustrous, brownish-golden flakes, m. p. 228° , is prepared by shaking together *p*-nitrobenzoyl chloride and formyl-*p*-phenylenediamine in an aqueous suspension containing some acid-fixing material, such as chalk, sodium carbonate, or sodium acetate, and then hydrolysing the diacylated diamine with dilute hydrochloric or sulphuric acid. The patent contains a tabulated summary of the physical properties of seven other nitrobenzoyldiamines obtained from *p*-phenylenediamine and 2:4-tolylenediamine. These products when diazotised and coupled with 6-amino- α -naphthol-3-sulphonic acid in alkaline solution give rise to nitroazo-compounds, which may be reduced with sodium sulphide, yielding diaminoazo-dyes which dye cotton directly, and on further diazotisation and development on the fibre with β -naphthol give bluish-red colours.

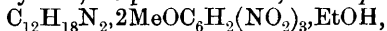
F. M. G. M.

Condensation of 2-Methylindole with Formaldehyde. E. VOISENET (*Bull. Soc. chim.*, 1909, [iv], 5, 736—742).—The action of aliphatic and aromatic aldehydes on 2-, 3-, and 7-methylindoles has been studied by Fischer (Abstr., 1888, 283), Freund and Lebach (Abstr., 1903, i, 278; 1905, i, 663), and Renz and Læw (Abstr., 1904, i, 190), but hitherto the aldehydes employed have not included formaldehyde. With the object of elucidating the sensitive colour reaction given by the latter aldehyde with protein substances in the presence of a weak oxidising agent and excess of acid (Abstr., 1906, ii, 59), the author is investigating its condensation with indole and the methylindoles. Unlike other aliphatic aldehydes, formaldehyde condenses quite readily with 2-methylindole. When the latter is treated with commercial formaldehyde, it is converted into *dimethyl-3-methylenedi-indole*, $CH_2 \left[C \begin{smallmatrix} \swarrow CMe \\ \searrow C_6H_4 \end{smallmatrix} > NH \right]_2$, a colourless substance crystallising from acetone in prisms and from alcohol or ether in needles, which soften at 230° and have m. p. 240° . On exposure to light and air, the crystals become coloured, first orange-red, and then deep red. Dimethylmethylenedi-indole is not decomposed by water; it dissolves in concentrated hydrochloric or glacial acetic acids, but the corresponding salts are too unstable to be isolated, and in the presence of hot concentrated hydrochloric acid, it tends to decompose into methylindole and methylenemethylindole. With platinic or auric chlorides, its hydrochloric acid solution gives a dark grey precipitate, becoming reddish-violet on exposure to air. Dimethylmethylenedi-indole is readily oxidised, when its acetone solution is boiled with an alcoholic solution of chloranil containing a few drops of hydrochloric acid, the magenta-red colouring matter, *dimethylmethylenediroindole*, being produced. The colour of the latter is destroyed by alkalis or reducing agents.

The condensation of formaldehyde with 2-methylindole takes place in the absence of any catalyst, although a trace of formic or other acid accelerates the reaction.

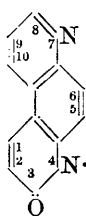
E. H.

ψ -Phenanthroline. ADOLF KAUFMANN and RADOSLAV RADOŠEVIĆ [with RICHARD HÜSSY and WULF DAMJE] (*Ber.*, 1909, 42, 2612—2622).—The author suggests replacing the accepted names phenanthroline, ψ -phenanthroline, and *isophenanthroline* by the terms *m*-phenanthroline, *p*-phenanthroline, and *o*-phenanthroline. A quantitative yield of ψ -phenanthroline may be obtained by warming on an oil-bath a mixture of 6-aminoquinoline, arsenic acid, glycerol, and concentrated sulphuric acid; by diluting the resulting liquid, and pouring it drop by drop into the calculated quantity of alkali hydroxide, the substance is precipitated in the form of colourless needles free from the resinous impurities commonly met with in this preparation; the anhydrous substance, dried at 110°, crystallises from light petroleum in needles, m. p. 177°. A *mercuric* salt is precipitated from aqueous solutions of ψ -phenanthroline by the addition of mercuric chloride; it crystallises from dilute hydrochloric acid in feathery aggregates, m. p. 182—185°. The *picrate* forms yellow needles, m. p. 249—250°; the *monomethiodide*, fine yellow needles, m. p. 257° (decomp.); the corresponding *chloride*, yellow needles, m. p. 218—221°; the *methyl picrate*, glistening needles, m. p. 235°; the *dimethiodide*, prepared by the action of potassium iodide on the methyl sulphate additive compound, large, reddish-brown prisms, m. p. 265° (decomp.); the corresponding *chloride*, from the methyl sulphate compound and sodium chloride, stout, brownish-yellow crystals, m. p. 218—220°; the *dipicrate*,

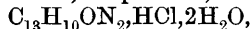


prepared by adding picric acid to an alcoholic solution of the dimethiodide or chloride, forms brown needles, m. p. 233—237°. Attempts to oxidise phenanthroline to the corresponding quinone, or to prepare a nitro-derivative, failed.

4-Methyl- ψ -phenanthrol-3-one, annexed formula, obtained by treating



ψ -phenanthroline methiodide with potassium ferricyanide and potassium hydroxide, separates from benzene in faintly yellow crystals, m. p. 239—240°; the *mercuric* salt forms yellowish-brown needles, m. p. 280°; the *hydrochloride*,



yellow needles, m. p. 297—298°; the *nitrate*, yellowish-red needles, m. p. 229—230°; the *methiodide*, obtained from the methylsulphate additive compound and potassium iodide, forms yellow needles, decomposes at 260°, and melts at 294—295°; the *methyl picrate* forms yellow needles and leaflets, m. p. 255°.

5-Nitro-4-methyl- ψ -phenanthrol-3-one, prepared by warming phenanthroline nitrate on a water-bath with a mixture of concentrated sulphuric acid and fuming nitric acid, crystallises from alcohol in yellow needles, m. p. 301—303°; forms a *picrate*, m. p. 225°, and a *platinum* salt.

5-Amino-4-methyl- ψ -phenanthrol-3-one, $\text{C}_{13}\text{H}_{11}\text{ON}_3 \cdot 2\text{H}_2\text{O}$, obtained by reducing the last-mentioned nitro-compound with ammonium sulphide, crystallises from water in brownish-yellow needles, m. p. 250°; the *hydrochloride*, red needles, decomposes above 300°; the *acetyl* derivative, silken needles, m. p. 280°; the *picrate*, dark red powder, decomposes at 263°.

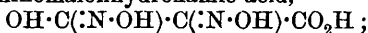
4 : 7-Dimethyl- ψ -phenanthroline-3 : 8-dione, prepared by oxidising ψ -phenanthroline dimethiodide with potassium ferricyanide in alkaline

solution, crystallises with $4\text{H}_2\text{O}$ in glistening needles, and melts above 320° ; when dried in a vacuum over sulphuric acid it loses H_2O , and when heated at 110 — 120 it becomes anhydrous, and is then very deliquescent; it yields no salts. P. H.

Furoxans. II. Degradation of Ethyl Furoxandicarboxylate (Ethyl Glyoxime-peroxide-dicarboxylate). HEINRICH WIELAND, LEOPOLD SEMPER, and ERWIN GMELIN (*Annalen*, 1909, 367, 52—79).—Mainly an amplification of work which has been described previously (compare Wieland and Semper, *Abstr.*, 1908, i, 108; Wieland and Gmelin, *ibid.*, 1013).

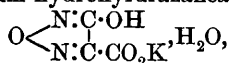
Furoxandicarboxylic acid cannot be obtained by treating the barium salt with acids, since it is very unstable, and dissociates immediately into carbon dioxide and furoxancarboxylic acid, $\text{O} \begin{array}{c} \text{CH}-\text{C}\cdot\text{CO}_2\text{H} \\ \diagup \quad \diagdown \\ \text{N}\cdot\text{O} \quad \text{N} \end{array}$

The latter substance is likewise unstable, and readily undergoes hydrolysis, yielding oximinomalonhydroxamic acid,



it is also decomposed by amines with the formation of aminoximes; thus, with aniline it yields oximinomalonanilideoxime (compare Wieland and Gmelin, *loc. cit.*). These changes take place with such ease that the transformation of the carboxylic acid into furoxan appears to be impracticable; even acetic anhydride, which in analogous cases is employed with success to effect the elimination of carbon dioxide, in this case leads to the destruction of the furazan ring.

It is probable that the salt obtained by Nef (*Abstr.*, 1895, i, 9) by hydrolysing oximinocyanoacethydroxamic acid with potassium hydroxide is not potassium hydroxyfuroxancarboxylate,



but potassium oximinomalonhydroxamate.

The authors criticise adversely the work of Jovitschitsch (*Abstr.*, 1906, i, 732). The supposed glyoxime-peroxide-dicarboxylic acid of this investigator is shown to be ethyl hydrogen furoxandicarboxylate, whilst the silver salts described in the same paper are probably mixtures.

Finally, the synthesis of *p*-methoxy- α -isatoxime and 5:5'-dimethoxy-indigotin has been effected by the method of Wieland and Gmelin (*loc. cit.*).

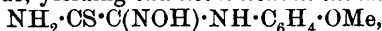
Barium furoxandicarboxylate, $\text{C}_4\text{H}_6\text{N}_2\text{Ba}\cdot\text{H}_2\text{O}$, crystallises in slender needles, and is extremely explosive when dry. It is converted by a 10% solution of hydrochloric acid ($1\frac{1}{2}$ mols.) into the *barium hydrogen salt*, $\text{C}_8\text{H}_2\text{O}_{12}\text{N}_4\text{Ba}$, crystallising in glistening leaflets. *Silver furoxandicarboxylate*, $\text{C}_4\text{O}_6\text{N}_2\text{Ag}_2$, is a pale yellow, highly explosive powder.

Furoxancarboxylic acid crystallises in stellate groups of colourless needles, m. p. 89 — 91° (decomp.); it may be kept for some time in a desiccator, but decomposes rapidly in solution; with calcium chloride it forms an *additive* compound of indefinite composition, obtained as a crystalline powder.

Oximinomalonhydroxamic acid is most readily obtained as its *barium*

salt, $C_3H_2O_5N_2Ba$, a heavy, pale yellow powder, by treating barium furoxandicarboxylate with excess of barium hydroxide solution; the acid crystallises in aggregates of prisms, m. p. 135° (decomp.). A brownish-green copper salt, lemon-yellow mercurous salt, pale yellow lead salt, and bright yellow, crystalline silver salt were prepared. The acid is rapidly decomposed by mineral acids, yielding carbon dioxide, hydroxylamine, and hydrogen cyanide.

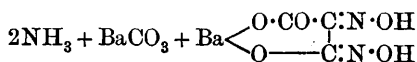
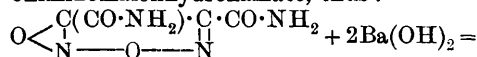
Synthesis of 5:5'-Dimethoxyindigotin.—Barium furoxandicarboxylate is converted by *p*-anisidine hydrochloride in aqueous solution and subsequent treatment with dilute hydrochloric acid into oximinomalon-*p*-anisidideoxime, $CO_2H \cdot C(N \cdot OH) \cdot C(N \cdot OH) \cdot NH \cdot C_6H_4 \cdot OMe$, which crystallises in white, glistening leaflets, m. p. 164° (decomp.), and is acted on by acetic anhydride at about 60° , yielding cyanofornanisidideoxime acetate, $OAc \cdot N : C(CN) \cdot NH \cdot C_6H_4 \cdot OMe$, crystallising in short needles, m. p. $171-172^\circ$ (decomp.). The latter substance reacts with ammonium sulphide, yielding oxanisidideoxime-thiamide,



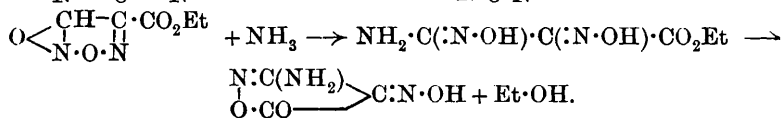
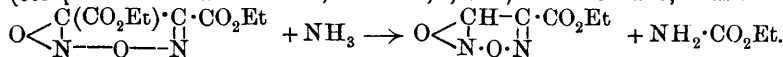
which crystallises in small, pale yellow needles, decomposes at 174° , and, when warmed with fuming sulphuric acid, yields 5-methoxy-

2-isatoxime, $OMe \cdot C_6H_3 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} C : N \cdot OH$, dark red needles with a bronzy reflex, sintering at 225° , m. p. 232° (decomp.); the sodium salt of the latter substance forms glistening, orange-yellow leaflets. 5:5'-Dimethoxyindigotin, $C_{18}H_{14}O_4N_2$, prepared by boiling the methoxyisatoxime with alcoholic ammonium sulphide, crystallises in glistening, dark blue needles and prisms. W. H. G.

Furoxans. III. Behaviour of Ethyl Furoxandicarboxylate towards Ammonia and Amines. HEINRICH WIELAND and ERWIN GMELIN (*Annalen*, 1909, 367, 80—99).—It is shown that the compound formed by the action of ammonia on ethyl furoxandicarboxylate is furoxandicarboxylamide, since it is hydrolysed by an aqueous solution of barium hydroxide, yielding barium carbonate, ammonia, and barium oximinomalonhydroxamate, thus:

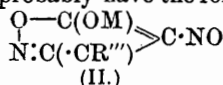
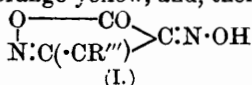


(compare Pröpper, Abstr., 1883, 573; Bouveault and Bongert, *Bull. Soc. chim.*, 1902, 27, 1170; Ulpiani and Ferreti, Abstr., 1902, i, 430; Wahl, Abstr., 1908, i, 141). The formation of the amide from the ester is accompanied by the production of amino-oximinooxazolone (compare Wieland and Hess, this vol., i, 369) and urethane, thus:



Homologues of amino-oximinoisooxazolone are formed analogously by the action of secondary aliphatic amines on ethyl furoxandicarboxylate (compare Bouveault and Bongert, *loc. cit.*).

Oximinoisooxazolones of the type (I) are colourless, whilst their salts are orange-yellow, and, therefore, probably have the formula (II).



The introduction of the amino-group is accompanied by the production of colour in the free isooxazolone derivatives, whilst the salts have practically the same colour. It is therefore probable that these compounds exist in the nitroso-enolic form, in agreement with which is the fact that they are readily reduced in the cold by zinc dust and dilute acetic acid.

Furoxandicarboxylamide forms colourless needles, m. p. 222—223°: Bouveault gives m. p. 253° (*loc. cit.*).

Cyanomethenylamino-oxime acetate, $\text{CN}\cdot\text{C}(\text{NH}_2):\text{N}\cdot\text{OAc}$, is prepared by the action of acetic anhydride on oximinomalonamino-oxime (Wieland and Hess, *loc. cit.*); it forms long, spear-shaped crystals, sinters at 125°, m. p. 137° (decomp.).

Oximinopiperidylisooxazolone, $\begin{array}{c} \text{O} \text{---} \text{CO} \\ | \quad \diagup \\ \text{N}:\text{C}(\text{C}_5\text{NH}_{10}) > \text{C}:\text{N}\cdot\text{OH} \end{array}$, prepared by the action of piperidine on ethyl furoxandicarboxylate, crystallises in orange-red needles and decomposes at 148°; the piperidine and barium salts are orange-red. It is converted by warm aqueous barium hydroxide into the barium salt of oximinomalonpiperidideoxime; attempts to obtain the corresponding acid were unsuccessful, since it passes immediately into oximinopiperidylisooxazolone; the barium salt is converted by acetic anhydride into cyanopiperidinomethylene-oxime acetate, $\text{CN}\cdot\text{C}(\text{C}_5\text{NH}_{10}):\text{N}\cdot\text{OAc}$, which crystallises in long, colourless needles, m. p. 53—54°, and is decomposed by 20% sulphuric acid, yielding acetic acid, hydrogen cyanide, piperidine, and hydroxylamine.

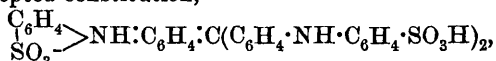
Anilino-oximinoisooxazolone, $\begin{array}{c} \text{N}:\text{C}(\text{NHPh}) \\ | \quad \diagup \\ \text{O} \text{---} \text{CO} > \text{C}:\text{N}\cdot\text{OH} \end{array}$, prepared by the action of hot glacial acetic acid on oximinomalonanilideoxime (compare Wieland and Gmelin, *Abstr.*, 1908, i, 1013), crystallises in dark red, rhombic leaflets and glistening, red needles, and decomposes at 148°.

p-Anisidino-oximinoisooxazolone, $\text{C}_{13}\text{H}_9\text{O}_4\text{N}_3$, prepared similarly from the corresponding anisidideoxime (preceding abstract), crystallises in glistening, brownish-red leaflets and decomposes at 136°.

Phenylhydrazino-oximinoisooxazolone, $\begin{array}{c} \text{CO}\cdot\text{C}(\text{NOH}) \\ | \quad \diagup \\ \text{O} \text{---} \text{N} > \text{C}\cdot\text{NH}\cdot\text{NHPh} \end{array}$, prepared by the action of phenylhydrazine on ethyl furoxandicarboxylate, crystallises in small, yellow needles, and decomposes at 183°. It is converted by aqueous alkalis into phenylhydrazideoximecarboxylic acid, $\text{NHPh}\cdot\text{NH}\cdot\text{C}(\text{NOH})\cdot\text{C}(\text{NOH})\cdot\text{CO}_2\text{H}$, obtained as an almost colourless substance; the benzoyl derivative, $\text{C}_{16}\text{H}_{14}\text{O}_5\text{N}_4$, forms long, yellow needles, sinters at 154°, m. p. 158°.

W. H. G.

Condition of Some Dyes in Aqueous Solution. EDMUND KNECHT and J. P. BATEY (*J. Soc. Dyers*, 1909, 25, 194—203).—The widely accepted view that many dyes, particularly those of high molecular weight, exist as colloids in aqueous solution is controverted by the authors. The molecular conductivities at 18° and at 90° of certain acid dyes, such as naphthol-yellow-S, benzopurpurin, soluble-blue, alkali-blue, erica-B, and chrysophenine, indicate that they are good electrolytes, and in dilute solution show a high degree of ionisation. In the trisulphonic acids prepared from Helvetia-blue and spirit-blue, it appears that only two of the three available hydrogen atoms are appreciably ionised, a result which accords with the generally accepted constitution,

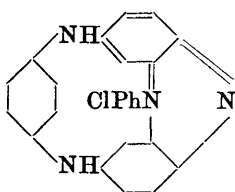


of dyes of this type. The results are confirmed by the ebullioscopic examination of aqueous solutions of naphthol-yellow-S and its calcium salt, soluble-blue, benzopurpurin, and chrysophenine, the molecular weights obtained showing that ionic dissociation has occurred except with naphthol-yellow-S. It is also shown that erica readily diffuses through parchment paper, and that the rates of simple diffusion of benzopurpurin and soluble-blue are high, indicating that they are undergoing ionic dissociation. C. S.

Chemical Technology of Aniline-Black. ARTHUR G. GREEN (*J. Soc. Dyers*, 1909, 25, 188—192).—Little definite is known regarding the chemical constitution of aniline-black, owing probably to its being produced exclusively on the fibre and not in substance. In the usual processes of dyeing, the cotton goods are steeped in a solution containing aniline hydrochloride, sodium chlorate, and a copper or vanadium salt or potassium ferrocyanide, and dried; by warming, an intermediate green shade is produced, which passes into black by treating the goods with a solution of sodium dichromate. Three stages of oxidation or condensation are usually distinguished, the predominating compounds being emeraldine, nigraniline, and un-greenable black; commercial aniline-black contains these compounds in variable proportions. Published analyses, which refer mainly to mixtures of emeraldine and nigraniline, are therefore widely divergent, but the balance of evidence favours the composition $\text{C}_{18}\text{H}_{15}\text{N}_2\text{·HCl}$ or $\text{C}_{18}\text{H}_{13}\text{N}_3\text{·HCl}$. There is little doubt that the aniline residues in the two substances are singly combined by para-nitrogen atoms in chain or ring form, and the constitution $\text{C}_6\text{H}_4\text{<}\begin{array}{c} \text{N·C}_6\text{H}_4 \\ \text{N·C}_6\text{H}_4 \end{array}\text{>NH}$ for emeraldine harmonises with the production of quinone by oxidation, of only di-*p*-nitrogen derivatives by complete reduction, with the stability of the substance to boiling dilute acids, and with Nietzki's synthesis of aniline-black by the oxidation of a mixture of aniline and di-*p*-aminodiphenylamine, or of diphenylamine and *p*-phenylenediamine. The close relationship of nigraniline chloride, $\text{C}_6\text{H}_4\text{<}\begin{array}{c} \text{N·C}_6\text{H}_4 \\ \text{N·C}_6\text{H}_4 \end{array}\text{>NCl}$, to emeraldine is shown by the facts: (1) emeraldine on the fibre is oxidised by cold potassium dichromate or persulphate to nigraniline. The colour of the latter is changed only slightly by acids or alkalis,

since the base and the salts are of the same type; (2) nigraniline on the fibre is reduced by cold sodium hydrogen sulphite to the original green emeraldine, and by further reduction by stannous chloride or sodium hyposulphite to colourless leuco-emeraldine; (3) nigraniline on the fibre, when treated with dilute mineral acids, is partly oxidised to quinone and partly reduced to emeraldine.

In deducing the constitution of ungreenable black, the following particulars must be considered. Ungreenable black is not reduced to emeraldine, and is unaffected by mineral acids, is reduced by sodium hyposulphite to a brown leuco-compound, which readily re-oxidises to the original black, and for its complete production by the further oxidation of emeraldine the presence of aniline or other primary aromatic amine is



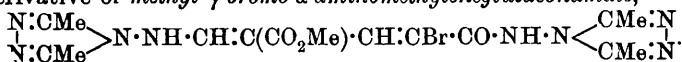
necessary. From the facts that the aniline cannot be replaced in the condensation by dimethylaniline, and that *p*-toluidine, which on account of the para-methyl group does not give rise to emeraldine or aniline-black on oxidation, can be employed to convert emeraldine or nigraniline into an ungreenable black, the conclusion is drawn that an unsubstituted amino-group is

concerned in the reaction. The annexed constitution for the chloride of ungreenable black best interprets these facts.

The author also discusses the theory of the oxidation of aniline to aniline-black by atmospheric oxygen in the presence of cupric chloride and *p*-diamines or *p*-aminophenols (Eng. Pat. 1907, 16189, A. G. Green). C. S.

Action of 1-Amino-1:3:4-triazole and its 2:5-Substitution Products on Methylbromocoumalic Acid. CARL BÜLOW and FRITZ WEBER (*Ber.*, 1909, 42, 1990—1996).—1-Amino-1:3:4-triazole has been proved to be the parent substance of the so-called *N*-dihydrotetrazines and similar compounds. To support this formula the behaviour of the aminotriazole and its homologues towards methylbromocoumalic acid is now studied. 1-Aminotriazole and the ester condense on heating in alcoholic solution for eight days at 45—55° to *methyl 3-bromo-1(1':3':4')-triazolyl-2-pyridone-5-carboxylate*, $\begin{matrix} \text{N:CH} \\ | \\ \text{N:CH} \end{matrix} > \text{N} \cdot \text{N} < \begin{matrix} \text{CO} \\ | \\ \text{CH:C(CO}_2\text{Me)} \end{matrix} > \text{CH}$, the crystals of which are colourless, m. p. 211°, decomp. 212°.

The 1-amino-2:5-dimethyl- or -diphenyl-triazoles could not be made to condense with ethyldiacetylsuccinate, but they combine with methylbromocoumalate, yielding, however, owing to the opening of the α -pyrone nucleus, derivatives of glutaconic acid. This reaction confirms the view that these 2:5-substitution products of the triazole contain a 1-amino-group. Apparently the activity of the *N*-amino-group of a heterocyclic ring is much reduced by the presence of two neighbouring alkyl groups. 1-Amino-2:5-dimethyl-1:3:4-triazole and methyl bromocoumalate yield the *di-2:5-dimethyltriazolyl* derivative of *methyl γ -bromo- α -aminomethyleneglutaconamate*,



This crystallises in needles, m. p. 205°.

The corresponding *di-2:5-diphenyltriazolyl* derivative separates in colourless, glistening crystals, m. p. 183—183.5°. E. F. A.

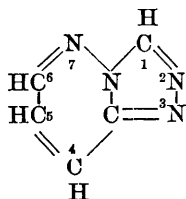
Triazolepyrrole and Triazolelutidone Derivatives. CARL BÜLOW and FRITZ WEBER (*Ber.*, 1909, 42, 2487—2494. Compare Abstr., 1906, i, 905; 1907, i, 99; preceding abstract).—1(1':3':4')-Triazolyl-2:5-dimethylpyrrole-3:4-dicarboxylic acid, $C_{10}H_{10}O_4N_4 \cdot H_2O$, obtained by hydrolysing the corresponding ester (Abstr., 1906, i, 906) with 5% potassium hydroxide solution, crystallises from water in slender, colourless needles, m. p. 290—295° (decomp.). When the acid is titrated with sodium hydroxide in the presence of phenolphthalein, only some 75% of the theoretical amount of alkali is required. When the acid is left in contact with an excess of concentrated ammonium hydroxide solution in a desiccator over sulphuric acid, the monoammonium salt, $C_{10}H_{13}O_4N_5$, is obtained, which crystallises from water in slender needles, m. p. 280—285° (decomp.). The addition of silver nitrate to a solution of the ammonium salt produces a precipitate of the silver salt, $C_{10}H_9O_4N_4Ag$.

Diacetylacetone, as a representative symmetrical 1:5-diketone, reacts readily with 1-amino-1:3:4-triazole, yielding 1-triazole-2:6-lutidone, $\begin{matrix} N:CH \\ | \\ N:N < \begin{matrix} CMe:CH \\ CMe:CH \end{matrix} > CO \end{matrix}$, which crystallises from absolute alcohol in colourless needles, melting and decomposing at a temperature above the b. p. of sulphuric acid. It yields a pale blue, crystalline precipitate with copper nitrate, a colourless, crystalline precipitate with silver nitrate, and well-developed crystals with mercuric chloride. Reducing agents have no action on the condensation product.

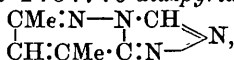
2:5-Dialkylated aminotriazoles do not condense with 1:5-diketones. J. J. S.

Action of 1-Amino-1:3:4-triazole on Diketones. CARL BÜLOW and FRITZ WEBER (*Ber.*, 1909, 42, 2208—2216. Compare Abstr., 1906, i, 905; 1907, i, 99; preceding abstract).—1-Amino-1:3:4-triazole condenses with a hot alcoholic solution of diacetyl, yielding the product, $\begin{matrix} N:CH \\ | \\ N:N < CMe \cdot CO \cdot CH_3 \end{matrix}$, which crystallises from alcohol and melts at 197—199°.

1-Amino-1:3:4-triazole condenses with 1:3-diketones, yielding compounds with two condensed heterocyclic nuclei (a 6 and a 5 ring) having a nitrogen and a carbon atom in common (annexed formula).



4:6-Dimethyl-2:3:7:0-diazpyridazine.



obtained by condensing an alcoholic solution of acetylacetone with aminotriazole in the presence of a few drops of piperidine, crystallises from a mixture of benzene and light petroleum, and has m. p. 122—123°. The compound is volatile without decomposition, and forms a nitrate,

$C_7H_8N_4.HNO_3$, which crystallises in colourless needles, m. p. 180—181° (decomp.).

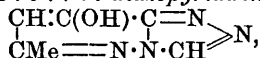
4:5:6-Trimethyl-2:3:7:0-diazopyridazine, $\begin{array}{c} CMe:N-N\cdot CH \\ CMe:CMe\cdot C=N \end{array} \gg N$, obtained from methyl acetylacetone and aminotriazole, has m. p. 129°, and crystallises from hot water, in which it is readily soluble, in long, glistening needles.

Benzoylacetone and 1-aminotriazole yield 4-phenyl-6-methyl-2:3:7:0-diazopyridazine, $\begin{array}{c} CMe:N-N\cdot CH \\ CH:CPh\cdot C=N \end{array} \gg N$, which crystallises from a mixture of benzene and light petroleum in colourless, slender needles, m. p. 152—153°. It forms additive compounds with cupric nitrate and mercuric chloride.

The condensation products are all strong poisons; they yield characteristic additive compounds with many metallic salts, and also form salts with certain acids. J. J. S.

Synthesis of Heterocyclic Dinuclear Compounds: Heterohydroxylic Acids. CARL BÜLOW [and FRITZ WEBER] (*Ber.*, 1909, 42, 2594—2603. Compare preceding abstract).—The pyridazine derivatives described in this paper have marked acid properties, comparable with those of the true carboxylic acids, and it is proposed to call them heterohydroxylic acids.

4-Hydroxy-6-methyl-2:3:7:0-diazopyridazine,



obtained by boiling together ethyl acetoacetate and aminotriazole for eight hours in glacial acetic acid solution, separates from alcohol in slender, colourless needles, which melt above the boiling point of sulphuric acid; in alcoholic solution it gives a claret-red colour with ferric chloride; the substance is soluble in potash, and can be titrated by means of phenolphthalein; when dissolved in water and treated with silver nitrate or mercuric chloride, it gives an amorphous silver salt or a crystalline mercuric salt; from the sodium salt, the manganous, zinc, nickel, cobalt, copper, lead, mercurous, mercuric, and silver salts have been prepared by double decomposition; their composition may be expressed by the formula $C_6H_5N_4O\cdot OX$, in which X represents the metal:

4-Hydroxy-5:6-dimethyl-2:3:7:0-diazopyridazine, $C_5N_4HMe_2\cdot OH$, obtained by boiling together aminotriazole, methyl acetoacetate, and glacial acetic acid for forty-eight hours, crystallises from water in small, snow-white needles, m. p. 252°; its sodium salt gives a number of characteristic precipitates with various metallic salts; the precipitates in many cases differ from those obtained by the interaction of the aqueous solution of the free acid with the same salts.

4-Hydroxy-6-phenyl-2:3:7:0-diazopyridazine, $C_5N_4H_2Ph\cdot OH$, prepared by heating a mixture of aminotriazole, ethyl benzoylacetate, and glacial acetic acid for eighteen hours, crystallises from methyl alcohol in colourless needles, m. p. 282°; this substance has also

marked acid properties, and its sodium salt likewise gives characteristic precipitates with most metallic salts.

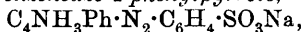
By boiling together slightly different proportions of aminotriazole, ethyl benzoylacetate, and glacial acetic acid for forty-eight hours, a pure white, crystalline substance, m. p. 243—244°, is obtained of the empirical formula $C_{15}H_{14}O_2N_8$; it appears to be a compound of hydroxyphenyldiazopyridazine, $C_{11}H_8ON_4$, with 1-acetylamino-triazole, $C_4H_6ON_4$; whereas the compound $C_{11}H_8ON_4$, m. p. 282°, gives in dilute alcoholic solution an immediate claret-red colour with ferric chloride, this substance, $C_{15}H_{14}O_2N_8$, m. p. 243—244°, produces under the same conditions only a faint colour change; the more fusible substance is, however, easily converted into the less fusible by boiling for half an hour with ethyl alcohol, or more rapidly by dissolving it in dilute aqueous alkali and precipitating with a slight excess of acetic acid. P. H.

Reduction of Triphenylmethane Dyes and of Azo-compounds by Sodium Hyposulphite. OTTO FISCHER, ADOLF FRITZEN, and S. EILLES (*J. pr. Chem.*, 1909, ii, 79, 562—568).—The reducing action of sodium hyposulphite is greatly accelerated by the addition of a little zinc dust. Crystal-violet, malachite-green, and *p*-rosaniline in hot alcoholic solution are reduced to the leuco-bases, whilst 1-benzeneazo-2:2'-dinaphthylamine in alcoholic-pyridine solution yields 1-amino-2:2'-dinaphthylamine, the *acetyl* derivative of which, $C_{22}H_{18}ON_2$, has m. p. 214°. C. S.

Azopyrroles and their Reduction. EUGEN KHOTINSKY and MAX SOLOWEITSCHIK (*Ber.*, 1909, 42, 2508—2515).—Various azopyrroles have been prepared and reduced with the hope of obtaining stable aminopyrroles; the latter are formed, but have not been isolated.

Di-4:4'-a-pyrrolylazodiphenyl, $C_{12}H_8(N_2 \cdot C_4NH_4)_2$, obtained by coupling diazotised benzidine hydrochloride and pyrrole in aqueous-alcoholic solution at 0° in the presence of sodium acetate, is a yellowish-brown powder, which decomposes on heating. The corresponding compound from *o*-tolidine, $C_{12}H_8Me_2(N_2 \cdot C_4NH_4)_2$, prepared below -6°, is light brown, and has m. p. 160—165° (decomp.). *2-Benzeneazo-5-phenylpyrrole*, $C_4NH_3Ph \cdot N_2Ph$, m. p. 112°, is brownish-yellow, whilst the sodium salt of *2-p-sulphobenzeneazo-5-phenylpyrrole*, obtained by salting out the solution obtained by coupling 2-phenylpyrrole and diazotised sulphanilic acid, is greyish-brown and carbonises without melting. *Di-4:4'-a-phenylpyrrolylazodiphenyl*, $C_{12}H_8(N_2 \cdot C_4NH_3Ph)_2$, is a dark red substance, which carbonises without melting, whilst the *N*-phenyl isomeride, m. p. 178°, is brick-red and has more pronounced basic properties. *Di-4:4'-N-phenylpyrrolyl-o-ditolyl*, $C_{12}H_8Me_2(N_2 \cdot C_4NH_3Ph)_2$, is dark red, and carbonises at 115°.

Sodium 2-p-sulphobenzeneazo-1-phenylpyrrole,

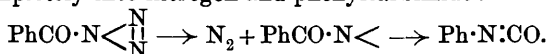


obtained by coupling diazotised sulphanilic acid and 1-phenylpyrrole in glacial acetic acid, and subsequent treatment with sodium carbonate,

forms golden-brown crystals containing $3\text{H}_2\text{O}$, which carbonise at $275\text{--}285^\circ$.

The preceding disazo-compounds are unsuited for reduction on account of their instability, but the sulphonated compounds, particularly the last, can be reduced by stannous chloride and hydrochloric acid or by sodium hyposulphite; the aminopyrroles, however, have not been isolated. C. S.

The Hofmann-Curtius, Beckmann, and Benzilic Acid Inter-molecular Rearrangements. GEORG SCHROETER (*Ber.*, 1909, **42**, 2336—2349).—Benzoylazouimide, when heated at 70° , decomposes nearly completely into nitrogen and phenylcarbimide:



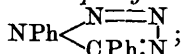
o-Nitrobenzazouimide, when heated at 50° , decomposes in a similar manner into nitrogen and *o*-nitrophenylcarbimide. Neither benzonitrile oxide nor its polymerisation products, diphenylglyoxime peroxide or tribenzonitrile oxide, could be detected as intermediate products of the decomposition of benzazouimide.

Benzophenone chloride reacts with sodium azouimide in cold methyl-alcoholic solution to form benzophenonedimethylacetal, m. p. 107° . In amyl ether, however, it reacts with silver azouimide, forming an oil, which decomposes on heating at $115\text{--}116^\circ$ in a stream of carbon dioxide, liberating nitrogen, and consists in part of benzophenonediazouimide. Decomposition takes place in accordance with the equation:



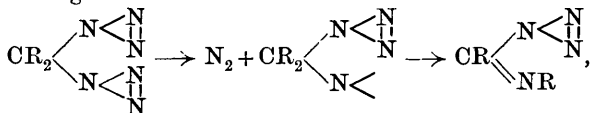
About one-third of the benzophenone chloride is converted into diazouimide and two-thirds into benzophenone, ammonia, and silver chloride.

The compound Ph_2CN_4 is 1 : 5-diphenyl-1 : 2 : 3 : 4-tetrazole,



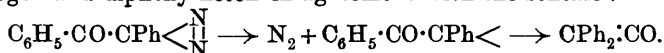
it crystallises in broad, colourless needles, m. p. 146° .

This reaction is in accord with the following scheme for the Beckmann rearrangement:



the alkyliminoazouimide finally undergoing rearrangement to the stable tetrazole.

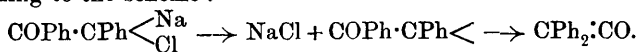
Azibenzil (benzoylphenylazomethylene) in benzene solution, when warmed at $50\text{--}60^\circ$ in a stream of carbon dioxide, decomposes into nitrogen and diphenylketen in agreement with the scheme:



This forms a very convenient method of preparing diphenylketen. The transformation of dibenzoylstilbene into tetraphenylcrotonolactone and of dibenzoylstryene into triphenylcrotonolactone are explained by similar schemes.

[With CARL CASPAR.]—Desyl chloride, m. p. 68·5°, is conveniently obtained by warming benzoin with the equivalent quantity of thionyl chloride. When distilled under reduced pressure, slight decomposition takes place, and a green vapour is formed, condensing to a green liquid, but which loses its colour when solid and yields pure colourless desyl chloride when crystallised.

Desyl chloride forms a sodium salt, which on warming in benzene solution loses sodium chloride and undergoes rearrangement in part according to the scheme :



E. F. A.

The Changes in Physical Conditions of the Colloids. VIII. Studies on Acid Albumin.

WOLFGANG PAULI and HANS HANDOVSKY (*Biochem. Zeitsch.*, 1909, 18, 340—371).—Measurements were made by means of the Ostwald viscometer of the internal friction of “amphoteric” protein solutions which had been prepared by prolonged dialysis of serum of different origins. It was found that the addition of acids increased the viscosity up to a certain concentration, after which further addition caused a decrease in this factor. In the case of weak acids, however, such as acetic and citric acids, the maximum of viscosity was not attained. Addition of salts to the acid proteins diminished the viscosity, and the authors have investigated quantitatively the effect of various salts in producing this diminution. They give in some detail a theory to account for the changes in the properties of the “amphoteric” proteins produced by the action of

acids and salts, which is founded on the assumption that the increased friction is due to the protein ion. By means of acids, the

“amphoteric” protein is converted into the “ionised” protein according to the annexed scheme. From the latter formula, salts can be

formed with acids, such as $\text{R} \begin{smallmatrix} \text{NH}_2 \\ \text{CO}_2\text{H} \end{smallmatrix} \begin{smallmatrix} \text{H} \\ \text{Cl} \end{smallmatrix}$, which can give rise to the

ions Cl^- and $\text{R} \begin{smallmatrix} \text{NH}_3^+ \\ \text{CO}_2\text{H} \end{smallmatrix}$. Addition of hydrochloric acid to solutions containing such ions will depress the dissociation, and thus diminish the amount of protein ion and the viscosity. The action of salts is also ascribed to the decrease of the protein ions in solution, resulting from interaction of the protein salt with the added salt, which action the authors discuss in some detail.

S. B. S.

The Electric Charge of Serum Albumin and of Ferments.

LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1909, 19, 181—185).—The earlier experiments of Hardy and of Pauli on the behaviour of serum-albumin in an electric field left it doubtful whether any migration takes place. This was a result of the apparatus employed by these authors, which did not completely exclude the formation of acid and alkali at the electrodes. By using the arrangement employed by the

present author in his work on ferments (this vol., i, 277), this is avoided, and the solution remains neutral throughout; in such a solution the proteins migrate exclusively to the anode. In that case the concentration of hydrogen ions is 10^{-7} ; with one part of acetic acid in 10,000 ($H^+ = 10^{-5}$), the migration is purely cathodic. The intermediate concentration of hydrogen ions ($H^+ = 10^{-6}$) was obtained by sodium phosphate; in it the albumin wandered to both electrodes (compare also Pauli and Handovsky, preceding abstract). G. B.

Refractive Indices of Solutions of the Caseinates and the Acid and Alkali Equivalents of Casein. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1909, 13, 469—489).—The refractive indices of solutions which differ only in their casein-content are connected by the formula $n - n_1 = ac$, where n is the observed refractive index of the solution, c is the concentration of the casein, n_1 is a constant which depends on the nature of the solvent used to dissolve the casein, and a is a constant. It follows that when the constants are known, the concentrations of solutions containing casein can be determined with considerable accuracy by measurements of the refractive index. The change in the refractive index of a solution of an acid or base produced by the addition of a definite weight of casein is practically independent of the nature and concentration of the base or acid. The difference between the refractive index of a solution of sodium caseinate and that of water at the same temperature, is independent of the temperature between 20° and 40° .

The quantity of hydrochloric acid which just dissolves 1 gram of casein (determined by dissolving casein in sodium hydroxide, adding a known excess of hydrochloric acid, filtering, and measuring the refractive index of the solution) is about 32×10^{-5} gram-mols.; the alkali equivalent of 1 gram of casein, determined by a somewhat similar method, is 11.4×10^{-5} mols.

Solutions of bases saturated with casein are between 10^{-5} and 10^{-6} normal with regard to hydrogen ions. G. S.

Production of Putrefaction Bases. D. ACKERMANN (*Zeitsch. physiol. Chem.*, 1909, 60, 482—501).—Attempts were made to obtain pentamethylenediamine, tetramethylenediamine, and δ -aminovaleric acid from lysine, ornithine, and arginine respectively by the action of putrefactive organisms, but without success. When, however, casein is decomposed by boiling with sulphuric acid and water, and the product freed from arginine, pentamethylenediamine is readily obtained by putrefaction, and as the amount produced depends on the amount of lysine present (an additional amount of lysine was added to the mixture), and is not affected by varying amounts of other products of the decomposition of casein, it is evident that lysine is the compound from which it is formed.

Tetramethylenediamine and δ -aminovaleric acid are produced only when arginine is present.

Experiments on the action of putrefaction organisms on aspartic and glutamic acids, glycine, alanine, and guanidine, show that the first two acids are readily attacked, whilst glycine and alanine

were only slightly decomposed. Guanidine was partly converted into carbamide. N. H. J. M.

Action of Pure Hydrogen Peroxide on Crystallised Oxyhæmoglobin. I. SZRETER (*Compt. rend.*, 1909, 148, 1776—1779. Compare Abstr., 1907, i, 807).—Several crystallisations are necessary to free oxyhæmoglobin from the substance which brings about catalytic decomposition of hydrogen peroxide (Senter's hæmase). A physiological solution of pure sodium sulphate is recommended instead of sodium chloride for washing oxyhæmoglobin, since this avoids the presence of chlorine in the product. W. O. W.

Guanylic Acid. PHÆBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1909, 42, 2469—2473. Compare Bang, Abstr., 1899, i, 179; 1901, i, 299; 1908, i, 70; Fürth and Jerusalem, Abstr., 1907, i, 993; 1908, ii, 119; Steudel, *ibid.*, 1908, i, 70; Levene and Mandel, *ibid.*, i, 587; Jones and Rowntree, *ibid.*, i, 487).—Guanylic acid appears to be similar to inosic acid (Abstr., 1908, i, 931; this vol., i, 164) in constitution. When hydrolysed by dissolving in a slight excess of sodium hydroxide solution, neutralising with acetic acid, and heating in sealed tubes at 130—135°, guanylic acid yields a guanine pentoside, $C_{10}H_{13}O_5N_5 \cdot 2H_2O$, analogous to inosine, and termed *guanosine*. It crystallises from water in long, silky needles resembling tyrosine. It contains no phosphorus, but gives the pentose reactions. When quickly heated, it decomposes at 237°. It dissolves in alkalis and in mineral acids, and in alkaline solution has $[\alpha]_D^{20} - 60.52^\circ$. When hydrolysed with 0.1*N*-sulphuric acid it yields carnose and guanine.

Carnose is also formed when guanylic acid is hydrolysed by dilute mineral acid.

Whereas both inosine and guanosine are lævorotatory, inosic and guanylic acids have opposite rotations. J. J. S.

Yeast Nucleic Acid. PHÆBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1909, 42, 2474—2478. Compare this vol., i, 447).—Guanosine (compare preceding abstract) has been isolated from the products obtained by hydrolysing the nucleic acid of yeast in neutral solution. The pentose obtained by the complete hydrolysis of the nucleic acid or of guanosine is not *l*-xylose, but *d*-ribose. The sugar termed carnose (preceding abstract) is *d*-ribose. J. J. S.

Lipoids. IV. Phosphatides of the Ox Pancreas. SIGMUND FRÄNKEL and G. A. PARI (*Biochem. Zeitsch.*, 1909, 17, 68—77. Compare this vol., i, 276).—From the pancreas of the horse a saturated phosphatide, m. p. 167°, has been isolated; ox pancreas, however, yields a different phosphatide, now termed *vesalthin*, soluble in acetone and in methyl acetate. This phosphatide is unsaturated; it forms a cadmium compound, $C_{32}H_{63}O_9NP \cdot CdCl_2$, contains no galactose, and yields myristic acid, $C_{14}H_{28}O_2$, and an unsaturated fatty acid having fewer carbon atoms than oleic acid. It contains, further, a base which, since it yields four methyl groups attached to nitrogen, is not choline. Vesalthin is optically active, having $[\alpha]_D + 118^\circ$ approximately.

From the alcoholic infusion of the pancreas, a compound,
 $C_7H_{15}N, CdCl_2$,
 has been obtained. This does not react with dimethylamino-
 benzaldehyde, but shows the orcinol reaction, and may represent an
 acetylpentosamine. E. F. A.

Lipoids. V. Phosphatide of the Ox Pancreas. SIGMUND FRÄNKEL, KURT LINNERT, and G. A. PARI (*Biochem. Zeitsch.*, 1909, 18, 37—39).—Further proof that the base contained in vesalthin (preceding abstract) is not choline is shown by the following further points: the platinichloride has m. p. 254°, and the ratio of chlorine to platinum is 5 : 1 (choline platinichloride, m. p. 241°, gives the ratio Cl : Pt = 6 : 1). W. D. H.

The Action of Pepsin on Egg-Albumin. REGINALD O. HERZOG and M. MARGOLIS (*Zeitsch. physiol. Chem.*, 1909, 60, 298—305). **The Relationship between Pepsin and Rennin.** REGINALD O. HERZOG (*ibid.*, 306—310).—The action of strong pepsin solutions on egg-albumin follows the Schütz law; the action of rennet solutions on the same protein follows the same law, but its reaction velocity is slower.

Not only is there this resemblance between the two enzymes, but it is pointed out that both are inhibited by the anti-pepsin of Weinland obtained from the worm *Ascaris*, and their diffusion coefficients are the same. If the two enzymes are not identical, they exhibit great parallelism. W. D. H.

The Maltase of Buckwheat. R. HUERRE (*Compt. rend.*, 1909, 148, 1526—1528).—The dry grains of buckwheat contain a soluble maltase which disappears at the commencement of germination, and an insoluble enzyme which persists during this process. The maltase acts between 3° and 70°, with an optimum at 55°. Its activity is increased by partial neutralisation of the alkalinity of the medium or by the addition of acetamide or amino-acids. W. O. W.

Influence of Boric Acid on Diastatic Actions. H. AGULHON (*Compt. rend.*, 1909, 148, 1340—1342. Compare Gerber, Abstr., 1908, i, 745).—Boric acid exerts as a rule a feebly retarding influence on the activity of diastatic ferments. In the case of sucrase, emulsin, trypsin, and pancreatic amylase, the action is slightly accelerated. The diastatic coagulation of milk is favoured by the presence of boric acid. W. O. W.

Electrical Migration of Enzymes. III. Malt Diastase. IV. Pepsin. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1909, 17, 231—234. Compare this vol., i, 345).—Malt diastase was dialysed and placed as middle element of the cell:

Silver in sodium chloride		Water		Ferment		Water		Copper in cupric chloride
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In neutral solution it migrates to the cathode, but a small quantity

passes to the anode. In acetic acid solution the migration is entirely cathodic; in dilute sodium carbonate solution it is entirely anodic. The undialysed ferment migrates exclusively to the cathode.

Diastase is accordingly amphoteric, as shown by adsorption experiments. Kaolin adsorbs it only in acid solution. Compared with amphoteric trypsin, diastase is more strongly positive, and shows positive properties in neutral solution; tryysin is more strongly negative, and shows positive properties only in distinctly acid solution.

Pepsin.—In the cell,

Silver in sodium chloride	Hydrochloric acid	Pepsin in hydrochloric acid	Hydrochloric acid	Copper in cupric chloride
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hydrogen ions travel with the current, and bring about a decrease in acidity, and so affect the behaviour of the pepsin. To get over this, the sodium chloride in the first compartment is replaced by hydrochloric acid. Under these conditions, pepsin migrates to the anode when the electric current is passed through the pure aqueous solution; it migrates to both anode and cathode in $N/200$ and weaker acid solution, and migrates only to the cathode in $N/50$ and $N/40$ hydrochloric acid.

Pepsin only acts as a proteoclast in presence of a considerable proportion of acid, whereas it acts similarly to rennet only in neutral solution. It is suggested that when cathodic it acts as a proteoclast, when anodic it is the same ferment as rennet. E. F. A.

Asymmetric Syntheses by means of Enzyme Action. LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1909, 17, 257—269. Compare this vol., i, 74).—The influence of a number of foreign substances on the reaction of benzaldehyde, hydrogen cyanide, and emulsin, leading to the formation of optically active benzaldehydecyanohydrin, has been studied, in order to detect differences in the behaviour of hydrolytic and synthetic emulsin.

The addition of large quantities of alcohol does not destroy the synthetic enzyme so long as the solution is not filtered. The addition of an equal volume of alcohol to a solution of emulsin gives a filtrate which causes the formation of optically active products; if the hydrogen cyanide is added before precipitation, these have a lower rotation. This is confirmatory evidence of a compound of hydrogen cyanide with the synthetic enzyme. Liquids not miscible with water, such as chloroform, ethyl acetate, and xylene, do not prevent the synthetic action. Alkali and phenol prevent action; formaldehyde has but little influence. Half saturation with ammonium sulphate produces a precipitate; the filtrate has no synthetic action, and contains only hydrolytic enzyme; the precipitate when dissolved in water contains active synthetic enzyme. The same result is obtained on complete saturation with magnesium sulphate. In this way the hydrolytic enzyme can be obtained free from the synthetic. The unpurified enzyme acting on benzaldehyde and hydrogen cyanide produces a product of maximum optical activity in about two and a-half hours, and the optical activity subsequently decreases. The purified synthetical

enzyme gives a product, of which the optical activity is as large after two and a-half as after twenty-four hours. Pepsin and trypsin in neutral solution destroy the synthetical enzyme.

A large number of other aldehydes yield, when shaken with hydrogen cyanide and emulsin, optically active nitriles, from which in some cases optically active acids were obtained on hydrolysis. Thus acetaldehyde, isobutaldehyde, heptaldehyde, octaldehyde, citral, furfuraldehyde, *o*-methoxybenzaldehyde, anisaldehyde, cumenaldehyde, piperonal, *o*- and *m*-nitrobenzaldehydes, cinnamaldehyde, phenylacetaldehyde, phthalaldehyde, isophthalaldehyde, and terephthalaldehyde gave active products. On the other hand, from salicylaldehyde, *m*- and *p*-hydroxybenzaldehydes, *p*-nitrobenzaldehyde, protocatechu-aldehyde, methyl ethyl ketone, and hyponone, inactive products resulted. Quantitative measurements show that in all cases the emulsin accelerates the addition of hydrogen cyanide, the acceleration being very marked in the case of anisaldehyde, furfuraldehyde, and dextrose. This acceleration is observed whether or no optically active products are formed.

A full explanation for the experimentally observed facts is found in the conclusion that emulsin consists of a synthetic enzyme, bringing about the asymmetric synthesis, and a hydrolytic enzyme acting to hydrolyse the optically active nitrile.

E. F. A.

Catalysing Constituents of Emulsin. LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1909, 19, 186—190).—The acceleration of the addition of hydrocyanic acid to aldehydes and ketones, due to emulsin preparations, is brought about by inorganic salts contained in the latter, and especially by magnesium compounds. Acids, which reduce the degree of dissociation of the hydrogen cyanide retard the additive reaction, from which it follows that hydrogen cyanide is added in the form of ions, a result already deduced by Lapworth (*Trans.*, 1903, 83, 995) from other experiments.

G. B.

Action of a Bulgarian Ferment on Certain Sugars. GABRIEL BERTRAND and F. DUCHACEK (*Compt. rend.*, 1909, 148, 1338—1340; *Ann. Inst. Pasteur*, 1909, 23, 402—414).—A study of the action of the "yoghourt" ferment which occurs in curdled Bulgarian milk. This ferment has no action on arabinose, xylose, sorbose, maltose, sucrose, and mannitol, but brings about a lactic fermentation in the case of dextrose, mannose, galactose, lævulose, or lactose.

Unlike the ordinary lactic fermentation, however, the decomposition is accompanied by the production of *d*- and *l*-lactic acids in equal proportions.

W. O. W.

The Properties and Classification of the Oxidising Enzymes, and Analogies between Enzymic Activity and the Effects of Immune Substances and Complements. BENJAMIN MOORE and EDWARD WHITLEY (*Bio-Chem. J.*, 1909, 4, 136—167).—The authors do not consider it necessary to assume the existence of oxygenase (the peroxide-forming ferment) or catalase, and regard peroxydase as the only enzyme of this class. Traces of organic peroxides are present in

the fresh juices of most plants; they are formed from a precursor, but there is no evidence that their production is due to enzymes. These peroxides react with various compounds (for example, α -naphthol, *p*-phenylenediamine, quinol, guaiacum, etc.) to produce colours, and the reaction is considerably accelerated by the enzyme peroxydase, which is widely distributed in plants. Where the organic peroxide is absent the reaction is only produced after the addition of hydrogen peroxide; it is thus possible by two tests (reagent + plant juice; reagent + hydrogen peroxide + plant juice) to discover whether both peroxide and peroxydase or peroxydase only are present. Guaiacum is less trustworthy than the other reagents, as it sometimes contains a peroxide.

An active peroxydase precipitate was analysed, and yielded C 46.8; H, 7.1; N, 10.8; O, etc., 35.3 (calculated ash-free). E. J. R.

Coaguloses. IV. D. LAWROFF (*Zeitsch. physiol. Chem.*, 1909, 80, 520—532. Compare Abstr., 1908, i, 844).—In the peptic digestion of casein two chief groups of coagulose-yielding substances are obtained: (1) of the type of proteoses with relatively little nitrogen; and (2) of the type of polypeptides; these yield hardly any bases. They yield coa-proteoses and coa-peptides respectively. The chemical individuality of these substances is still an open question. W. D. H.

Action of Different Antiseptics on the Enzymes of Yeast-Juice. FRANZ DUCHÁČEK (*Biochem. Zeitsch.*, 1909, 18, 211—227).—Small quantities of phenol (0.1%) have no deleterious action on the enzyme. Small quantities of chloroform (0.5%) and chloral hydrate (0.7%) increase the activity. The action is due to the deleterious influence of the antiseptic on the proteolytic enzyme which acts on the zymase. Benzoic and salicylic acids were found to exert, in low concentrations (0.1%); but small action on the fermentative capacity of the juice. The experiments as a whole demonstrate that the action of yeast-juice is due to the zymase, and not to any contamination with living protoplasm. The fermentation takes place in concentrations of antiseptic high enough to totally inhibit the action of any living matter. S. B. S.

Action of Yeast Enzymes. EDUARD BUCHNER and HUGO HAEHN (*Biochem. Zeitsch.*, 1909, 19, 191—218).—A discussion on the course of the action of yeast enzymes in special relationship to the work of Harden and Young and others on the co-enzyme of zymase. The loss of activity which occurs when yeast juice is kept is attributed to the action of a proteolytic enzyme (endo-tryptase) on the zymase, and the point to which special attention is directed is that the co-enzyme protects zymase from this harmful influence. The co-enzyme is particularly sensitive to the action of potassium, and the view is advanced that it is an easily saponifiable organic ester of phosphoric acid. W. D. H.

Organic Chemistry.

Hydration of Hydrocarbons of the Acetylene Series by means of Cadmium, Zinc, and Magnesium Salts. M. G. KUTSCHEROFF (*Ber.*, 1909, 42, 2759—2762).—The author has previously shown (Abstr., 1881, 883; 1884, 719) that hydrocarbons of the acetylene series can be hydrated by the agency of mercury salts. It is now found that when acetylene is heated to 100° with solutions of cadmium or zinc salts (acetate, chloride, and bromide), acetaldehyde is formed, and when the latter metal is used (as chloride or bromide), probably crotonaldehyde. *iso*Propylacetylene when heated at 150° with cadmium or zinc chlorides gives a quantitative yield of methyl propyl ketone. J. C. C.

Glutaric Pinacone, $\text{OH}\cdot\text{CMe}_2\cdot[\text{CH}_2]_3\cdot\text{CMe}_2\cdot\text{OH}$ [$\beta\zeta$ -Dimethylheptane- $\beta\zeta$ -diol]. PIERRE BRUYLANTS (*Bull. Acad. roy. Belg.*, 1909, 276—282).—By the action of magnesium methyl bromide on ethyl glutarate, $\beta\zeta$ -dimethylheptane- $\beta\zeta$ -diol, $\text{OH}\cdot\text{CMe}_2\cdot[\text{CH}_2]_3\cdot\text{CMe}_2\cdot\text{OH}$, is formed; it crystallises with a molecule of water in fine tufts, m. p. 60—61°. When heated at 140°, the hydrate loses water, giving the anhydrous pinacone, m. p. 76—77°, which re-absorbs water quite readily. Like succinic pinacone (Henry, Abstr., 1906, i, 922), but much less readily, glutaric pinacone is dehydrated by dilute sulphuric acid, giving tetramethylpentamethylene oxide, $\text{CH}_2\langle\text{CH}_2\cdot\text{CMe}_2\rangle\text{O}$, a colourless, mobile liquid, b. p. 141—143°, with a pronounced terpene-like odour, which reacts readily with hydrochloric acid, giving a dichlorohydrin, m. p. 41—42°. The latter can also be obtained by the action of concentrated hydrochloric acid or acetyl chloride on the pinacone itself. The dichlorohydrin is decomposed slowly by cold, and very rapidly by hot, water.

Succinic pinacone (*loc. cit.*) also crystallises with water. When silky needles, m. p. 92°, of the anhydrous pinacone are moistened with a few drops of water, they are rapidly transformed into small, hard, brittle crystals of the hexahydrate, m. p. 41—42°, analogous to that of oxalic pinacone. This hydrate, however, is very unstable, losing water even by prolonged contact with a porous tile. E. H.

Purification of Ethyl Ether. GUIDO GARBARINI (*Bull. Assoc. chim. Sucr. Dist.*, 1909, 26, 1165—1168).—The researches of Schoenbein, Babo, Hingzet, Buchner, Legler, Richardson, and Dymond have shown that ethyl ether is peroxidised when exposed to the air, and that this peroxidation is accelerated by light. A special arrangement of the receiver used in distillation to reduce the contact of the ether with air to a minimum is described. The author finds that the peroxide compound unavoidably formed is not affected by manganese dioxide, but can be completely removed by treating the ether for twenty-four hours with ferrous hydroxide. The latter is prepared in a dry

form, in order to avoid wetting the ether, in the following manner. Crystallised ferrous sulphate is powdered and mixed with a equimolecular weight of finely powdered lime. If the ferrous sulphate has not effloresced, the reaction takes place readily by virtue of its water of crystallisation, considerable heat being developed, but in some cases the addition of a small quantity of water (15—20 c.c. per 20 kilos. of mixture) is necessary. When the reaction is complete and the ferrous hydroxide commences to oxidise, the mixture is covered with lime. The crude ether is treated with this product in the proportion of 20 kilos. per 10 hectolitres. E. H.

Dynamical Study of Two Alkyl Derivatives of Phosphoric Acid. TH. VAN HOVE (*Bull. Acad. roy. Belg.*, 1909, 282—294).—The author has measured the electrical conductivity of, and the rate of inversion of sucrose by, diethyl hydrogen phosphate and tetrafluorodiethyl hydrogen phosphate (Swarts, this vol., i, 202). A detailed description of the purification of the two acids is given. The conductivity at 25° of tetrafluorodiethyl hydrogen phosphate varies from μ_{16} 326.9 to μ_{1024} 379.2, whilst that of diethyl hydrogen phosphate varies from μ_{16} 263 to μ_{1024} 373. From measurements of the conductivities of their sodium salts, the limiting values μ_{∞} 382 and μ_{∞} 379 have been deduced respectively for the two acids. The limiting conductivities give the means of determining the degree of ionisation. The latter increases from 85.57% to 99.26% in the case of tetrafluorodiethyl hydrogen phosphate when the dilution varies from 16 to 1024, and from 69.4% to 98.41% in the case of diethyl hydrogen phosphate for the same increase in dilution. With the former acid the degree of ionisation is too great at the small dilutions to allow of the calculation of the dissociation constant, but in the case of diethyl hydrogen phosphate the value 9.84 is obtained for K at dilution 16. A table is given comparing the conductivities and degrees of ionisation of the above acids with those of phosphoric acid. This indicates that the replacement of the basic hydrogen in phosphoric acid by an alkyl group enhances the acid character, whilst the more negative difluoroethyl radicle has a still greater effect. (*N*/16-Phosphoric acid solution is ionised only 32.4%.) The rates of inversion of sucrose by tetrafluorodiethyl hydrogen phosphate and diethyl hydrogen phosphate have been compared with that of dichloroacetic acid, the dissociation constant of which was found by Ostwald to be 5.14. By aid of the latter value, the degree of ionisation of dichloroacetic acid at the dilution employed (*N*/8) is found to be 0.468, and from this and the velocity constants of the sucrose inversions by the three acids, the values 0.5803 and 0.8536 are obtained for the degrees of ionisation of diethyl hydrogen phosphate and tetrafluorodiethyl hydrogen phosphate respectively at the same dilution (*N*/8). The dissociation constants are thence found to be 10.03 and 62.2 for the two acids, of which the former agrees with the value obtained by conductivity measurements. E. H.

Decomposition of Formic Acid by Concentrated Sulphuric Acid. JULIUS MEYER (*Zeitsch. Elektrochem.*, 1909, 15, 506—509).—The rate of evolution of carbon monoxide from solutions of different

concentrations of formic acid and of sodium formate in 90% sulphuric acid at 18° and 25° is measured. The solutions were well stirred during the measurements. The equation of the unimolecular reaction applies very well to the results; the mean values of the constants are with formic acid 0.00297 and 0.00867, with sodium formate 0.00348 and 0.00881, at 18° and 25° respectively. T. E.

Effect of Neutral Salts on Hydrolysis by Water. DAVID R. KELLOGG (*J. Amer. Chem. Soc.*, 1909, 31, 886—900).—It has been shown in an earlier paper (this vol., i, 203) that the rate of hydrolysis of ethyl acetate by water is considerably affected by the addition of potassium chloride, an acceleration being produced by solutions containing from 1 to 20% of the salt, and a retardation by stronger solutions.

The investigation has now been continued, and a study made of the influence of potassium chloride, bromide, and iodide at a fixed temperature (100°) and with a fixed concentration of ethyl acetate (0.4021*N*). The concentrations of the salts have been varied from 0.1*N* to 4*N*.

The results show that the specific influence of the salts is greater in somewhat dilute solutions. As the concentration increases, the effect gradually becomes less until it reaches zero, and then becomes negative in character, so that a 4*N*-solution of potassium chloride hydrolyses the ester more slowly than does pure water. A series of curves is given showing the relations between the concentrations of the three salts and the time required by each to hydrolyse 25, 50, and 75% of the ester. The maximum accelerating power is at about 1.8*N* for potassium chloride, 0.5*N* for the bromide, and 0.25*N* for the iodide. The reactions show a distinct period of induction at the commencement, but after they have well started, the velocity is much greater than in the earlier stages, whilst towards the close of the reactions the rate decreases considerably.

Various hypotheses are suggested to explain the influence of the salts on the hydrolysis, but it is shown that none of them is capable of fully explaining all the facts of the case. E. G.

Catalysis of Saturated Fatty Acids. JEAN B. SENDERENS (*Compt. rend.*, 1909, 149, 213—215. Compare this vol., i, 286).—A further study of the action of heated metallic oxides on fatty acids whereby symmetrical ketones are produced. The ketone arises from decomposition of a salt first formed by the action of the acid on the oxide. Thorium oxide is the most satisfactory catalyst, but the oxides of uranium are little inferior in this respect. Since the formation and destruction of the salt takes place with equal readiness in these cases, a good yield of the pure ketone is obtained.

With the oxides of iron, aluminium, and chromium the formation of the salt takes place less readily than its decomposition, and a good yield of ketone is only obtained when acetic acid is employed. Owing to the stability of the salts of calcium and zinc and the high temperature necessary for their decomposition, the oxides of these metals are unsuitable as catalysts. The ketone is formed in small quantity, and

is accompanied by complex pyrogenic products. The oxides of copper and cadmium behave in a similar manner, but the reaction is further complicated by reduction of the oxide to the metallic state.

W. O. W.

Optically Active Cyanopropylisopropylacetic Acid. EMIL FISCHER and ERICH FLATAU (*Sitzungsber. K. Akad. Wiss. Berlin*, 1909, 876—883).—Propylisopropylacetic [isopropylvaleric] acid presents a simple case in which the magnitude of the optical activity cannot depend on the differences in the weight of the substituting groups. The racemic acid has now been carefully purified and resolved into the optically active components by means of brucine. The dextro-acid has been obtained pure; it has the high optical rotatory power $[\alpha]_D + 11.4^\circ$ in toluene. This indicates that the structural difference between the propyl and isopropyl groups is sufficient to cause a relatively marked asymmetry of the molecule; in general, isopropyl exercises in chemical changes an influence quite different from that of the propyl group.

Ethyl α -cyanoisovalerate, $C_8H_7 \cdot CH(CN) \cdot CO_2Et$ (compare Henry, *Bull. Acad. roy. Belg.*, 1889, [iii], 18, 679), is obtained as an oil by the condensation of ethyl cyanoacetate with isopropyl bromide. It has b. p. 106—109°/13 mm., 218—219° (corr.)/745 mm., and reacts further with propyl bromide and sodium, forming ethyl α -cyano- α -isopropylvalerate, $CN \cdot CPr^{\alpha} \cdot Pr^{\beta} \cdot CO_2Et$, a colourless oil with a bitter taste, $D^{20}_D 0.943$, b. p. 113—114°/11—12 mm., 242—243°/749 mm. (corr.). When hydrolysed with potassium hydroxide it is converted into dl-cyanoisopropylvaleric acid, b. p. 168—169.5°/13 mm. The lead salt forms minute, colourless prisms concentrically arranged; when reconverted into the acid, a thick, transparent, odourless syrup, b. p. 168—169°/13 mm., was obtained, which, on prolonged standing, solidifies to a crystalline mass, m. p. 40—48°. The acid forms soluble, crystalline calcium and barium salts and a colourless silver salt. It is more stable towards alkali than cyanoacetic acid, the presence of the two propyl groups hindering the hydrolysis of the cyano-group.

The brucine salt of d-cyanoisopropylvaleric acid crystallises in colourless, glistening, microscopic, rectangular plates, m. p. 121° (corr.), and in 10% solution in alcohol has $\alpha - 0.29^\circ$. The corresponding acid, prepared by hydrolysis with sulphuric acid, has m. p. 94—95° (corr.) and $[\alpha]_D^{20} + 11.4^\circ (\pm 0.2^\circ)$ in toluene, whilst the value of α in 10% solution in other solvents varies from $+0.28^\circ$ in alcohol to $+1.52^\circ$ in bromobenzene.

E. F. A.

The Detergent Action of Soap Solutions. WALTHER SPRING (*Bull. Acad. roy. Belg.*, 1909, 187—206).—The author criticises the theories put forward by W. S. Jevons (*Chem. Zeit.*, 1878, 2, 457), Hillger (*J. Amer. Chem. Soc.*, 1903, 25, 511), Falk (*Zeitsch. Elektrochem.*, 1904, 10, 834), and Knapp to account for the cleansing power of soap, pointing out that all of them are inadmissible as they seek only to explain the removal of fatty impurities.

When lamp-black, which has been freed from fatty impurities by prolonged exhaustion with hot benzene, is shaken with a 2% soap

solution, it is deposited almost as quickly as from pure water, whilst with soap solutions containing less than 0.5% of soap, deposition requires about ten days. From a 1% solution, however, deposition is not complete in two months, thus showing that an optimum concentration of soap exists for retaining lamp-black in suspension. Dilute acids have not, but alkalis even of the dilution of 1 in 6,000,000,000 have, greater powers of suspension than water. Methyl and ethyl alcoholic solutions of soap also exhibit optimum concentrations analogous to that of water; 0.02% and 0.005% solutions respectively having the greatest powers of suspension. When water containing lamp-black in suspension is filtered, all the lamp-black remains on the paper, but when a soap solution having lamp-black in suspension is filtered, the paper is not even blackened, thus showing that carbon forms a colloidal combination with soap and also with cellulose, the former being the more stable.

The existence of the latter colloidal combination is confirmed by the fact that the carbon is not removed from the filter-paper by washing after reversal. When the soap solution from which lamp-black has been deposited is evaporated to dryness and the residue incinerated, a greater proportion of ash is obtained than on similarly treating the soap solution to which no lamp-black has been added, thus indicating that the lamp-black causes a decomposition of the soap into an acid soap and a basic soap, and agglutinates with the former, leaving a larger proportion of basic soap in solution. Alcoholic soap solutions do not exhibit this phenomenon. The probability of carbon combining with the acid soap is strengthened by the observation that they are of opposite electrical polarity; thus when lamp-black suspended in water to which a trace of alkali has been added is submitted to electrical cataphoresis, it collects round and is deposited on the cathode, whilst a 2% soap solution on similar treatment forms a white deposit on the anode, which contains a smaller proportion of ash than that left in solution, thus indicating its acid nature. The deposit obtained from soap solutions in which lamp-black has been suspended is actually of an oily, viscous nature, quite different from the lamp-black as originally used. From the above experimental observations the conclusion is drawn that the cleansing action of soap is merely an example of substitution, and can be represented by the equation $OD + S = DS + O$, in which O represents the object defiled by the dirt D , and S is the soap. Both OD and DS are colloidal absorption compounds. The lack of cleansing power of alcoholic soap solutions is explained by the fact that in alcoholic solution soap is not decomposed into an acid part and a basic part.

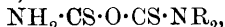
E. H.

Montana (Montan) and Montanin Waxes. HUGH RYAN and THOMAS DILLON (*Sci. Proc. Roy. Dubl. Soc.*, 1909, 12, 202—208).—Irish Montana wax is found to be different from Peat wax recently described by Zaloziecki and Hausmann (*Abstr.*, 1907, i, 674), but identical with montan wax prepared from lignite by Boyen (*Abstr.*, 1902, i, 72). It is a yellow, crystalline, waxy solid having a faint odour of petroleum, m. p. 76°, acid number 73.3, saponification number 73.9, Hübl-Waller iodine number 16.0. This

wax consists of 53% of a free acid, called by Boyen montanic acid (*loc. cit.*), and 47% of a non-saponifiable portion. Montanic acid, $C_{28}H_{56}O_2$, has m. p. 83° , acid number 131.6. The non-saponifiable portion crystallises in glistening, curved needles, m. p. $58-59^\circ$, and does not appear to be a saturated hydrocarbon, neither does it react with hot acetic anhydride; the Hübl-Waller iodine number is 31.13. Montanin wax has also been investigated; it is similar in chemical composition, although different in physical properties, to montana wax. It is a white, hard wax, m. p. $95-97^\circ$, acid number 56.9, ester number 1.0, saponification number 57.9, and contains 34.8% of non-saponifiable matter identical with that contained in montana wax, also 41.33% of montanic acid and 23.87% of sodium montanate. Irish lignite wax is found to have m. p. 72° , acid number 70.28; the free acid has m. p. 80° .

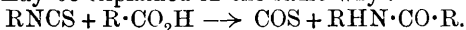
J. V. E.

Stability Relationships of the Anhydrides and Thioanhydrides of Organic Acids. JULIUS VON BRAUN (*Ber.*, 1909, 42, 2743—2745).—The author points out that compounds of the general type $E_1 \cdot C(\cdot E_2) \cdot E_3 \cdot C(\cdot E_2'') \cdot E_1'$ (compare Herzog, this vol., i, 568), where E_2 , E_2' , and E_2'' denote the bivalent atoms :O and :S, and E_1 and E_1' the univalent groups R, OR and NR_2 (NH_2 and NHR) can be divided into two sharply-defined groups, namely, (1) the ordinary acid anhydrides, $R \cdot CO \cdot O \cdot CO \cdot R$, the thiocarbamino-oxides,



and the thiuram sulphides, $NR_2 \cdot CS \cdot S \cdot CS \cdot NR_2$, and (2) the extremely labile and characteristic yellow condensation products of dithiocarbamates with acid chlorides (and esters of chlorocarbonic acid), $NR_2 \cdot [CS \cdot S] \cdot CO \cdot R \cdot OR$, and the additive products of acids with isocyanic ester, $NHR \cdot [CO \cdot O] \cdot CO \cdot R$, which on decomposition eliminate the group shown in square brackets. The formation of acid amides by warming diphenylcarbamyil chloride with acids, and of acid esters by warming esters of chlorocarbonic acid with acids, is probably accompanied by the intermediate formation of unstable anhydrides, which readily lose carbon dioxide (shown by square brackets): $NR_2 \cdot [CO \cdot O] \cdot CO \cdot R$, $OR \cdot [CO \cdot O] \cdot CO \cdot R$.

The well known formation of carbonyl sulphide and acid amides from thiocarbimides or thiocyanic acid and carboxylic acids at higher temperatures may be explained in the same way:



The different behaviour of the two groups is attributed to the fact that the compounds belonging to the first are symmetrical, whilst those of the second are unsymmetrical, and are, therefore, more labile.

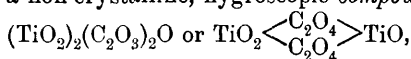
J. C. C.

Additive Di-iodo-derivatives of Higher Fatty Acids of the $C_nH_{2n-4}O_2$ Series. ALBERT ARNAUD and SWIGEL POSTERNAK (*Compt. rend.*, 1909, 149, 220—222).—Di-iodo-derivatives of the higher members of the $C_nH_{2n-4}O_2$ series of acids are most conveniently prepared by adding the calculated quantity of iodine to a solution of the acid in acetic acid. Tetra-iodo-derivatives cannot be prepared by a direct method. The di-iodo-derivatives are not altered by light

or by boiling with alcoholic alkali hydroxides; they are stable towards oxidising agents, but are readily reduced to the original acids. Their preparation serves as a convenient method for characterising the acids, and has been employed in isolating new members of the series from complex mixtures.

Di-iodotariric acid, $\text{CH}_3 \cdot [\text{CH}_2]_{10} \cdot \text{Cl} \cdot \text{Cl} \cdot [\text{CH}_2]_4 \cdot \text{CO}_2\text{H}$, crystallises in slender needles, m. p. 48.5° ; the *ammonium* salt forms long needles, and is distinguished from the corresponding salt of di-iodoelaidic acid by its sparing solubility in alcohol. Di-iodobrassicic acid has m. p. $50-51^\circ$ (Liebermann and Sachse give 47°). W. O. W.

Complex Ozo-salts of Titanium. ARRIGO MAZZUCHELLI and ENRICO PANTANELLI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 518—522. Compare Abstr., 1907, i, 891).—The addition of excess of hydrogen peroxide to a solution obtained by heating freshly-precipitated titanium hydroxide in less than the calculated quantity of oxalic acid results in the formation of a non-crystalline, hygroscopic compound,



which is partly hydrolysed by water.

The authors have also prepared the complex *ozolitanotartrate*, $\text{TiO}_2 \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{C}_4\text{H}_5\text{O}_6\text{K} \cdot 10\text{H}_2\text{O}$. T. H. P.

Solubility of Some Comparatively Insoluble Salts of the Rare Earths. EBERHART RIMBACH and ALWIN SCHUBERT (*Zeitsch. physikal. Chem.*, 1909, 67, 183—202).—The solubilities of the salts in question have been determined by Kohlrausch's electrical conductivity method at temperatures between 18° and 26° . The temperature-coefficient of the conductivity in the neighbourhood of 25° was determined in each case, and the results at 25° obtained by interpolation. The specific conductivity, λ , and the solubility, s , in mgs. per litre of the different salts at 25° are as follows. (1) *Oxalates* of the type $\text{M}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$: cerium, $\lambda = 0.651 \times 10^{-6}$, $s = 0.41$; lanthanum, $\lambda = 0.954 \times 10^{-6}$, $s = 0.62$; praseodymium, $\lambda = 1.165 \times 10^{-6}$, $s = 0.74$; neodymium, $\lambda = 0.765 \times 10^{-6}$, $s = 0.49$; samarium, $\lambda = 0.820 \times 10^{-6}$, $s = 0.54$; ytterbium, $\lambda = 4.853 \times 10^{-6}$, $s = 3.34$; and yttrium with $9\text{H}_2\text{O}$, $\lambda = 1.741 \times 10^{-6}$, $s = 1.00$. (2) *Tartrates*: cerium,

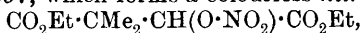
$\text{Ce}_2(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 4\frac{1}{2}\text{H}_2\text{O}$, $\lambda = 51.66 \times 10^{-6}$, $s = 50.01$; lanthanum, $\text{La}_2(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 3\text{H}_2\text{O}$, $\lambda = 58.55 \times 10^{-6}$, $s = 58.80$. (3) *Iodates*: cerium, $\text{Ce}(\text{IO}_3)_3 \cdot 2\text{H}_2\text{O}$, $\lambda = 636.8 \times 10^{-6}$, $s = 1636$; lanthanum, $\lambda = 692.6 \times 10^{-6}$, $s = 1871$.

In a saturated solution the oxalates are almost completely ionised; the tartrates to the extent of 89%, and the iodates to 76—77%.

G. S.

Synthesis of Unsymmetrical Dialkylmalic Esters and Diethyl-oxalacetic Esters. BERTHOLD RASSOW and R. BAUER (*J. pr. Chem.*, 1909, [ii], 80, 87—102. Compare Zeltner, Abstr., 1908, i, 316).—Interaction between ethyl oxalate (1 mol.), ethyl α -bromoisobutyrate (1 mol.), and zinc ($2\frac{1}{2}$ mols.) containing a little amalgamated zinc, for twenty-four hours at $60-65^\circ$, and treatment of the product with

water and dilute sulphuric acids, yields *ethyl $\alpha\alpha$ -dimethylmalate*, $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{Et}$, b. p. 248—250° or 123—124°/12—13 mm., D^{15}_D 1.076, n^{21}_D 1.4357, which forms a colourless *nitrate*,

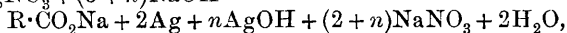
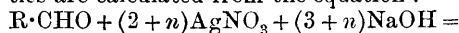


b. p. 128°/11 mm., n^{23}_D 1.4371, by treatment with concentrated nitric and sulphuric acids at 0°, and is hydrolysed by alcoholic potassium hydroxide to Baeyer and Villiger's dimethylmalic acid.

The interaction of ethyl oxalate, ethyl α -bromoisobutyrate, and magnesium in ethereal solution leads to the formation of *ethyl dimethyl-oxalacetate*, $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, b. p. 230° or 115—120°/11 mm., D^{15}_D 1.05, n^{23}_D 1.4313, which is hydrolysed by alcoholic potassium hydroxide to oxalic and isobutyric acids, and by warm dilute sulphuric or hydrochloric acid to isobutyrylformic acid, forms a *semicarbazone*, m. p. 95°, and by heating with phenylhydrazine, initially at 100° and finally at 190—200°, yields *ethyl 1-phenyl-4:4-dimethylpyrazolone-3-carboxylate*, m. p. 81°.

Ethyl diethyloxalacetate, $\text{CO}_2\text{Et}\cdot\text{CEt}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, prepared in a similar manner from ethyl α -bromo- α -ethylbutyrate, has b. p. 134—136°/12 mm., and forms a *phenylhydrazone*, m. p. 86°. C. S.

Oxidation of Aldehydes by Silver Oxide. MARCEL DELÉPINE and PIERRE BONNET (*Compt. rend.*, 1909, 149, 39—41).—When silver oxide is employed in oxidising aldehydes to acids, it is unnecessary to isolate and wash the oxide as usually recommended. The following process has been found to give almost theoretical yields of the acids in the pure state. Silver nitrate is added to an aqueous solution of the aldehyde containing sufficient alcohol to keep it in solution. A $N/2$ or $N/3$ solution of sodium, potassium, or preferably barium hydroxide is added at frequent intervals during two hours, with constant shaking. After twelve hours the liquid is filtered and treated with carbon dioxide. Alcohol is removed by distillation, and, if necessary, any neutral products may be removed by extraction with ether. Quantities are calculated from the equation:



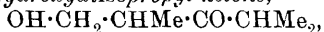
where $n = 0.1$ to 1.0 .

This method is the only one that gives satisfactory results in the case of the polymeride of crotonaldehyde, $\text{C}_8\text{H}_{12}\text{O}_2$; in this instance it is necessary to add more than $(2+n)$ equivalents of alkali.

W. O. W.

$\alpha\alpha$ -Dialkyl- β -keto-alcohols. EDMOND É. BLAISE and I. HERMAN (*Ann. Chim. Phys.*, 1909, [viii], 17, 371—398).—Mainly a recapitulation of work previously published (compare *Abstr.*, 1904, i, 218, 219; 1905, i, 505; 1907, i, 749; 1908, i, 78, 248, 318, 596; this vol., i, 85). The following new compounds are described: *β -Acetoxy- $\alpha\alpha$ -dimethylpropionyl chloride*, $\text{OAc}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{COCl}$, b. p. 84°/12 mm.; the *anilide*, white needles, m. p. 87°; and the *p-toluidide*, needles, m. p. 79°. *Ethyl hydroxy-tert-butyl ketoxime*, $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CEt}\cdot\text{N}\cdot\text{OH}$, small crystals, m. p. 80°; the *phenylhydrazone*, clear yellow needles, m. p. 104—105°; the *semicarbazone*, small crystals, m. p. 122°; and the

phenylurethane, small, colourless crystals, m. p. 62.5° . *Ethyl isopropyl ketone semicarbazone* forms needles, m. p. 92.5° . α -*Methylhydracrylic acid*, $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, a colourless, viscous liquid; the *ethyl ester* has b. p. $76^{\circ}/7$ mm.; the *phenylhydrazide* forms brilliant white spangles, m. p. 143° ; the *phenylurethane*, white needles, m. p. 122° . β -*Acetoxyisobutyric acid*, $\text{OAc}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, b. p. $132^{\circ}/8$ mm.; the *ethyl ester*, b. p. $84\text{--}85^{\circ}/9$ mm.; the *chloride*, b. p. $75^{\circ}/7$ mm.; the *anilide*, slender needles, m. p. 100° ; the α -*naphthylamide*, small crystals, m. p. 104° ; the *p-toluidide*, needles, m. p. 99° . β -*Bromodiisopropyl ketone*, $\text{CHMe}_2\cdot\text{CO}\cdot\text{CBrMe}_2$, formed by the action of hydrogen bromide on isopropyl methylvinyl ketone, has b. p. $65^{\circ}/9$ mm.; it does not give a semicarbazone. β -*Hydroxydiisopropyl ketone*,



has b. p. $80^{\circ}/10$ mm.; the *acetyl* compound has b. p. $87^{\circ}/8$ mm.

E. H.

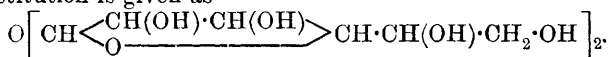
Colorimetric Determination of the Molecular Weights of Carbohydrates. Differentiation of Primary from Secondary and Tertiary Alcohols. II. LEONHARD WACKER (*Ber.*, 1909, 42, 2675—2680).—The colorimetric method described previously (*Abstr.*, 1908, i, 135) has been improved by the use of stronger, 33%, sodium hydroxide whereby the coloration is rendered more durable. The molecular weights of carbohydrates are somewhat greater when dextrose is used as standard in place of maltose. The colour reaction is determined by the terminal $\cdot\text{CHO}$ or $\cdot\text{CH}_2\cdot\text{OH}$ group, since secondary and tertiary alcohols practically do not give a coloration with phenylhydrazinesulphonic acid. The method is being employed in the examination of starch and its degradation products. C. S.

Synthesis of New Disaccharides of the Type of Trehalose.

EMIL FISCHER and KONRAD DELBRÜCK (*Ber.*, 1909, 42, 2776—2785).—The following method promises to be of great importance in the synthesis of disaccharides. β -Bromoacetodextrose and silver carbonate in dry ether are shaken with a small quantity of water so long as carbon dioxide is evolved. The precipitate contains *tetra-acetyldextrose*, $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}(\text{OAc})\\ \text{O}\cdot\text{CH}(\text{OH})\end{smallmatrix}\right\rangle\text{CH}\cdot\text{OAc}$, m. p. 118° (corr.), whilst the ethereal filtrate leaves a viscous residue of an octa-acetyl compound. Tetra-acetyl dextrose exhibits mutarotation, an alcoholic solution (0.2521 in 4.4480 grams), D^{20} 0.8043, giving in a 1-dcm. tube at 22° a rotation of 0.10° after ten minutes and 3.77° after thirty-eight hours, reduces Fehling's solution, and is easily soluble in dilute sodium hydroxide.

The octa-acetyl compound, which is obtained in better yield by repeatedly shaking silver carbonate and β -bromoacetodextrose in dry ether with a few drops of water, or by shaking a chloroform solution of tetra-acetyldextrose with phosphoric oxide, is separated by boiling water into two constituents, a soluble, crystalline *octa-acetylisotrehulose*, $\text{C}_{28}\text{H}_{38}\text{O}_{19}$, m. p. 181° (corr.), and an insoluble, amorphous substance, $\text{C}_{28}\text{H}_{38}\text{O}_{19}$. The latter softens at 80° , has m. p. 115° , and $[\alpha]_D^{25}$ 31.1° in benzene, scarcely affects Fehling's solution, and is probably a

mixture, which is hydrolysed by barium hydroxide to a mixture of disaccharides. Octa-acetylisotrehalose has $[\alpha]_D^{22} - 17.2^\circ$ in benzene, does not reduce Fehling's solution, and is hydrolysed by barium hydroxide solution at the ordinary temperature to a disaccharide, $C_{12}H_{22}O_{11}$, an amorphous, hygroscopic powder, which does not reduce Fehling's solution, has $[\alpha]_D^{23} - 39.4^\circ$ in aqueous solution, and yields dextrose by heating with 10% hydrochloric acid; by reason of the similarity of its properties to those of trehalose, the disaccharide is named isotrehalose. Its constitution is given as



C. S.

Constitution of Perseulose. GABRIEL BERTRAND (*Compt. rend.*, 1909, 149, 225—227. Compare Abstr., 1908, i, 715).—When perseulose is reduced by sodium amalgam in acid solution there is formed persitol, together with a new laevorotatory heptitol distinguished from persitol by its solubility in water and alcohol. The name *perseulitol* is proposed for this substance. The formation of two stereoisomeric sugars in this way, coupled with the fact that it resists oxidation by bromine water, indicates that perseulose is a hepta-ketose, this being the first instance of one recorded.

W. O. W.

Two New Carbohydrates from Asparagus. GEORGES TANRET (*Compt. rend.*, 1909, 149, 48—50).—A description of two new sugars occurring in approximately equal quantities in the roots of asparagus. The roots are boiled with water, after defecation with barium hydroxide and lead acetate, followed by treatment with sulphuric acid to remove lead, the liquid is neutralised, concentrated at a low temperature, and the sugars isolated by fractional precipitation with barium hydroxide.

Asparagose crystallises in spherical aggregates or in fine, microscopic needles, having the composition $(C_6H_{10}O_5)_n \cdot H_2O$, where $n = 15$ or 16 . It is insoluble in absolute alcohol, but soluble in two parts of cold water, $\alpha_D - 35.1^\circ$. On the Maquenne block it softens at 185° , and has m. p. 198 — 200° . *Asparagose* does not reduce Fehling's solution, gives no coloration with iodine, and on hydrolysis yields dextrose and laevulose. The barium compound, $(3C_6H_{10}O_5 \cdot BaO)_n$, is moderately soluble in water. The second carbohydrate, *ψ-asparagose*, has $\alpha_D 30.3^\circ$, and occurs as a white, slightly hygroscopic mass, which is much more soluble than asparagose. Like asparagose, it is hydrolysed by invertin, yielding dextrose and laevulose.

W. O. W.

Coloration of the Particles of Colloidal Starch and of Perfectly Soluble Starch with Iodine and Potassium Iodide. NICOLA CASTORO (*Gazzetta*, 1909, 39, i, 603—607).—Treatment of pea-flour starch with dilute sulphuric acid yields a pseudo-solution of starch, which is precipitated in white flocks by absolute or 95% alcohol. Part of this precipitate is soluble in water; the insoluble part is coloured bluish-violet by a solution of iodine in potassium iodide, and consists of amylopectin, whilst the dissolved part, in the form of a

pseudo-solution, is coloured intensely blue, and is in part diffusible through parchment and in part colloidal. The latter consists of amylose, and is coloured a characteristic blue by iodine in potassium iodide, whilst the diffusible part is coloured a wine-violet.

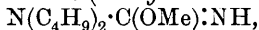
These results, and others obtained with potato starch, show that the different colorations obtained depend on the magnitude of the particles, which are larger for pseudo-solutions than for true solutions of starch.

T. H. P.

Oxygen Ethers of the Dialkylcarbamides. RALPH H. MCKEE (*Amer. Chem. J.*, 1909, 42, 1—29).—In an earlier paper (Abstr., 1901, i, 755) some aromatic isocarbamide derivatives were described. The present paper gives an account of methyl- and ethyl-dialkylisocarbamides, $\text{NR}_2 \cdot \text{C}(\text{OMe}) \cdot \text{NH}$, in which R is CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , or C_5H_{11} . These compounds, obtained by the action of sodium alkyl-oxides on dialkylcyanamides, are colourless oils, the densities and solubilities of which decrease as R increases from CH_3 to C_5H_{11} . They are strong bases, uniting with one equivalent of the strong acids to form neutral salts, attacking the skin in the same way as potassium hydroxide, and being capable of dissolving aluminium hydroxide. When a solution of one of these bases in ether or light petroleum is treated with dry hydrogen chloride, the hydrochloride is precipitated, which, on heating, decomposes quantitatively into methyl chloride and the carbamide: $\text{NR}_2 \cdot \text{C}(\text{OMe}) \cdot \text{NH} \cdot \text{HCl} = \text{NR}_2 \cdot \text{CO} \cdot \text{NH}_2 + \text{CH}_3\text{Cl}$. If the bases are heated alone, they are decomposed into the cyanamide and alcohol from which they were prepared, whilst if heated in aqueous solution, the following reaction takes place:

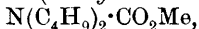
$\text{NR}_2 \cdot \text{C}(\text{OMe}) \cdot \text{NH} + \text{H}_2\text{O} = \text{NR}_2 \cdot \text{CO} \cdot \text{NH}_2 + \text{CH}_3 \cdot \text{OH}$,
but neither ammonia nor a urethane is formed.

Methyldiisobutylisocarbamide (methyl diisobutyliminocarbamate),



b. p. $102^\circ/14$ mm., $116^\circ/22$ mm., $135^\circ/42$ mm., and $218\text{—}222^\circ$ (decomp.)/742 mm., obtained by the action of sodium methoxide on diisobutylcyanamide, has $D_{18.5}^{20} 0.8933$, and is soluble in 100 parts of water to the extent of 1.14 parts at 0° , 0.94 at 10° , 0.61 at 21° , 0.49 at 30° , and 0.32 at 85° ; the *hydrochloride* and *ferrocyanide* are described. *Diisobutylcarbamide*, $\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CO} \cdot \text{NH}_2$, b. p. $180^\circ/25$ mm., m. p. $72\text{—}74^\circ$, may be prepared by the action of potassium isocyanate on diisobutylamine hydrochloride; its *oxalate*, m. p. 115° (decomp.), and *picrate*, m. p. $90\text{—}91^\circ$, are described. *Benzoylmethyldiisobutylisocarbamide*, $\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{C}(\text{OMe}) \cdot \text{NBz}$, forms a viscid oil, and, when heated with dilute hydrochloric acid at 100° , is converted into methyl chloride and benzoyldiisobutylcarbamide; the *hydrochloride* decomposes rapidly at the ordinary temperature with formation of the same products. *Benzoyldiisobutylcarbamide*, $\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CO} \cdot \text{NHBz}$, m. p. $123\text{—}123.5^\circ$, crystallises in stout, rhombic plates.

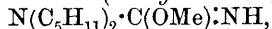
Methyl diisobutylcarbamate (methyldiisobutylurethane),



b. p. $204^\circ/753$ mm., obtained by the action of methyl chlorocarbonate on diisobutylamine in presence of potassium hydroxide, has a characteristic odour, and is soluble at 18° in 4000 parts of water, 1200 parts

of 3*N*-hydrochloric acid, or 200 parts of 12*N*-hydrochloric acid. The corresponding *ethyl* ester, b. p. 100°/13 mm. and 203°/757 mm., is soluble at 17° in 1600 parts of water, 640 parts of 3*N*-hydrochloric acid, or 320 parts of 12*N*-hydrochloric acid.

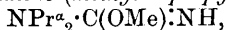
Methyldiisocarbamide (*methyl diisocarbaminocarbamate*),



b. p. 125°/7 mm., 133°/12 mm., and 153°/30 mm., has D_{15}^{20} 0.8860, and is soluble in 1500 parts of water at 15°; the *hydrochloride* melts at 104° (decomp.). *Diisocarbamide*, $\text{N}(\text{C}_5\text{H}_{11})_2 \cdot \text{CO} \cdot \text{NH}_2$, was obtained as an oil; its *oxalate*, m. p. 102.5° (decomp.), and *picrate* are described.

Ethyldiisocarbamide (*ethyl diisocarbaminocarbamate*) has b. p. 158°/28 mm.; its aqueous solution blackens mercurous chloride, and gives a white precipitate with solution of mercuric chloride. The *hydrochloride* has m. p. 125° (decomp.).

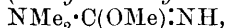
Methyldipropylisocarbamide (*methyl dipropyliminocarbamate*),



behaves with mercury salts in the same way as *ethyl diisocarbaminocarbamide*; its *hydrochloride* decomposes at the ordinary temperature. *Methyl dipropylcarbamate* (*methyldipropylurethane*), $\text{NPr}^a_2 \cdot \text{CO}_2\text{Me}$, b. p. 191°/751 mm., is soluble at 18° in 300 parts of water or 160 parts of 3*N*-hydrochloric acid. *Ethyl dipropylcarbamate* boils at about 200°/749 mm.

Ethyldipropylisocarbamide (*ethyl dipropyliminocarbamate*), b. p. 92°/10 mm., does not decompose at 100°.

Trimethylisocarbamide (*methyl dimethyliminocarbamate*),



b. p. 60.5°/27 mm., 86°/98 mm., and 146.5° (decomp.)/755 mm., is readily volatile with the vapour of ether or alcohol, and is completely miscible with all solvents; its salts are deliquescent, and undergo rapid decomposition at the ordinary temperature. A slightly impure specimen had D_{40}^{20} 0.9708. This compound dissolves silver oxide and aluminium hydroxide, but not cupric hydroxide. It gives a black precipitate with mercurous nitrate and a white precipitate with mercuric chloride. The *hydrochloride* melts at 91° (decomp.).

Pinner has shown that imino-ethers decompose slowly at the ordinary temperature, and more quickly on heating, into the nitrile and alcohol from which they were prepared. An analogous decomposition has now been observed with some of the *isocarbamides*. Thus when *trimethylisocarbamide* is heated at 100° in a sealed tube, it decomposes into *dimethylcyanamide* and *methyl alcohol*. Under similar conditions, *ethylisocarbamide* yields *ethyl alcohol* and *melamine*, together with small quantities of *dicyanodiamide*. E. G.

Guanidine Perchromate. KARL A. HOFMANN and KARL BUCHNER (*Ber.*, 1909, 42, 2773—2776).—When *guanidine carbonate*, water, and chromium trioxide are warmed at 30—35° to expel carbon dioxide, and then treated at 0° with 33% hydrogen peroxide, a precipitate of *guanidine perchromate*, $(\text{CN}_3\text{H}_3)_2\text{CrO}_5 \cdot \text{H}_2\text{O}$, is obtained. It forms small, brownish-yellow, double-refracting prisms, yields 7 equivalents of oxygen with 2% sodium hydroxide, 13 equivalents

with alkaline potassium permanganate, 9 equivalents with 15% sulphuric acid, 12 equivalents with acidified potassium permanganate, forms the usual blue solution with ether and dilute sulphuric acid, and is decomposed by boiling water, forming guanidine chromate. Since the *potassium* salt, K_3CrO_8 , is obtained by treatment with 15% potassium chloride at a low temperature, guanidine perchromate is a true salt and not a metal ammonia. C. S.

New Method of Preparing Ammonium Thiocyanate and Thiocarbamide. GIUSEPPE INGHILLERI (*Gazzetta*, 1909, 39, i, 634—639).—When 6 grams of carbon disulphide and 8 grams of ammonium carbonate are heated together in a sealed tube at 100—110°, they react, giving ammonium dithiocarbamate, thus: $CS_2 + NH_4 \cdot O \cdot CO \cdot O \cdot NH_4 = H_2O + CO_2 + NH_2 \cdot CS \cdot S \cdot NH_4$. If, however, the temperature is kept at 120—130°, ammonium thiocyanate is formed: $NH_2 \cdot CS \cdot S \cdot NH_4 = H_2S + NH_4 \cdot NCS$, whilst at 160° a quantitative yield of thiocarbamide is obtained.

The interaction of carbon disulphide and ammonium carbonate in presence of alcohol at the ordinary pressure gives a quantitative yield of ammonium thiocyanate, whilst at 160° in a sealed tube these compounds give a product having the same m. p. as diethylthiocarbamide. T. H. P.

Reaction between Ferric Compounds and Thiocyanates. CORRADO BONGIOVANNI (*Boll. Chim. Farm.*, 1909, 48, 483—485).—Reply to Brioni's criticisms (this vol., i, 92) on the author's work on this subject (*Abstr.*, 1908, i, 770, 859). T. H. P.

Hexathiocyano-salts of Molybdenum. JOHANNA MAAS and JULIUS SAND (*Ber.*, 1909, 42, 2642—2646. Compare *Abstr.*, 1908, i, 397, 513, 961; Rosenheim and Garfunkel, *ibid.*, i, 614; Rosenheim, this vol., i, 558).—The potassium and ammonium salts have not similar compositions, as stated by Rosenheim, but are to be represented by the formulæ $K_3Mo(SCN)_6 \cdot H_2O, 4H_2O$ and $(NH_4)_3Mo(SCN)_6 \cdot H_2O, 3H_2O$.

The corresponding acetates are strictly isomorphous, and have the analogous formulæ $K_3Mo(SCN)_6 \cdot H_2O, HOAc$ and $(NH_4)_3Mo(SCN)_6 \cdot H_2O, HOAc$.

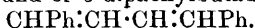
The thiocyanate can be determined accurately in the case of the complex molybdenum salts, although not with complex thiocyanochromium compounds. J. J. S.

Prussian Blue and Turnbull's Blue. KARL A. HOFMANN (*J. pr. Chem.*, 1909, ii, 80, 150—152).—In reply to Müller and Stanisch (this vol., i, 142), the author reaffirms his opinion that soluble Prussian blue and soluble Turnbull's blue are identical. They have the composition $KFe'''[Fe(CN)_6]_x \cdot H_2O$, and behave alike optically and towards water, ammonium hydroxide, oxalic acid, ammonium oxalate, and ammonium tartrate. C. S.

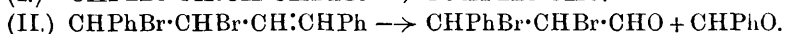
New Method of Preparing Nitrosobenzene. BERNARDO ODDO (*Gazzetta*, 1909, 39, i, 659—661).—Nitrosobenzene may be prepared

in 56% yield by the action of nitrosyl chloride on magnesium phenyl bromide: $\text{MgPhBr} + \text{NOCl} = \text{MgBrCl} + \text{Ph}\cdot\text{NO}$. T. H. P.

Course of the Addition of Bromine to Conjugated Ethylene Linkings. FRITZ STRAUS (*Ber.*, 1909, 42, 2866—2885).—With the object of testing the accuracy of Thiele's theory that in the formation of a bromine additive compound of a substance containing the conjugated ethylene linking, the bromine atoms attach themselves in the $\alpha\delta$ -position, the author has studied the action of ozone on the bromine additive compound of *s*-diphenylbutadiene,

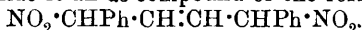


A substance of the formula (I) should on oxidation with ozone break at the double linking to give two molecules of bromophenylacetaldehyde, whereas a substance of the constitution (II) should give a mixture of dibromocinnamaldehyde with benzaldehyde:



The latter reaction was found to take place on passing a current of ozone through a solution of the dibromide in carbon tetrachloride solution, and it follows from this that the bromine atoms were added in the 1:2-position, and not in the $\alpha\delta$ -position as required by the theory. The dibromocinnamaldehyde was identified by conversion into the crystalline monobromo-derivative or into β -bromostyrene, whilst the benzaldehyde was identified in the form of benzoic acid.

Similarly, by subjecting the dibromo-additive compound of monophenylbutadiene, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$, to the action of ozone, the author obtained a mixture of benzaldehyde with a brominated aliphatic aldehyde, which, however, could not be identified. Since these substances must have been produced by the oxidation of a compound of the constitution $\text{CHPh}\cdot\text{CH}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$, it follows that the bromine atoms were added in the $\gamma\delta$ -position. The addition of hydrogen to both mono- and di-phenylbutadiene, however, takes place in accordance with Thiele's theory in the $\alpha\delta$ -position, and when butadiene itself is exposed to the action of bromine, both the $\alpha\delta$ - and the $\alpha\beta$ -dibromides are produced; it has further been shown by Wieland that the additive compound formed from diphenylbutadiene and nitrogen peroxide is an $\alpha\delta$ -compound of the formula



The similarity in action which is thus seen to subsist between hydrogen and nitrogen peroxide as opposed to bromine may be explained by assuming that hydrogen is added on in the atomic form, and that the nitrogen peroxide when dissolved in organic solvents acts as a simple molecule, and, accordingly, in both cases the substance to be added is present in the form in which it is to be added on, whereas in the case of bromine the addition is molecular. P. H.

Cyanobenzylamines. OTTO FISCHER and H. WOLTER (*J. pr. Chem.*, 1909, [ii]. 80, 102—112).—During unsuccessful attempts to prepare *o*-cyanobenzaldehyde, the following new compounds have been

obtained. *o*-Cyanobenzylaniline does not form a nitroso-derivative. *p*-Cyanobenzylaniline, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NHPh}$, m. p. 86° , obtained from aniline and *p*-cyanobenzyl chloride at 90° , forms a *hydrochloride*, $\text{C}_{14}\text{H}_{12}\text{N}_3\cdot\text{HCl}$, m. p. 215° (decomp.), and a *nitroso-derivative*, $\text{C}_{14}\text{H}_{11}\text{ON}_3$, m. p. 90° , and is oxidised in acetone by aqueous potassium permanganate to *p*-cyanobenzanilide, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHPh}$, m. p. 178 — 179° ; *Di-p*-cyanobenzylaniline, $\text{C}_{22}\text{H}_{17}\text{N}_3$, m. p. 181 — 182° , is a by-product in the preparation of *p*-cyanobenzylaniline. *m*-Cyanobenzylaniline, m. p. 70° , is prepared in a similar manner to the para-isomeride, and forms a *hydrochloride*, *picrate*, m. p. 158° , and *nitrosoamine*, m. p. 63° . *o*-Cyanobenzylmethylamine, m. p. 100 — 105° , prepared from *o*-cyanobenzyl chloride and 33.5% methylamine, forms a *hydrochloride*, $\text{C}_9\text{H}_{10}\text{N}_2\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$, and an *aurichloride*, but not a nitrosoamine. *o*-Cyanobenzyltrimethyl-*p*-phenylenediamine, $\text{C}_{16}\text{H}_{17}\text{N}_3$, m. p. 135° , forms a *hydrochloride*, $\text{C}_{16}\text{H}_{17}\text{N}_3\cdot\text{HCl}\cdot 3\text{H}_2\text{O}$, an orange-red *picrate*, darkening at 185° and decomposing at 200° , and with nitrous acid a red *nitro*-compound, $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_4$, m. p. 139° .

p-Cyanobenzyltrimethyl-*p*-phenylenediamine, m. p. 183° , forms a yellow *nitrosoamine*, $\text{C}_{16}\text{H}_{16}\text{ON}_4$, m. p. 105 — 106° , which is converted by dilute sulphuric acid into *p*-cyanobenzaldehyde. C. S.

Constituents of Coal Tar. Ethylbenzene. GUSTAV SCHULTZ and A SANDER (*Ber.*, 1909, 42, 2633—2636. Compare Noelting and Palmar, *Abstr.*, 1891, 1197).—Dinitroethylbenzene (Weisweiler, *Abstr.*, 1900, i, 291) has b. p. $163^\circ/10$ mm., $167.8^\circ/13$ mm., $178.5^\circ/18$ mm., $187^\circ/24.5$ mm., and $195.5^\circ/33$ mm., and when reduced with ammonium sulphide yields 2-nitro-4-amino-1-ethylbenzene, $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Et}\cdot\text{NH}_2$, which crystallises from light petroleum in orange-yellow prisms, m. p. 43 — 44° . The *acetyl* derivative, $\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_2$, forms yellowish-brown crystals, m. p. 100 — 101° .

Trinitroethylbenzene (Weisweiler, *loc. cit.*) yields coloured additive compounds with arylamines and aromatic hydrocarbons.

With aniline it yields light red prisms, m. p. 45° ; with *p*-toluidine, blood-red needles, m. p. 25° . The corresponding compound of trinitrotoluene and *p*-toluidine has m. p. 69 — 70° .

Trinitroethylbenzene and *o*-toluidine yield blood-red prisms, m. p. 35° . With monomethylaniline the nitro-compound yields red prisms, m. p. 44° ; with *m*-4-xylydine, red prisms, m. p. 52° ; with benzidine, black prisms, m. p. 73° ; with *o*-toluidine, violet-black prisms, m. p. 85° ; with α -naphthylamine, wine-red plates, m. p. 72 — 73° ; with β -naphthylamine, purplish-red needles, m. p. 61 — 63° , and with naphthalene, yellow prisms, m. p. 58° . All these compounds contain 1 molecule of nitro-compound united with 1 molecule of amine or hydrocarbon, and they are all comparatively unstable (compare *Trans.*, 1901, 79, 522; 1903, 83, 1334).

When reduced with ammonium sulphide, the trinitro-compound yields *s*-dinitroaminoethylbenzene, $\text{C}_8\text{H}_9\text{O}_4\text{N}_3$, which crystallises from light petroleum in lemon-yellow prisms, m. p. 110° . J. J. S.

Abnormal Salts. II. ANTONI KORCZYŃSKI (*Bull. Acad. sci. Cracow*, 1909, 610—627. Compare *Abstr.*, 1908, i, 977).—It has been

shown previously that the tendency of substituted phenols to form abnormal ammonium salts at the ordinary temperature or at 0° to -17° is conditioned by the presence and the position of certain atoms or groups in the acidic substance, and that substituents in the di-ortho-positions exert the greatest influence. The investigation has been extended to include fifty-eight substituted phenols, cresols, naphthols, benzoic and cinnamic acids, the substituents being nitro-groups and halogens, with the following results. In nitrophenols and nitrobenzoic acids the tendency to abnormal salt formation is greatest when the nitro-group is in the para-position, but in nitrocinnamic acids when the substituent is in the ortho-position, and so also in monohaloid benzoic acids. In dinitrophenols the tendency is greatest in the 2:6-compound, but in halogen disubstituted cresols, abnormal salt formation is most marked when the halogen atoms are in the *o*:*p*-positions with respect to the hydroxyl group. The fact that 2:4-dinitro-1-naphthol absorbs 1 mol. NH_3 , whilst 1:6-dinitro-2-naphthol absorbs 2, is explicable by Kaufler's stereo-formula of naphthalene, according to which positions 1 and 6 are di-ortho with respect to position 2. When a halogen atom in 2:4:6-trihalogenphenols is replaced by a nitro-group, the tendency is, or is not, diminished according as the nitro-group is in the ortho- or the para-position to the hydroxyl group. When a nitro-group in 2:4:6-trinitrophenol is replaced by a halogen atom, the tendency is not diminished when the halogen is in the ortho-position, and in the para-position only when the halogen atom is iodine.

It is remarkable that the addition of ammonia to nitrophenols is most favoured when the nitro-group is in that position in which it most hinders the addition of hydrogen chloride to the corresponding nitro-aniline.

C. S.

The Oxidation of Phenol. The Effect of Some Forms of Light and of Active Oxygen on Phenol and Anisole. HARRY D. GIBBS (*Philippine J. Sci.*, 1909, 4, 133—151. Compare this vol., i, 221, and Kohn and Freyer, *J. Soc. Chem. Ind.*, 1893, 12, 111).—Pure phenol remains colourless in sunlight when in contact with the indifferent gases, hydrogen, nitrogen, and carbon dioxide, but is coloured in the presence of oxygen. In the dark, the rate is not appreciable at the ordinary temperature, but increases with rise of temperature. It can be measured at 100° , and at the boiling point of phenol is fairly rapid. In sunlight the rate of coloration is rapid, and increases directly with the temperature. The coloration is due to oxidation, and the principal products formed are quinol, *p*-benzoquinone, and catechol, together with some carbon dioxide. The coloration itself is probably due to the formation of quinone condensation products, of which the red compound, phenoquinone, is one.

Ozone reacts readily with phenol, yielding quinol, *p*-benzoquinone, catechol, glyoxylic acid, and carbon dioxide. An ozonide was not isolated. Anodic oxygen also reacts readily with phenol, yielding *p*-benzoquinone. The experiments lead to the conclusion that the activity is not due to oxygen gaseous ions.

The nature of the glass through which the sunlight passes has an

influence on the rate of the reaction. Glasses which absorb ultra-violet rays most completely have the greatest retarding effect.

Ozone could not be detected in pure dry oxygen sealed in a glass tube and exposed to sunlight. The altitude of the sun, the thickness of the atmosphere through which it passes, and the atmospheric conditions influence the rate of coloration.

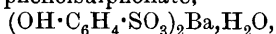
Anisole is not coloured by oxygen or ozone in the presence of sunlight.

The reactivity of phenol is augmented by the absorbed wave-lengths at about λ 291 to λ 243.

The purest phenol can only be obtained by distillation in an atmosphere free from oxygen. J. J. S.

Phenolsulphonic Acid Method for the Estimation of Nitrates in Water. I. Composition of the Reagent and of the Reaction Product. EMIL M. CHAMOT and D. S. PRATT (*J. Amer. Chem. Soc.*, 1909, 31, 922—928).—A study of the standard phenolsulphonic acid employed for the estimation of nitrates in water has shown that it contains phenol-2:4-disulphonic acid, together with small quantities of *p*-phenolsulphonic acid, and that the yellow coloration produced in the reaction is not due to picric acid, as is generally supposed, but to an alkali nitrophenol-sulphonate.

An investigation has been made of the barium salts of the phenol-sulphonic acids, and the observations of Obermiller (*Abstr.*, 1907, i, 910) on barium *o*-phenolsulphonate and phenol-2 : 4-disulphonate are confirmed. Barium *p*-phenolsulphonate,



forms rosettes of slender, white, silky needles. It is shown that mixtures of the phenolsulphonic acids can be analysed micro-chemically by means of these salts, the crystalline forms of which are depicted by micro-photographs.

When *o*-phenolsulphonic acid is added to nitrates and afterwards diluted and rendered alkaline, a dark green solution is obtained without any yellow tint. *p*-Phenolsulphonic acid does not react with nitrates in the cold, but on heating it behaves in the same way as the ortho-acid. Phenol-2 : 4-disulphonic acid reacts to form pure yellow solutions. If the mono-acids are submitted to prolonged heating with the nitrate, greenish-yellow solutions are produced, owing to the conversion of some of the mono-acid into the di-acid.

A bibliography of the subject is appended.

E. G.

Dibenzylideneacetone [Distyryl Ketone] and Triphenylmethane. ADOLF VON BAEYER (*Ber.*, 1909, 42, 2624—2633).—Phenol crystals turn brown immediately when brought into contact with triphenylmethyl chloride. When gently warmed, a deep brown solution is obtained; when this is heated more strongly, the colour disappears, but is restored on cooling.

The reaction between the two compounds is accompanied by the evolution of hydrogen chloride. It has not been found possible to isolate a definite additive compound from the brown solution, as the

addition of diluents immediately destroys the colour. The addition of water produces hydrogen chloride and triphenylcarbinol, or, if the mixture has stood for some time, hydroxytetraphenylmethane (Abstr., 1902, i, 769). The coloration is not due to the presence of hydroxytetraphenylmethane or to *α*-phenoxytriphenylmethane. The latter compound, $\text{CPh}_3\cdot\text{OPh}$, prepared by the action of triphenylmethyl chloride on potassium phenoxide, crystallises from a mixture of ether and light petroleum in six-sided plates or prisms, m. p. 103° . This ether is stable towards alkalis, but is immediately hydrolysed by acids.

The following phenols produce intense brown colorations with triphenylmethyl chloride: phenol, *m*- and *p*-cresols, *p*- and *o*-chlorophenols, *p*-nitrophenol, quinol, and its monomethyl ether, resorcinol and its monomethyl ether, catechol, pyrogallol, ethyl *p*-hydroxybenzoate, *p*-hydroxybenzaldehyde, α - and β -naphthol. With *o*-cresol and 1:3:4-xenol it is necessary to use a large amount of chloride in order to produce an intense coloration, and *o*-nitrophenol, picric acid, trichlorophenol, thymol, guaiacol, ethyl salicylate, and salicylaldehyde do not give a coloration. Some of the latter, however, give a brown coloration with the chloride in the presence of a little stannic chloride.

Tri-*p*-chloro- and tri-*p*-bromo-phenylmethyl chlorides dissolve in phenol to brown solutions, whereas the corresponding iodo-derivative gives a reddish-violet coloration. Tri-*o*-anisylmethyl chloride gives a blue coloration with phenol or guaiacol. The additive compounds, which are undoubtedly formed, do not appear to be quinonoid compounds, as suggested by Gomberg.

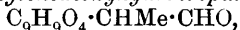
Hydroxymethoxytetraphenylmethane, $\text{CPh}_3\cdot\text{C}_6\text{H}_5(\text{OH})\cdot\text{OMe}$, prepared by the action of triphenylmethyl chloride on guaiacol in the presence of stannic chloride, crystallises in colourless needles or prisms, m. p. 220° .

It is suggested that in triphenylmethyl the free linking of the carbon atom unites with the centric valencies of the benzene rings, thus destroying the symmetry of these rings and producing colour.

J. J. S.

Presence of 5:6-Dimethoxy-3:4-methylenedioxy-1-allylbenzene in Oil of Samphire. MARCEL DELÉPINE (*Compt. rend.*, 1909, 149, 215—217.* Compare Borde, *Bull. Sci. pharm.*, 1909, 16, 132).—The portion of the oil of samphire (*Crithmum maritimum*) boiling above 200° at ordinary pressure has been separated into two fractions: (1) a dextrorotatory fraction, b. p. $90\text{--}95^\circ/13$ mm., constituting 5% of the original oil; (ii) an optically inactive fraction, b. p. $157\text{--}158^\circ/13$ mm., D_4^{20} 1.1753, which constitutes 40% of the oil and has been identified with 5:6-dimethoxy-3:4-methylenedioxy-1-allylbenzene (Thoms, Abstr., 1904, i, 742).

Oxidation of *isoapiole* with mercuric oxide and iodine furnishes 5:6-dimethoxy-3:4-methylenedioxyhydratropaldehyde,



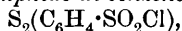
b. p. $189^\circ/17$ mm., D_4^{20} 1.2567, n_D^{25} 1.53191; its *oxime* has m. p. 102° ; the *semicarbazone* has m. p. 148° . Oxidation of the aldehyde leads

* and *Bull. Soc. chim.*, 1909, [iv], 5, 926—930.

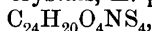
to the formation of the corresponding acid, $C_{12}H_{14}O_6$, m. p. 119° , and 5 : 6-dimethoxy-3 : 4-methylenedioxyacetophenone, $C_9H_8O_4 \cdot COMe$, m. p. $88-89^\circ$, which can be further oxidised to the ketonic acid,



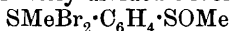
Dithioquinol. THEODOR ZINCKE and W. FROHNEBERG (*Ber.*, 1909, 42, 2721—2736).—The authors have prepared a number of derivatives of dithioquinol. 4 : 4'-Disulphido-di-benzenesulphonyl chloride,



prepared by treating the corresponding potassium salt with phosphoryl chloride, forms large, square crystals, m. p. 142° ; the dianilide,

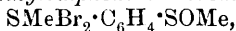


crystallises in white needles, m. p. $189-190^\circ$. On reduction with zinc dust and hydrochloric acid in alcoholic solution, the dichloride yields dithioquinol, $SH \cdot C_6H_4 \cdot SH$; the diacetyl derivative, $C_{10}H_{10}O_2S_2$, of which crystallises in white tablets, m. p. 126° . Oxidising agents convert dithioquinol into a yellow, amorphous sulphide, $(C_6H_4S_2)_n$, which is also the first product of the action of chlorine or bromine. On chlorination, dithioquinol is converted into benzene-1 : 4-disulphonyl chloride, m. p. 138° (Körner and Monselise, this Journ., 1877, i, 81, give 131°). Benzene-1 : 4-disulphonanilide forms colourless tablets, m. p. 248° . Bromination of dithioquinol leads to the formation of benzene-1 : 4-disulphonyl bromide, $C_6H_4(SO_2Br)_2$, colourless needles, m. p. 148° . 1 : 4-Dimethylthiolbenzene, $C_6H_4(SMe)_2$, prepared by methylating dithioquinol, best with methyl sulphate, crystallises in colourless, pearly leaflets, m. p. 85° , and has a characteristic odour. On oxidation with nitric acid, or by treating the tetrabromide (see below) with dilute alkali, phenylene 1 : 4-dimethyldisulphoxide, $C_6H_4(SOMe)_2$, is formed; this crystallises in large, colourless, rhombic tablets or stumpy needles, m. p. 188° , and with mercuric chloride gives a characteristic compound, $C_6H_4(SOMe)_2 \cdot HgCl_2$, crystallising in white needles, m. p. 220° . On oxidising the disulphoxide with nitric and hydrochloric acids, it is converted into phenylene-1 : 4-dimethyldisulphone, $C_6H_4(SO_2Me)_2$, which crystallises in colourless, rhombic tablets, m. p. $258-260^\circ$. 1-Methylthiolphenyl 4-methylsulphoxide, $SMe \cdot C_6H_4 \cdot SOMe$, prepared by the action of finely divided silver on the dibromide,



(see below), crystallises in long, colourless needles, m. p. 102° ; with mercuric chloride it gives a compound crystallising in long needles. 1 : 4-Dimethylthiolbenzene tetrabromide, $C_6H_4(SMeBr_2)_2$, prepared either by the action of hydrogen bromide on phenylene 1 : 4-dimethyldisulphoxide or by the addition of bromine to 1 : 4-dimethylthiolbenzene, forms dark red needles, m. p. $87-90^\circ$ (decomp.); the compound occurs in two modifications, the second being obtained by recrystallising the dark red needles just described from carefully dried chloroform, and forming thick tablets or columns, m. p. $107-109^\circ$ (decomp.), which are almost black in reflected, and dark garnet-red in transmitted, light. On exposure to moist air, the tetrabromide decomposes into hydrogen bromide and the disulphoxide; when the solution is evaporated in a vacuum, however, the tetrabromide is regenerated. With mercuric chloride the compound, $C_6H_4(SOMe)_2 \cdot HgBr_2$, large needles, m. p. 225° ,

is obtained. On treating the tetrabromide with 33% alkali, bromine is removed and 1:4-dimethylthiolbenzene is formed. By the action of sodium methoxide and methyl alcohol on the tetrabromide, the chief product is 1:4-dimethylthiolbenzene, some 1-methylthiolphenyl 4-methylsulphoxide is also formed, and on one occasion a *substance* crystallising in stout, rhombic tablets, m. p. 148°, was obtained. *1-Methylthiolphenyl 4-methylsulphoxide dibromide*,



prepared by passing hydrogen bromide into a chloroform solution of phenylene 1:4-dimethyldisulphoxide, forms yellow needles, m. p. 74° (decomp.). *1:4-Dimethylthiolbenzene tetraiodide*, $\text{C}_6\text{H}_4(\text{SMeI}_2)_2$, is prepared by treating the disulphoxide with concentrated hydriodic acid or by the addition of iodine to 1:4-dimethylthiolbenzene. It crystallises in long, almost black needles, m. p. 82—89° (decomp.). In distinction from the tetrabromide it is very stable, but the iodine is readily eliminated by the usual agents. When mixed with glacial acetic acid and subjected to the action of a stream of chlorine, it dissolves, and iodine trichloride and benzene-1:4-disulphonyl chloride are formed; when chlorinated in presence of chloroform, however, a yellow, crystalline *compound*, $\text{C}_8\text{H}_{10}\text{O}_2\text{Cl}_6\text{I}_2\text{S}_2$, is produced, which, in presence of methyl alcohol, yields phenylene 1:4-dimethylsulphone. *1:4-Dibromo-2:5-dimethylthiolbenzene*, $\text{C}_6\text{H}_2\text{Br}_2(\text{SMe})_2$, prepared by heating a mixture of dimethylthiolbenzene, bromine, and glacial acetic acid, crystallises in colourless needles, m. p. 198°. On treatment with zinc dust and hydrochloric acid in glacial acetic acid solution, dimethylthiolbenzene is regenerated, and the dibromo-compound forms an additive *compound* with bromine, which crystallises in long, dark red needles, m. p. 80—90° (decomp.). The dibromo-compound also yields an additive *compound* with iodine, which on treatment with chlorine furnishes dibromobenzenedisulphonyl chloride. *1:4-Di-trichloromethylthiolbenzene*, $\text{CCl}_3 \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{CCl}_3$, prepared by chlorinating the corresponding dimethylthiolbenzene in chloroform solution, crystallises in white needles, m. p. 148°; on reduction with zinc dust in glacial acetic acid solution, it yields dithioquinol and dimethyl sulphide; with alcoholic potash it gives dithioquinol, and, on warming with aniline, dithioquinol and triphenylguanidine are produced. *Phenylene 1:4-di-trichloromethylsulphoxide*, $\text{CCl}_3 \cdot \text{SO} \cdot \text{C}_6\text{H}_4 \cdot \text{SO} \cdot \text{CCl}_3$, prepared by chlorinating the disulphoxide or by oxidising 1:4-di-trichloromethylthiolbenzene with hydrogen peroxide in glacial acetic acid solution, crystallises in colourless tablets or leaflets, m. p. 192°; on reduction with zinc dust in acetic acid solution, dimethyl sulphide is produced. J. C. C.

Addition of Dimethyl Sulphate to Thiophenol Ethers.

KARL AUWERS and F. ARNDT (*Ber.*, 1909, 42, 2713—2715).—In the interaction between *p*-methylthioltoluene and dimethyl sulphate (this vol., i, 175) a by-product is always obtained, which has now been found to be the additive product, *p-tolyldimethylsulphonium methyl sulphate*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{SMe}_2 \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OMe}$. It is readily prepared by warming equimolecular quantities of its components on the water-bath. It crystallises in glistening leaflets, m. p. 97°. The compound dissociates on distillation, and is decomposed on heating with alkalis. When

p-ethylthioltoluene is substituted for the methyl compound in this reaction, *p*-tolylmethyl ethylsulphonium methyl sulphate, a colourless, odourless, viscid oil, solidifying at a low temperature to a transparent, glassy mass, is produced. On heating alone or with soda-lime, it decomposes into *p*-methylthioltoluene and methyl ethyl sulphate. In this way it is possible to convert the ethyl ether of a thiophenol into the corresponding methyl ether. No similar additive products are obtained when diethyl sulphide or methyl iodide are used instead of dimethyl sulphate.

J. C. C.

A Reaction of Aromatic Inner Anhydrides and Anhydride-forming Compounds. BRUNO BARDACH (*Zeitsch. anal. Chem.*, 1909, 48, 438—448).—The reaction of proteins recently described (Abstr., 1908, ii, 332) has been more fully investigated, and it is found that the thin, yellow needles which are obtained as precipitate in place of iodoform, although they have not yet been obtained perfectly pure, contain 91.78% iodine, and have m. p. about 141—143° (decomp.). In the presence of internal aromatic anhydrides, or substances which under given conditions form anhydrides, iodine and potassium iodide in alkaline acetone solution do not yield iodoform, but a similar yellow, crystalline iodine compound. From numerous experiments the conclusion is drawn that aromatic hydroxy-acids containing long side-chains in positions favourable to anhydride formation, also polyhydroxy-ketones, form anhydrides under the conditions of this test. It is found possible by using this test to ascertain directly whether an aromatic substance forms an anhydride.

J. V. E.

New Method of Ester Formation by the Action of Chloro-carbonic Esters on Acids. ALFRED EINHORN (*Ber.*, 1909, 42, 2772—2773).—Herzog's claim (this vol., i, 568) is not original, since the author has already shown (this vol., i, 568) that esters and anhydrides of benzoic and *p*-nitrobenzoic acids are obtained by the action of ethyl chlorocarbonate on the two acids.

C. S.

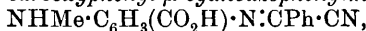
Aromatic Nitroso-compounds, Azomethinecarboxylic Acids, and the Preparation of Benzoquinoneoximecarboxylic Acid. JOSEF HOUBEN, WALTER BRASSERT, and LEO ETTINGER (*Ber.*, 1909, 42, 2745—2759).—5-Nitroso-*N*-methylantranilic acid (Houben and Brassert, Abstr., 1908, i, 27), in aqueous alkaline solution, apparently undergoes intramolecular change, thus: $\text{NO} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{H}) \cdot \text{NHMe} \rightarrow \text{NOH} : \text{C}_6\text{H}_3(\text{CO}_2\text{H}) : \text{NMe}$. Confirmation of this is afforded by the fact that, in anhydrous solvents, such as sodium alkyl oxides, the acid condenses quantitatively with compounds containing an "acidic" methylene group, whilst in aqueous alkaline solution only a small yield is obtained. It is possible, also, to condense the ester of the acid, in presence of sodium alkyl oxide, to azomethine compounds without hydrolysis taking place. Dyes analogous to those of the phenazine series are also produced by condensing the acid or its ester with aniline hydrochloride, β -phenylnaphthylamine, β -ethylnaphthylamine, diphenyl-*m*-phenylenediamine, ditolylnaphthylenediamine, tolylenediamine, etc., in glacial acetic acid solution in the presence of hydrogen chloride. On

treatment with magnesium or zinc in ammonium chloride solution, the acid is first decolorised, and is then gradually transformed into an intensely blue dye. The authors have also discovered that *p*-benzoquinoneoximecarboxylic acid can readily be prepared in good yield by treating nitrosomethylantranilic acid with cold dilute alkali hydroxide for a short time.

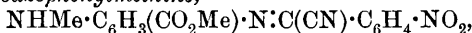
The acid can be condensed with various agents in a similar manner to nitrosomethylantranilic acid.

5-Nitroso-*N*-methylantranilic acid is readily prepared by treating a hydrochloric acid solution of methylantranilic acid with sodium nitrite; the *methyl* ester crystallises in small, bright green needles, m. p. 119° (corr.), and the *ethyl* ester forms small, grass-green needles, m. p. 87—88°.

5-Nitroso-*N*-ethylantranilic acid, $\text{NO}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{NH}\text{Et}$, prepared by the action of a cold alcoholic solution of hydrogen chloride on *o*-ethylnitrosoaminebenzoic acid, or by treating ethylantranilic acid with concentrated hydrochloric acid and sodium nitrite, crystallises in bright green, rectangular, prismatic rods, m. p. 152° (decomp.). The condensation of 5-nitroso-*N*-methylantranilic acid with phenylacetonitrile in the presence of sodium ethoxide leads to the production of 4-methylamino-3-carboxyphenyl- μ -cyanoazophenylmethine,



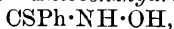
which is a yellowish-red dye, m. p. 223—224°; the sodium salt forms red needles. 4'-Nitro-4-methylamino-3-carboxyphenyl- μ -cyanoazophenylmethine, similarly obtained from the nitroso-acid and *p*-nitrophenylacetonitrile, crystallises in dark red needles, m. p. 260°; the sodium salt is dark red. Ethyl 4-methylamino-3-carboxyphenyl- μ -cyanoazomethinecarboxylate, $\text{NHMe}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{N}:\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, prepared by condensing 5-nitrosomethylantranilic acid and ethyl cyanoacetate, is a red substance, m. p. 203—204°. 4'-Nitro-4-methylamino-3-carbomethoxyphenyl- μ -cyanoazophenylmethine,



prepared by condensing methyl 5-nitrosomethylantranilate with *p*-nitrophenylacetonitrile, crystallises in reddish-brown needles with a blue reflex, m. p. 200—201°; it forms a colourless salt with concentrated sulphuric acid. Reduction of 5-nitrosomethylantranilic acid in ammoniacal solution with ammonium chloride and magnesium furnishes a blue dye resembling indigotin, which probably has the constitution $\text{NHMe}\cdot\text{C}_6\text{H}_2(\text{CO}_2\text{H})(\text{NH}_2)\cdot\text{N}:\text{C}_6\text{H}_2(\text{CO}_2\text{H})\cdot\text{NMe}$.

[With ERICH KELLNER.]—*p*-Benzoquinoneoximecarboxylic acid may readily be prepared by the action of cold concentrated sodium hydroxide on 5-nitrosomethylantranilic acid. When condensed with *p*-nitrophenylacetonitrile it yields 4'-nitro-4-hydroxy-3-carboxyphenyl- μ -cyanoazophenylmethine, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{N}:\text{C}(\text{CN})\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, forming dull yellow crystals, m. p. 231—236°. J. C. C.

Thiohydroxamic Acids. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 687—690).—Thiobenzhydroxamic acid,



prepared by the action of hydroxylamine on dithiobenzoic acid: $\text{Ph}\cdot\text{CS}_2\text{H} + \text{NH}_2\cdot\text{OH} = \text{CSPh}\cdot\text{NH}\cdot\text{OH} + \text{H}_2\text{S}$, is very unstable,

decomposing mostly according to the equation: $\text{CSPH}\cdot\text{NH}\cdot\text{OH} = \text{Ph}\cdot\text{CN} + \text{S} + \text{H}_2\text{O}$. Its solution gives with ferric chloride a violet-blue coloration, or with excess, a black precipitate. Its *benzyl* ester, $\text{OH}\cdot\text{N}:\text{CPh}\cdot\text{S}\cdot\text{CH}_2\text{Ph}$, m. p. 120—122°, yields a *benzoyl* derivative, $\text{OBz}\cdot\text{N}:\text{CPh}\cdot\text{S}\cdot\text{CH}_2\text{Ph}$, separating from alcohol in crystals, m. p. 135°. Its *dibenzoyl* derivative, $\text{OBz}\cdot\text{N}:\text{CPh}\cdot\text{SBz}$, crystallises from alcohol in small, colourless prisms, m. p. 90—92°. This dibenzoyl compound, like that of β -benzhydroxamic acid, is not hydrolysed by dilute hydrochloric acid, but is decomposed by alcoholic potassium hydroxide, partly with formation of thiobenzhydroxamic and benzoic acids: $\text{NOBz}\cdot\text{CPh}\cdot\text{SBz} + 2\text{H}_2\text{O} = \text{OH}\cdot\text{N}:\text{CPh}\cdot\text{SH} + 2\text{Ph}\cdot\text{CO}_2\text{H}$, and partly into benzhydroxamic, thiobenzoic, and benzoic acids: $\text{OBz}\cdot\text{N}:\text{CPh}\cdot\text{SBz} + 2\text{H}_2\text{O} = \text{OH}\cdot\text{N}:\text{CPh}\cdot\text{OH} + \text{Ph}\cdot\text{CO}\cdot\text{SH} + \text{Ph}\cdot\text{CO}_2\text{H}$. T. H. P.

Saponification of Phenylisonitroacetoneitrile to the Amide by means of Hydrogen Peroxide. A. J. VAN PESKI, jun. (*Ber.*, 1909, 42, 2763—2764).—When sodium phenylisonitroacetoneitrile is treated with hydrogen peroxide in presence of sodium hydroxide, *sodium phenylisonitroacetamide*, $\text{NO}_2\text{Na}:\text{CPh}\cdot\text{CO}\cdot\text{NH}_2$, is formed; it separates on evaporation of its alcoholic solution in a vacuum in small, white rods. With bromine it yields *α -bromonitrophenylacetamide*, $\text{NO}_2\cdot\text{CBrPh}\cdot\text{CO}\cdot\text{NH}_2$, which crystallises in small, white needles, m. p. 113°, and when heated above its m. p. decomposes into bromine, nitric oxide, and phenylglyoxylamide. J. C. C.

Cinnamic Acids of Different Origin. EMIL ERLÉNMEYER [with OTTO HERZ and G. HILGENDORFF] (*Ber.*, 1909, 42, 2649—2655. Compare this vol., i, 156).—Small amounts of hetero- β -cinnamic acid appear to be present in storax-cinnamic acids obtained from different natural sources. The presence of this acid was shown by fractionating the ester carefully and hydrolysing the residue, when either synthetic cinnamic or hetero-cinnamic acid is obtained. Control experiments proved that the storax ester is not transformed into the hetero-ester when heated.

The cinnamic acid obtained from styryl methyl ketone is a mixture of the storax and hetero-acids. Benzylidenemalononic acid appears to exist in two forms, one of which yields storax acid by the loss of carbon dioxide, and the other, under similar conditions, the hetero-acid.

The acid obtained by Perkin's synthesis and also by Claisen's condensation (*Abstr.*, 1890, 891) is a mixture of the storax and hetero-acids (synthetical cinnamic acid).

When phenylpropionic acid is reduced, some 50% of storax-cinnamic acid is obtained; the remainder of the propionic acid undergoes decomposition, yielding phenylacetylene. The propionic acid prepared from storax-cinnamic acid gives a much better yield of storax acid when reduced. The phenylpropionic acid, prepared from the hetero- β -acid, has m. p. 138°, and when reduced yields the hetero-acid or mixtures of the hetero- and storax acids. J. J. S.

Differences in the Cinnamic Acids due to the Synthetical Materials Used. EMIL ERLÉNMEYER [with OTTO HERZ and G. HILGENDORFF] (*Ber.*, 1909, 42, 2655—2675. Compare preceding abstract).—Ordinary benzaldehyde contains two constituents, the more volatile of these yields storax-cinnamic acid by Perkin's synthesis, and the less volatile, hetero- β -cinnamic acid. The separation of the two constituents can be accomplished by repeated fractionation.

Natural benzaldehyde, which contains hydrogen cyanide, yields as chief condensation product storax acid, whereas the same aldehyde when freed from hydrogen cyanide yields synthetical cinnamic acid.

When hetero-cinnamic acid is oxidised to benzaldehyde and this is then condensed with sodium acetate and acetic anhydride, the product formed is the hetero-acid.

When heated with acetic anhydride the synthetical acid is converted into the storax acid or its anhydride, and a similar conversion occurs when the synthetical acid or the hetero- β -acid is sublimed.

The storax acid is stable towards alkalis or acetic anhydride, but when its solution in cold concentrated sulphuric acid is kept for some five weeks and then poured into water, it is partly transformed into hetero- β -acid or hetero- α -acid. If the benzaldehyde, obtained by oxidising the storax acid with warm permanganate whilst steam is blown through, is subjected to Perkin's synthesis, the product is synthetical cinnamic acid.

Storax acid can be obtained from ordinary synthetical benzaldehyde by Perkin's synthesis provided copper or copper acetate is present. The aldehyde recovered in the ordinary Perkin's synthesis also yields pure storax acid when condensed again with acetic anhydride and sodium acetate.

Crystallographic measurements of the dibromides from storax-, synthetical-, and hetero-cinnamic acids indicate that the dibromides from the storax- and hetero-acids are distinct, and that the dibromide of the synthetical acid is not homogeneous.

[With K. BUBE].—Determinations of the affinity constants of storax- α -, storax- β -, hetero- α -, and hetero- β -acids indicate that all four acids have much the same value; $K = 0.0036 - 0.0040$. The acids do not appear to yield saturated solutions at 25° even when left in contact with water for several days and shaken.

J. J. S.

3:5-Dinitro-4-hydroxybenzoic Acid. HEINRICH SALKOWSKI (*Annalen*, 1909, 367, 348—353).—The author has repeated and confirmed Reverdin's work (*Abstr.*, 1908, i, 537). It is shown that the potassium salt, $OK \cdot C_6H_2(NO_2)_2 \cdot CO_2K$, crystallises with $2\frac{1}{2}H_2O$ in yellow needles, with $2H_2O$ in red plates (compare this *Jour.*, 1872, 555), and with $1\frac{1}{2}H_2O$ in orange-red needles. The last two pass into the stable hydrate with $2\frac{1}{2}H_2O$ when kept in contact with the solution at the ordinary temperature.

W. H. G.

Crystallographic Study of *o*-Thymotic Acid and of Two Isomeric Thymotides. ARISTIDE ROSATI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 534—537).—The author gives crystallographic data of

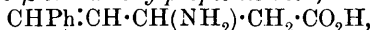
the following compounds, prepared by Spallino and to be described shortly.

o-Thymotic acid, $C_{11}H_{12}O_3$, m. p. 129° , crystallises from light petroleum in prisms belonging to the monoclinic system: $a:b:c = 1.0724:1:0.9039$, $\beta = 93^\circ 24'$.

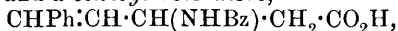
The thymotide, $C_{22}H_{24}O_4$, m. p. 174° , crystallises from benzene in hexagonal prisms belonging to the rhombohedral system: $a:c = 1:1.1092$, $\alpha = 94^\circ 11'$.

The thymotide, $C_{22}H_{24}O_4$, m. p. 209° , crystallises in a biaxial system.
T. H. P.

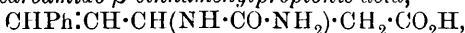
Unsaturated Compounds. VII. Addition of Hydroxylamine to Unsaturated Acids containing Conjugate Double Linkings. THEODOR POSNER and KARL ROHDE (*Ber.*, 1909, 42, 2785—2794. Compare this vol., i, 583).—Riedel and Schulz's work (this vol., i, 581), which encroaches on that of the authors', had already been done by them; it contains two errors. The compound obtained by the action of free hydroxylamine on the ester of cinnamenylacrylic acid in the cold is β -hydroxylamino- β -cinnamenylpropionhydroxamoxime hydroxide, $CHPh:CH:CH(NH\cdot OH)\cdot CH_2\cdot C(OH)(NH\cdot OH)_2$, and not hydroxylamine β -hydroxylamino- β -cinnamenylpropionylhydroxamate. Riedel and Schulz are incorrect in stating that hydroxylamine and cinnamenylacrylic acid only react to form an unstable hydroxylamine salt, for when the two substances are heated in methyl alcohol for 240 hours, β -amino- β -cinnamenylpropionic acid,



m. p. 238° (decomp.), is formed. The acid, which is obtained after thirty hours' heating when methyl cinnamenylacrylate is used in place of the acid itself, forms a silver salt, a hydrochloride, $C_{11}H_{13}O_2N\cdot HCl$, m. p. 195 — 196° , and a benzoyl derivative,



m. p. 205° , the methyl ester of which, $C_{19}H_{19}O_3N$, has m. p. 142 — 145° . β -Amino- β -cinnamenylpropionic acid and potassium cyanate in hot water yield β -carbamido- β -cinnamenylpropionic acid,



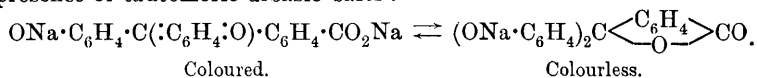
m. p. 187° (decomp.), which on heating forms cinnamenyldihydrouracil, $NH\langle\begin{smallmatrix} CO\cdot CH_2 \\ CO\cdot NH \end{smallmatrix}\rangle CH:CH:CHPh$, m. p. 231.5 — 232.5° . This fact and the formation of benzoic acid by the oxidation of β -benzoylamino- β -cinnamenylpropionic acid by cold alkaline potassium permanganate are proofs that hydroxylamine is added on at the $\alpha\beta$ -position in cinnamenylacrylic acid.
C. S.

Hofmann's Reaction. V. Action of Sodium Hypochlorite and a Little Alkali on Phthalimide. ERNST MOHR, FR. KÖHLER, and H. ULRICH (*J. pr. Chem.*, 1909, [ii], 80, 1—33. Compare this vol., i, 420).—The authors have continued the series of experiments which show that in the Hofmann reaction slight variations in the quantity of alkali, in the temperature, or in the method of mixing may materially affect the yield and even the nature of the product. The present paper deals with the claim (D.R.-P. 127138) that sodium

hypochlorite and phthalimide in the absence of free alkali yield, not anthranilic acid, but isatoic acid. This result, unexpected in view of the instability of carbamic acids towards acids, is confirmed by the authors. When equal molecular quantities of phthalimide and 2*N*-sodium hydroxide are treated rapidly at 7—8° with an equal molecular quantity of sodium hypochlorite, free from alkali, the temperature rises to 40—45°, and the solution turns dark brown. When a sample, tested every ten seconds, does not liberate iodine from acidified potassium iodide, the solution is poured into hydrochloric or acetic acid at 0°, whereby a precipitate of isatoic anhydride is obtained. When the same solutions, with or without a small excess of sodium hydroxide, are mixed so slowly at -5 to -10° that the final temperature does not exceed 2°, and then kept for six to eight hours at 0°, four crystalline fractions are obtained, the first being almost pure isatoic anhydride and the last, sodium anthranoylanthranilate. Finally, when a solution of sodium hypochlorite containing a small excess of sodium hydroxide, at 14°, is added slowly to a solution of equal molecular quantities of phthalimide and 2*N*-sodium hydroxide at -3°, the final temperature is 45—50°; the mixture is warmed until carbon dioxide ceases to be evolved, and then cooled, whereby a precipitate of sodium anthranoylanthranilate is obtained. This is the best method of obtaining the substance; the *potassium*, *barium*, and *copper* salts are described.

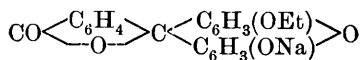
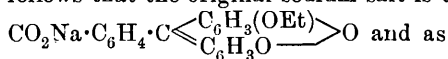
C. S.

Theory of Indicators and Reactions of Phthaleins and their Salts. SALOMON F. ACREE and E. A. SLAGLE (*Amer. Chem. J.*, 1909, 42, 115—147. Compare Abstr., 1908, i, 423, 653).—The authors show briefly the inadequacy of the quinone theory, of Baeyer's theory of halochromy, and of Ostwald's theory of electrolytic dissociation, to explain the colour phenomena of phenolphthalein and its salts. Stieglitz's view that the red salts of phenolphthalein are carboxylic and not phenolic is opposed by Meyer and Spengler's proof that the coloured salts are dibasic salts. The theory that the chief cause of the colour of the salts of aurin, phenolphthalein, etc., is not a quinonoid but a quinonephenol group, $\text{OK} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{O})$, proposed by Acree and adopted by many investigators, is explained at length and supported by numerous illustrations. The same theory explains the behaviour of the salts of phenolphthalein and fluorescein on alkylation; both the colour phenomena and the alkylation reactions point to the presence of tautomeric dibasic salts:

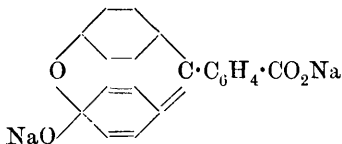


The presence of such tautomeric salts in the case of fluorescein is shown as follows. The *sodium* salt, $\text{CO}_2\text{Na} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{c} \text{C}_6\text{H}_3(\text{OEt}) \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_3\text{O} \end{array} \text{O}$, is obtained by treating a solution of sodium hydroxide with an excess of fluorescein ethyl ether and evaporating the filtrate after extracting it with carbon tetrachloride. The salt is much less coloured than that of fluorescein, and by treatment with alcoholic ethyl iodide yields a mixture of the colourless fluorescein diethyl ether and the coloured fluorescein

diethyl ester-ether. Since it is proved experimentally that these two are not interconvertible under the conditions of their formation, it follows that the original sodium salt is tautomeric, reacting as



The authors incline to the view that the ultimate cause of the colour of the salts of phenolphthalein, etc., is a third tautomeric salt of the annexed constitution, formed by intramolecular rearrangement between the CO of the quinone group and the phenolic $\cdot\text{ONa}$. Salts of analogous constitution have been obtained by Acree in the triazole series, and assumed by Hantzsch in the salts of nitrophenols, *p*-hydroxybenzaldehyde, and *p*-hydroxybenzophenone. The chief reason for

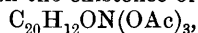


believing that such an intramolecular salt is the cause of the colour of the salts of phenolphthalein is the work of Jackson and others, who have shown that in non-aqueous solution, quinones and sodium phenoxide, sodium β -naphthoxide, or dimethylaniline yield intensely coloured additive double salts. It has indeed been shown that benzoquinone or anthraquinone yields deeply coloured compounds with salts of *o*-cresol, *p*-cresol, phenol, quinol, pyrogallol, resorcinol, or dimethylaniline, the colours being destroyed by the addition of acid.

The latter part of the paper deals with the solubility of phenolphthalin, tetrabromophenolphthalin, *p*-hydroxydiphenylphthalide, and their derivatives in dilute sodium hydroxide. Experiments to determine the affinity constants of these weak acids by Koelichen's dilatometric method show that the catalytic influence of the hydroxyl ions of the alkali on a 10% solution of diacetone alcohol is materially diminished by the presence of the salt of the weak acid. A new metallic dilatometer is described, with which very concordant results are obtained.

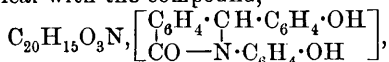
C. S.

Phthaleinoximes. RICHARD MEYER and S. M. KISSIN (*Ber.*, 1909, 42, 2825—2838).—The authors attempt to settle the constitutions of the oximes of phenolphthalein and quinolphthalein, and propose formulæ which harmonise with the properties of the oximes, but, it is admitted, present one or two difficulties. Friedländer's original quinonoid formula of phenolphthaleinoxime has been abandoned, and the lactonoid formula, $\text{C}(\text{C}_6\text{H}_4 \cdot \text{OH})_2 \begin{array}{c} \swarrow \text{C}_6\text{H}_4 \\ \searrow \text{N}(\text{OH}) \end{array} \text{CO}$, does not account for the colour of the oxime, or for its ready hydrolysis, since the similarly constituted anilides are stable to hydrolysing agents. The formula $\text{C}(\text{C}_6\text{H}_4 \cdot \text{OH})_2 \begin{array}{c} \swarrow \text{C}_6\text{H}_4 \\ \searrow \text{O} \end{array} \text{C} : \text{N} \cdot \text{OH}$ contains the chromophore, $:\text{C} : \text{N} \cdot$, and harmonises with the existence of a *triacetate*,



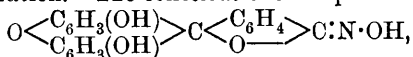
m. p. 229—230°, and *tribenzoate*, m. p. 175°, but presents the following difficulty.

Friedländer reduced the yellow oxime to a colourless substance, $C_{20}H_{17}O_3N$, identical with the compound,



synthesised by H. Meyer from hydroxyphenylphthalide and *p*-aminophenol; the authors have confirmed the composition $C_{20}H_{15}O_3N$ for the substance obtained by both methods, but cannot state during which preparation the intramolecular change has taken place, which must have occurred if the preceding formula of phenolphthaleinoxime is correct.

Of the three oximes of quinolphthalein, the α -isomeride has almost certainly the constitution $O < \begin{array}{c} C_6H_3(OH) \\ | \\ C_6H_3(OH) \end{array} > C < \begin{array}{c} C_6H_4 \\ | \\ N(OH) \end{array} > CO$, since it is colourless, forms a *trimethyl ether*, m. p. 123—124°, a *triacetate*, m. p. 210°, and a *tribenzoate*, m. p. 226—227°, and, like the analogously-constituted phthaleinanilides, is not attacked by zinc and sodium hydroxide. The yellowish-brown β - and γ -quinolphthaleinoximes are probably stereoisomerides, the γ -oxime, being the stable form, having the anti-configuration. The constitutions are probably



since the γ -oxime forms a *tribenzoate*, m. p. 275—280°, and the β -isomeride yields by treatment with zinc and sodium hydroxide a reduction product which re-oxidises to the γ -oxime. This reduction, however, presents a difficulty, since the similarly-constituted phenolphthaleinoxime suffers reduction in a different manner.

Although hydroxylamine does not, as a rule, attack lactones and similarly constituted compounds, there seems to be little doubt that such a reaction occurs with the phthaleins (possibly by reason of their solubility in alkalis), since hydroxyphenylphthalide forms an *oxime* (colourless leaflets containing 1 mol. MeOH from methyl alcohol), m. p. 215—216° (*dibenzoate*, m. p. 233—234°), and hydroxydiphenylphthalide also forms an *oxime*, m. p. 204—205°, which separates from ether in colourless, and from alcohol in yellow, crystals, and forms a *dibenzoate*, m. p. 150—151°. The aliphatic lactone of α -hydroxy- α -methylglutaric acid, which is also soluble in alkali hydroxides, does not yield an oxime. C. S.

New Preparation of spiroCyclanes. DON RADULESCU (*Ber.*, 1909, 42, 2770—2772).—When equal molecular quantities of ethyl succinate and ethyl cyclopropane-1:1-dicarboxylate in ether at 0° are treated with sodamide, the product, decomposed by cold water, yields the spirocycpane derivative, $\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array} > C < \begin{array}{c} CO \cdot CH \cdot CO_2Et \\ | \\ CO \cdot CH \cdot CO_2Et \end{array}$, m. p. 151—152° (decomp.). The substance and that from ethyl cyclobutandicarboxylate are being investigated. C. S.

Behaviour of *N*-Alkylaldoximes towards Iodine and the Condition of Iodine in Solutions. ERNST BECKMANN [and, in part, M. EBERT, HANS NETSCHER, and E. SCHULZ] (*Annalen*, 1909, 367, 271—303).—This investigation was commenced with the object of

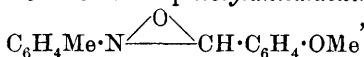
ascertaining whether *N*-alkylaldoximes, like oximino-compounds, are converted into their isomerides by the action of iodine. It is found, however, that when treated with iodine in an indifferent solvent, such as benzene, they at first yield soluble, simple iodine additive products, but subsequently hydrogen periodides separate, which, as a rule, consist of 2 mols. of the *N*-ether combined with 1 mol. of hydrogen iodide and 1 mol. of iodine, less frequently with 1 mol. of hydrogen iodide and 2 mols. of iodine. Sunlight and heat accelerate the formation of the hydrogen periodides, probably because they induce the production of hydrogen iodide at the cost of part of the *N*-ether.

The compounds containing 3 atoms of iodine in the mol. are generally yellow, brown, or red, whilst those with a higher proportion of iodine are green to steel-blue. The iodine is only loosely bound, and the compounds are dissociated in solution to a more or less degree depending on the temperature, likewise on the nature and quantity of the solvent. Aqueous solutions of sulphites and thiosulphates decompose the hydrogen periodides with elimination of hydrogen iodide and iodine and regeneration of the *N*-ether.

The latter part of the paper is devoted to a discussion of the work of various investigators relative to the state of iodine in solutions. The accumulated evidence supports the author's view that in brown solutions of iodine most of the halogen is combined with the solvent, whilst in violet solutions the greater part of it exists in an uncombined state.

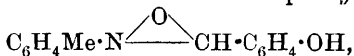
Bis-N-phenylbenzaldoxime hydrogen tri-iodide, $2C_{13}H_{11}ON, HI_3$, is a brownish-red substance, m. p. $101-102^\circ$; the *N-p-tolyl* compound, $2C_{14}H_{13}ON, HI_3$, is yellowish-red, and has m. p. $137-138^\circ$; the isomeric *N-o-tolyl* compound crystallises in small, slender, yellowish-red needles, m. p. $93-94^\circ$, whilst the *N-m-tolyl* derivative forms small, golden-green, felted needles, m. p. $85-86^\circ$; the analogous *N-benzyl* compound, $2C_{14}H_{13}ON, HI_3$, forms reddish-brown crystals, m. p. $108-109^\circ$.

N-Phenyl-p-anisaldoxime yields a *hydrogen penta-iodide*,
 $2C_{14}H_{13}O_2N, HI_5$,
 green crystals, m. p. $110-111^\circ$, and a *hydrogen tri-iodide*,
 $2C_{14}H_{13}O_2N, HI_3$,
 red crystals, m. p. $133-134^\circ$. *N-p-Tolylanisaldoxime*,



crystallises in white needles, m. p. $128-129^\circ$; the *hydrogen tri-iodide* forms yellowish-red needles, m. p. $121-122^\circ$. *Bis-N-o-tolylanisaldoxime hydrogen tri-iodide*, $2C_{15}H_{15}O_2N, HI_3$, m. p. $115-116^\circ$, is reddish-violet; the *hydrogen penta-iodide* is green, m. p. $102-103^\circ$. *N-m-Tolylanisaldoxime*, $C_{15}H_{15}O_2N$, crystallises in white needles, m. p. $88-89^\circ$; the *hydrogen tri-iodide* forms yellowish-green needles, m. p. $120-121^\circ$. *Bis-N-benzylanisaldoxime hydrogen tri-iodide*, $2C_{15}H_{15}O_2N, HI_3$, crystallises in orange-yellow needles, m. p. $174-175^\circ$.

Hydrogen periodides of the *N*-phenyl, *N-m-tolyl*, and *N-benzyl* ethers of salicylaldoxime could not be isolated. *N-p-Tolylsalicylaldoxime*,



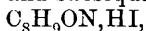
forms golden-yellow crystals, m. p. $112-113^\circ$; the *hydrogen penta-*

iodide forms very dark green needles, m. p. 156—157°. *N*-o-Tolylsalicylaldoxime crystallises in small, yellow needles, m. p. 99—100°; the *hydrogen tri-iodide* crystallises in small, dark green, felted needles, m. p. 167—168°.

N-Phenyl-o-nitrobenzaldoxime, $C_{13}H_{10}O_3N_2$, m. p. 94°, and *N*-p-tolyl-o-nitrobenzaldoxime, $C_{14}H_{12}O_3N_2$, colourless needles, m. p. 113—114°, do not yield crystalline hydrogen periodides. *N*-Benzyl-o-nitrobenzaldoxime yields the *hydrogen periodides*: $2C_{14}H_{12}O_3N_2 \cdot HI_3$, a red substance, m. p. 113—114°; $2C_{14}H_{12}O_3N_2 \cdot HI_5$, compact, steel-blue crystals, m. p. 81—82°; $3C_{14}H_{12}O_3N_2 \cdot HI_5$, compact, golden-green crystals, m. p. 94—95°.

When hydrogen iodide is passed into a solution of *N*-phenyl-anisaldoxime, a pale yellow precipitate of the *hydriodide*, $C_{14}H_{13}O_2N \cdot HI$, is obtained; the addition of more hydrogen iodide results in the formation of a *periodide* (41.1% iodine), crystallising in golden-green needles, m. p. 123—124°. *N*-p-Tolylbenzaldoxime, when similarly treated, yields at first the above hydrogen tri-iodide, m. p. 137—138°; the action of more hydrogen iodide leads to the formation of a red *hydrogen penta-iodide* (?), m. p. 188—189°. *N*-p-Tolylanisaldoxime does not liberate iodine from hydrogen iodide, consequently a periodide is not formed by the action of hydrogen iodide on this *N*-ether; the *hydriodide* is a pale yellow substance, m. p. 77—78°.

An ethereal solution of *N*-methylbenzaldoxime yields with hydrogen iodide at first the *hydriodide*, $2C_8H_9ON \cdot HI$, a yellow, crystalline substance, m. p. 128° (decomp.), and subsequently the *hydriodide*,



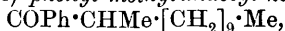
a pale yellow substance, m. p. 78—79°. The *N*-ether, when treated with iodine in benzene, yields a dark violet *hydrogen penta-iodide*, $2C_8H_9ON \cdot HI_5$, m. p. 92°, and a reddish violet *hydrogen tri-iodide*, $2C_8H_9ON \cdot HI_3$, m. p. 118°. The former passes into the latter by repeated crystallisation from ethyl iodide.

Hydrogen bromide, chloride, and fluoride combine with the *N*-alkylaloximes in equivalent proportions, yielding salts. Bromine, analogously to iodine, yields perbromides, which have not been thoroughly investigated.

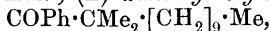
W. H. G.

New Trialkylacetophenones and Trialkylacetic Acids Derived from Them. ALBIN HALLER and ED. BAUER (*Compt. rend.*, 1909, 149, 5—10. Compare Abstr., 1908, i, 987; this vol., i, 131; Lucas, this vol., i, 488).—The authors have prepared several new trialkylacetophenones by the method already described (this vol., i, 108) with the object of ascertaining the influence of the alkyl groups on the manner in which the ketone undergoes fission when boiled with sodamide. It is found that the decomposition is quite independent of the nature of these groups, and that the products always consist of benzene with the amide of a trialkylacetic acid. *aa*-Dimethyl- α -isopropylacetophenone, $COPh \cdot CMe_2Pr^B$, b. p. 125—126°/11 mm., forms an *oxime*, crystallising in needles, m. p. 152—153°; on treatment with sodamide it yields *aa* β -trimethyl-*n*-butyramide, $CMe_2Pr^B \cdot CO \cdot NH_2$, pearly leaflets, m. p. 133—134°, forming on hydrolysis with sodium nitrite and sulphuric acid, *aa* β -trimethyl-*n*-butyric acid, $C_7H_{14}O_2$, a

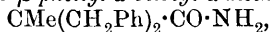
crystalline mass, m. p. 50°, b. p. 104—105°/13 mm. *Phenyl undecyl ketone*, $\text{COPh} \cdot [\text{CH}_2]_{10} \cdot \text{Me}$, obtained by the action of lauryl chloride on benzene in presence of aluminium chloride, forms a crystalline mass with an orange-like odour, m. p. 45°, b. p. 201—202°/9 mm.; on methylation it yields (i) *phenyl methylundecyl ketone*,



b. p. 199—200°/9—10 mm.; (ii) *dimethyldecylacetophenone*,



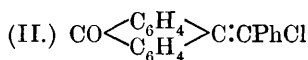
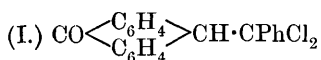
b. p. 198—199°/9 mm. The latter has been converted into *aa-dimethyl-lauric acid*, $\text{C}_{10}\text{H}_{21} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$, m. p. 27°, b. p. 184°/12 mm., the *amide* of which crystallises in pearly scales, m. p. 95—96°. *a-Benzyl-aa-dimethylacetophenone*, $\text{COPh} \cdot \text{CMe}_2 \cdot \text{CH}_2\text{Ph}$, has b. p. 180—185°/11 mm., and forms an *oxime*, m. p. 191°. *β-Phenyl-aa-dimethyl-propionic acid*, $\text{CH}_2\text{Ph} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$, m. p. 57°, b. p. 172—174°/19 mm., forms an *amide*, crystallising in needles, m. p. 62—63°, and a yellow *nitro-derivative*, $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}$, m. p. 134°, b. p. 220—230°/20 mm. *aa-Dibenzyl-a-methylacetophenone*, $\text{C}_{23}\text{H}_{23}\text{O}$, occurs in prisms, m. p. 61°; it has been converted into *β-phenyl-a-benzyl-a-methylpropionamide*,



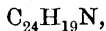
prisms, m. p. 149°; the corresponding acid could not be obtained.

W. O. W.

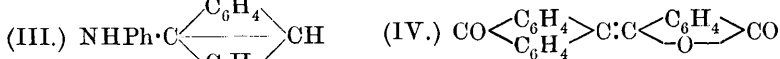
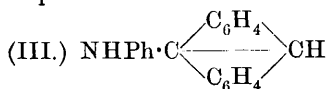
Reactions of Anthranol. ROBERT PADOVA (*Compt. rend.*, 1909, 149, 217—220. Compare this vol., i, 167).—When anthranol is heated with tri-*ω*-chlorophenylmethane in toluene, hydrogen chloride is evolved and a small quantity of dianthrone formed together with *dichlorobenzylanthrone* (formula I), small, grey prisms, m. p. 158—159°. Hot pyridine eliminates hydrogen chloride and produces *ω-chlorophenylanthraquinomethane* (formula II), small, rose-coloured prisms, sintering at 128°, m. p. 130—131°; it develops a deep red coloration with sulphuric acid.



When anthranol is heated for thirty minutes with excess of an aromatic amine, condensation occurs, with formation of arylanthramines, compounds crystallising from toluene in yellow needles showing intense fluorescence. *Phenylanthramine* (formula III) sinters at 191°, and has m. p. 197—198°. *α-Naphthylanthramine*,



has m. p. 199—201°; *β-naphthylanthramine* sinters at 205°, and has m. p. 213°.



Anthranol reacts with phthalylchloride, forming *phthalylideneanthrone* (formula IV), which crystallises in brown spangles, sintering at 259°, m. p. 262—264°, and giving a deep red solution with alcoholic potassium hydroxide.

A 75% yield of dianthrone is obtained by oxidising anthranol with phenanthraquinone (compare Dimroth, Abstr., 1901, i, 198; Meyer, this vol., i, 168).

Diphenylmethylenanthraquinone (Abstr., 1906, i, 741) forms, on reduction with acetic anhydride and zinc dust, 10-acetoxy-9-anthryl-

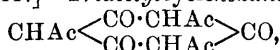
diphenylmethane, $\text{OAc} \cdot \text{C} \begin{array}{c} \swarrow \text{C}_6\text{H}_4 \\ \searrow \text{C}_6\text{H}_4 \end{array} \text{C} \cdot \text{CHPh}_2$. This has m. p. 228—229°;

its solutions show an intense violet fluorescence.

Phosphorus pentachloride attacks anthranol, forming a compound, m. p. 298—300°. W. O. W.

Transformation of a Phloroglucinol Derivative into one of cycloHexantrione. GUSTAV HELLER (*Ber.*, 1909, 42, 2736—2742).—The author has found that when phloroglucinyl triacetate is heated with zinc chloride to 130°, a molecular change takes place, whereby the triacetate is converted into triacetylcyclohexantrione; this compound yields a tribenzoyl derivative, and with hydroxylamine a monoxime.

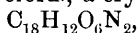
[With OTTO LANGKOPF.]—Triacetylcyclohexantrione,



crystallises in colourless, felted needles, m. p. 156°; it gives an intense blood red coloration with ferric chloride, and a green copper salt; the substance is also produced when a mixture of phloroglucinol, acetic anhydride, and zinc chloride is heated in a closed tube at above 150°.

Triacetyltribenzoylcyclohexantrione, $\text{CAcBz} \begin{array}{c} \swarrow \text{CO} \cdot \text{CAcBz} \\ \searrow \text{CO} \cdot \text{CAcBz} \end{array} \text{CO}$, has m. p. 220° (decomp.); it gives no coloration with ferric chloride; on hydrolysis with 80% sulphuric acid it yields phloroglucinol. The monoxime of triacetylcyclohexantrione, $\text{C}_{12}\text{H}_{13}\text{O}_6\text{N}$, has m. p. 187° (decomp.). Triacetylcyclohexantrione forms two monophenylhydrazones; the α -compound forms bushy, yellow needles, m. p. 154°, and the β -compound (produced at a higher temperature) forms yellow needles, m. p. 184°. J. C. C.

Attempts to Convert Oxalyldiacetophenone and other Oxalyl Compounds into Hexaketones. OSKAR WIDMAN and ERIK VIRGIN (*Ber.*, 1909, 42, 2794—2806).—In the hope of directly oxidising the two methylene groups in oxalyldiacetophenone to carbonyl groups, the substance has been warmed with nitric acid, D 1.4, but the products are Holleman's diphenyldinitrosacyl and isodiphenyldinitrosacyl and an unexamined oil; the first-mentioned compound, which, with the oil, results by the action of nitric acid, D 1.5, at 0°, forms with hydrazine hydrochloride an azine, $\begin{array}{c} \text{N} : \text{CPh} \cdot \text{C} : \text{N} \cdot \text{O} \\ | \qquad \qquad | \\ \text{N} : \text{CPh} \cdot \text{C} : \text{N} \cdot \text{O} \end{array}$, m. p. 207° (decomp.). When nitrous fumes are passed into a suspension of oxalyldiacetophenone in chloroform, a crystalline substance,



m. p. 130° (decomp.), is obtained, which has the composition of dioximino-oxalyldiacetophenone, but since it is not attacked by nitrous acid or amyl nitrite and does not form a quinoxaline derivative, it receives the annexed constitution, which is in harmony with the decomposition of the substance into oxalic acid and benzoyl cyanide by cold phenylhydrazine, aniline, hydroxylamine, or pyridine. It is stable to strong mineral acids, and is not attacked by acetyl chloride, acetic anhydride, or phenylcarbimide.

$$\begin{array}{c} \text{N} \text{-----} \text{O} \\ || \quad \quad \quad | \\ \text{C} \text{Bz} \cdot \text{C}(\text{OH}) \cdot \text{C}(\text{OH}) \cdot \text{C} \text{Bz} \\ | \quad \quad \quad | \\ \text{O} \text{-----} \text{N} \end{array}$$

2:4:2':4'-*Tetramethyloxalyldiacetophenone*, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_3\text{Me}_2$, m. p. 169—170°, obtained from acetyl-*m*-xylene, ethyl oxalate, and sodium ethoxide, and 4:4'-*dimethoxyoxalyldiacetophenone*, m. p. 182°, form dioximino-derivatives, m. p. 113—114° (decomp.) and 122—123° (decomp.) respectively, the properties of which are quite similar to those of the preceding substance.

Tetrabromo-oxalyldiacetophenone, $\text{C}_2\text{O}_2(\text{CBr}_2\cdot\text{COPh})_2$, m. p. 196—197°, prepared by the action of bromine on a chloroform solution of oxalyldiacetophenone containing anhydrous sodium carbonate, crystallises in stout, yellow prisms, retains the halogen very firmly, and is hydrolysed by sodium hydroxide, yielding methylene bromide and oxalic and benzoic acids.

Dibromo-oxalyldiacetophenone, $\text{C}_2\text{O}_2(\text{CHBr}\cdot\text{COPh})_2$, m. p. 124—125°, is obtained by passing air and bromine vapour into a chloroform solution of oxalyldiacetophenone containing calcium carbonate.

C. S.

Action of Sodium Hydroxide on Tetrabromo-*o*-benzoquinone. C. LORING JACKSON and AUGUSTUS H. FISKE (*Ber.*, 1909, 42, 2636—2638. Compare Zincke, *Abstr.*, 1887, 808).—When tetrabromo-*o*-benzoquinone is treated with cold sodium hydroxide solution (1:5), the products are tetrabromocatechol, m. p. 190—191°, and the *carboxylic acid* derived from the ether of bromotrihydroxycyclopentadiene, $\text{C}_5\text{HBr}(\text{OH})_3\cdot\text{O}\cdot\text{C}_5\text{Br}(\text{OH})_3\cdot\text{CO}_2\text{H}$, which separates from glacial acetic acid in pale yellow crystals, m. p. 174° (decomp.). When *N*-sodium hydroxide at 6° is used, the product crystallises from benzene in colourless prisms with acid properties, m. p. 217° (decomp.).

With 0.5*N*-sodium hydroxide at 15° the products are two acids. The one crystallises from benzene, in which it is sparingly soluble, as pale yellow needles, m. p. 207° (decomp.), and the other in colourless, rhombic prisms, m. p. 121° (decomp.).

J. J. S.

Tribromoresoquinone. RICHARD MEYER and KURT DESAMARI (*Ber.*, 1909, 42, 2814—2824).—The molecular weight of tribromoresoquinone in benzene (compare this vol., ii, 721) points to the bimolecular formula and therefore confirms Zincke and Schwabe's constitution, $\text{CO} \begin{array}{c} \text{CBr}\cdot\text{CH} \\ \text{CBr}_2\cdot\text{CO} \end{array} \text{C}:\text{C} \begin{array}{c} \text{CH}\cdot\text{CBr} \\ \text{CO}\cdot\text{CBr}_2 \end{array} \text{CO}$, for this substance. By treatment with tin and hydrochloric acid, hydriodic acid, chloroform, *as*-methyl- or benzoyl-phenylhydrazine, or semicarbazide, it yields 3:5:3':5'-*tetrabromo-2:4:2':4'-diresorcinol*, m. p. 280° (*tetra-acetate*,

m. p. 195°; *tetrabenzoate*, m. p. 188°), identical with the substance obtained by the bromination of Bayer & Co.'s 2:4:2':4'-diresorcinol (*tetra-acetate*, m. p. 120°; *tetrabenzoate*, m. p. 163°), which yields tribromoresoquinone by treatment with bromine in dilute acetic acid. Attempts to debrominate tetrabromodiresorcinol have been unsuccessful, but by prolonged heating of its alcoholic solution with zinc dust a *dibromodiresorcinol*, $C_{12}H_8O_4Br_2$, m. p. 195°, has been obtained, which forms a *tetra-acetate*, m. p. 154°, and a *tetrabenzoate*, m. p. 174°.

3:5:3':5'-Diresorcinol (*tetrabenzoate*, m. p. 200°), by bromination in glacial acetic acid, yields *hexabromodiresorcinol*, $C_{12}H_4O_4Br_6$, darkening at 180° (*tetra-acetate*, m. p. 259—264°), and by bromination in carbon disulphide forms a *tetrabromodiresorcinol*, $C_{12}H_6O_4Br_4$, m. p. 187—195° (*tetra-acetate*, m. p. 170°; *tetrabenzoate*, m. p. 265°). C. S.

Oxidation of Fenchyl Alcohol. A. BLUMANN and OTTO ZEITSCHEL (*Ber.*, 1909, 42, 2698—2702).—In the oxidation of fenchyl alcohol to fenchone by sodium dichromate and dilute sulphuric acid, a crystalline substance, m. p. 77—78°, has been obtained in 1—2% yield, which proves to be Czerny's lactone of α -hydroxydihydrofencholenic acid. The identity is confirmed by converting the lactone into the hydroxy-acid, the hydrochloride, and α -fencholenic acid. The last appears to be a mixture of isomeric acids differing in the position of the double linking. Attempts to oxidise fenchone to the lactone have been unsuccessful. C. S.

Philippine Terpenes and Essential Oils. III. RAYMOND F. BACON (*Philippine J. Sci.*, 1909, 4, 93—132. Compare Abstr., 1908, i, 814, 815; also Clover, *ibid.*, 1907, i, 542).—The source of Manila elemi is *Canarium luzonicum*. When fresh it is soft, but when left on trees exposed to the sun becomes quite hard. The terpenes obtained by distilling more than one hundred different specimens of elemi under reduced pressure have been isolated. The boiling point or specific rotatory powers of the different terpenes vary considerably. Some consist of limonene, others (90%) of phellandrene.

Phellandrene nitrite (Wallach, Abstr., 1904, i, 1035), when crystallised from cold solvents, has m. p. 120—121°. β -Phellandrene also appears to yield the same nitrite. In addition to α - and β -phellandrenes there appears to be a higher boiling phellandrene in elemi resin. It has b. p. 175—178°, D_4^{20} 0.8375, n_D^{30} 1.4685. The resin obtained after the distillation of the terpenes from elemi has been examined, and also subjected to destructive distillation. As a rule, the neutral product of distillation is an ordinary resin oil, but in two cases the terpene obtained was nearly pure pinene. Others again gave limonene and phellandrene. The halogen derivatives of terpenes react with magnesium, but the Grignard compounds, so formed, do not react normally with ethyl orthoformate.

α -Phellandrene can be transformed into dipentene by boiling its chloride for six hours in a reflux apparatus with excess of alcoholic potassium hydroxide.

Experiments have been made with lemon grass oil; *cinnamomum mercadoi*, which yields safrole, but practically no cinnamaldehyde;

petroleum nuts (fruits of *Pittosporum resiniferum*, which gave heptane and dihydroterpene; vetiver oil, from the roots of *Andropogon squarrosus* (compare Abstr., 1903, i, 187), which yielded an acid $C_{14}H_{24}O_2$; balao resin from *Dipterocarpus vernicifluus* and *D. grandiflorus*, which yields a sesquiterpene, b. p. 118—119°/8 mm., D_4^{20} 0.9104, n_D^{20} 1.4956, $[\alpha]_D^{30} + 116.4^\circ$; *Lantanna camara*; oil of Ylang-ylang.

J. J. S.

Constitution of isoPinene. OSSIAN ASCHAN (Reprint from *Öfversigt Finska Vetensk. Soc. Förhandl.*, 1908–1909, 51, A, No. 9).—The terpene described previously as pinolene (Abstr., 1907, i, 630) is shown to be a mixture of two hydrocarbons, since part of it (α -pinolene) is removed by treatment with aqueous potassium permanganate, whilst the remainder, β -pinolene, remains unattacked. β -Pinolene is a colourless liquid, b. p. 142—144°, D_4^{20} 0.8588, $[\eta]_D + 0.28^\circ$, n_D^{20} 1.44769, mol. ref. 42.37. The latter value indicates that the mol. of β -pinolene is built up of three carbon ring systems, of which one is a cyclopropane ring. The hydrochloride has m. p. 25—26°, and is apparently different from the hydrochloride obtained from crude pinolene (*loc. cit.*); however, when treated with aniline it yields isopinene. The acid formed by the oxidation of α -pinolene with potassium permanganate has been identified as *r*-camphoric acid.

isoPinene has b. p. 154.5—155.5°, D_4^{20} 0.8658, $\alpha_D + 2.61^\circ$ (in 1-dcm. tube), n_a 1.470253, mol. ref. 43.48, and is therefore probably a dicyclic terpene with a double linking. In fact, isopinene probably has the annexed constitution, since it is converted by aqueous potassium permanganate into apocamphoric acid and fenchonic acid, which has

the formula $\begin{array}{c} \text{CH}_2 \cdot \text{CH} - \text{CMe}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} - \text{CH} \end{array}$ $\begin{array}{c} \text{CMe}_2 \\ || \\ \text{CH}_2 \cdot \text{CH} \cdot \text{COMe} \end{array}$, for it yields apocamphoric acid when

treated with potassium hydroxide and bromine. Fenchonic acid crystallises in small, thick leaflets and prisms, m. p. 126—128°, and yields a somewhat unstable phenylhydrazone, crystallising in orange-yellow, long, six-sided leaflets, m. p. 70—100°. It is proposed to use von Baeyer's nomenclature, whereby isopinene becomes 2:7:7-trimethyl-2-norcamphene.

W. H. G.

Chitin. D. H. WESTER (*Arch. Pharm.*, 1909, 247, 282—307).—The author gives an exhaustive list of the researches on chitin since 1811, and a full account of its distribution in the animal and vegetable kingdoms. The chitin from different sources is shown to be one and the same substance. The method of isolation differs slightly from the following, according to the nature of the source. Shrimp shells are treated with cold 5% acetic acid, to destroy carbonates, and with 5% hydrochloric acid, at first for three hours at the ordinary temperature and finally for fifteen minutes on the water-bath with a fresh portion of the acid, whereby the next operation, the extraction of the colouring matters by hot alcohol, is facilitated. The residue is treated on the water-bath for five hours with frequently renewed 5%, and finally for one hour with 10%, potassium hydroxide, collected, washed, dried, and

extracted with ether. After treatment with dilute acid to remove chitosan, the residue is fairly pure chitin; its complete purification has probably not yet been accomplished. The susceptibility to the attack of alkali hydroxides, whereby chitosan is formed, is probably the reason for the frequent inaccuracies in the literature regarding the properties and reactions of chitin. Chitin free from chitosan does not decolorise an iodine-starch solution, does not respond to Millon's or the biuret test, does not give a violet coloration with iodine and dilute sulphuric acid, and remains unchanged after six hours' treatment with gastric and pancreatic juices. It is only slowly attacked by dilute mineral acids; from its solutions in 37% hydrochloric acid, or 50% nitric acid, it can be more or less recovered by careful neutralisation at 0°, even after many hours, but is decomposed by 95% sulphuric acid in less than thirty minutes. As tests for chitin, the author uses (1) its conversion by potassium hydroxide into chitosan, which (a) gives a violet coloration with 0.5% iodine and 1% sulphuric acid solution, (b) is precipitated as the sulphate from acetic acid solution by 1% sulphuric acid; (2) solubility in, and recovery from, 50% nitric acid; (3) formation of glucosamine hydrochloride by boiling concentrated hydrochloric acid.

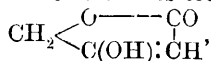
A 5% solution of potassium hydroxide in one hour at 160° converts chitin into chitosan, ammonia, acetic and oxalic acids, and smaller amounts of formic, butyric, and tartaric acids. Saturated potassium hydroxide at 250° for one hour yields a non-nitrogenous residue, indole, ammonia, acetic, formic, and oxalic acids, and traces of butyric and tartaric acids. When treated with 40–60% potassium hydroxide, chitin is completely changed into chitosan, within one hour at 110–160° and after 90–100 days at the ordinary temperature.

Chitosan, $C_{14}H_{26}O_{10}N_2$, is best prepared by treating chitin with 50% potassium hydroxide at 160–170° for one hour, dissolving the mass in 2.5–3% acetic acid, and reprecipitating the chitosan by a slight excess of alkali. It is soluble in many organic acids, and is precipitated from such solutions by 1% sulphuric acid. Its nitrogen is evolved quantitatively by nitrous acid. C. S.

Assamin. JOSEF HALBERKANN (*Biochem. Zeitsch.*, 1909, 19, 310–367).—*Assamin*, $C_{30}H_{46}O_{15}$ or $C_{60}H_{93}O_{30}$, a neutral saponin prepared from Assam tea seeds, is obtained as a yellowish-white, amorphous powder, is optically inactive, and yields an *acetyl* derivative, probably $C_{30}H_{36}O_{15}Ac_{10}$, which is also amorphous. On acid hydrolysis it yields a mixture of sapogenins, galactose, arabinose, and probably some butyric acid. A full description of its pharmacological characters is given. It is a strong hæmolytic agent. W. D. H.

The Benztetronic Acid [4-Hydroxycoumarin] Group. I. RICHARD ANSCHÜTZ (*Annalen*, 1909, 367, 169–270).—An account of an exhaustive investigation on the preparation and properties of benztetronic acid and its derivatives. Benztetronic acid is 4-hydroxycoumarin, C_6H_4 $\begin{smallmatrix} \text{O} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \text{:CH} \end{smallmatrix}$, but the use of the former name is

advocated, since this substance resembles tetronic acid,



to a remarkable degree, not only in its structure, but in its reactions. A new synthesis of coumarin is also described.

[With RICHARD ANSPACH, REMIGIUS FRESENIUS, and REINHOLD CLAUS.]—I. *Condensations with Acetylsalicylyl Chloride*.—3-Carbethoxybenzotetronic acid (ethyl 4-hydroxycoumarin-3-carboxylate),

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) : \text{C} \end{smallmatrix} \begin{smallmatrix} \text{CO} \\ \diagdown \quad \diagup \\ \text{CO}_2\text{Et} \end{smallmatrix}$, is prepared by the condensation of acetylsalicylyl chloride with ethyl sodiomalonate; it crystallises in white, prismatic needles, m. p. 101° ; the ammonium salt, $\text{C}_{12}\text{H}_{13}\text{O}_5\text{N}$, forms tufts of white needles; the sodium salt, $\text{C}_{12}\text{H}_9\text{O}_5\text{Na}$, is a white powder; the copper salt, $(\text{C}_{12}\text{H}_9\text{O}_5)_2\text{Cu}$, is a blue, crystalline powder; the silver salt is a white powder.

Ethyl sodiocyanoacetate and acetylsalicylyl chloride interact, yielding ethyl α -cyano-o-acetoxycarboxylate, $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$ or $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) : \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$, which crystallises in small, white leaflets, m. p. 65° . It is converted by ammonium hydroxide into ammonium 3-cyanobenzotetronate, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{ONH}_4) : \text{C} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CN} \end{smallmatrix}$; the acid (3-cyano-4-hydroxycoumarin), $\text{C}_{10}\text{H}_5\text{O}_3\text{N}$, forms crystalline nodules, m. p. 242° .

3-Carboxylamidobenzotetronic acid (4-hydroxycoumarin-3-carboxylamide), $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{OH}) : \text{C} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$, is prepared by the action of concentrated sulphuric acid on the nitrile just described; it crystallises in tufts of needles, m. p. 219° .

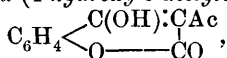
3-Ethylcarboxybenzotetronic acid is converted by phosphorus pentachloride into the corresponding chloride (ethyl 4-chlorocoumarin-3-carboxylate), $\text{C}_{12}\text{H}_9\text{O}_4\text{Cl}$, crystallising in almost white, flat needles, m. p. 83.5° . The latter substance, when treated with an alcoholic solution of sodium ethoxide, yields ethyl 4-ethoxycoumarin-3-carboxylate, $\text{C}_{14}\text{H}_{14}\text{O}_5$, a crystalline substance, m. p. 123.5 — 124.5° , which is hydrolysed by alcoholic potassium hydroxide, yielding 4-ethoxycoumarin-3-carboxylic acid, $\text{C}_{12}\text{H}_{10}\text{O}_5$, white needles, m. p. 86° . Attempts to prepare 4-ethoxycoumarin from the latter substance by elimination of carbon dioxide were unsuccessful.

Benzotetron-3-carboxylanilide (4-hydroxycoumarin-3-carboxylanilide), $\text{C}_{16}\text{H}_{11}\text{O}_4\text{N}$, is prepared by the action of boiling aniline on ethyl 4-hydroxycoumarin-3-carboxylate; it crystallises in tufts of slender, white needles, m. p. 213° ; the sodium derivative, $\text{C}_{16}\text{H}_{10}\text{O}_4\text{NNa}$, formed by the action of sodium on a solution of the substance in benzene, is a white, amorphous substance, which turns brown at 300° ; the silver derivative, $\text{C}_{16}\text{H}_{10}\text{O}_4\text{NAg}$, is a white powder; it is not known whether the metal in these compounds is attached to oxygen or nitrogen. 3-Carbethoxybenzotetronanilide (ethyl 4-anilinocoumarin-3-carboxylate), $\text{C}_{18}\text{H}_{15}\text{O}_4\text{N}$, is formed by the action of an alcoholic solution of aniline on ethyl 4-chlorocoumarin-3-carboxylate; it forms flat, pale yellow, prismatic needles, m. p. 128° . 4-Anilinocoumarin-3-carboxylanilide, $\text{C}_{22}\text{H}_{16}\text{O}_3\text{N}_2$, is formed by boiling the substance just described with an alcoholic solution of aniline; it crystallises in tufts of slender, yellow needles, m. p. 194° . The following compounds are

prepared by using phenylhydrazine instead of aniline: *4-hydroxycoumarin-3-carboxylic acid phenylhydrazide*, $C_{16}H_{12}O_4N_2$, feathery, pale yellow crystals, m. p. 210° ; *ethyl 4-phenylhydrazinocoumarin-3-carboxylate*, $C_{18}H_{16}O_4N_2$, small, felted needles, m. p. about 220° (decomp.); *4-phenylhydrazinocoumarin-3-carboxylic acid phenylhydrazide*,

$C_{22}H_{18}O_3N_4$, faintly yellow, slender crystals, m. p. $189-190^\circ$ (decomp.).

3-Acetobenzotetronic acid (4-hydroxy-3-acetylcoumarin),



is prepared by the action of acetylsalicylyl chloride on ethyl sodio-acetoacetate; it forms slender, white needles, m. p. 134° ; the ammonium, sodium, and silver salts were analysed.

Benzotetronic acid (4-hydroxycoumarin) may be prepared by heating ethyl 4-hydroxycoumarin-3-carboxylate with aqueous potassium hydroxide; similarly, from ethyl 4-ethoxycoumarin-3-carboxylate, 3-cyano-4-hydroxycoumarin and 4-hydroxy-3-acetylcoumarin; the silver salt, $C_9H_5O_3Ag$, is a white powder, which, when heated with ethyl iodide, yields 4-ethoxycoumarin, $C_{11}H_{10}O_3$, crystallising in pale yellow leaflets, m. p. 136° , b. p. $174^\circ/14$ mm. *4-Acetoxy coumarin*, $C_{11}H_8O_3$, prepared by the action of acetic anhydride on benzotetronic acid, crystallises in slender needles, m. p. 103° . *Benzotetronyl chloride (4-chlorocoumarin)*,

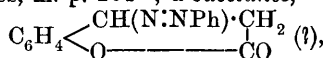
$C_6H_4 \begin{array}{c} \diagup CCl:CH \\ \diagdown O \text{---} CO \end{array}$, is formed by the action of phosphorus pentachloride on a solution of benzotetronic acid in chloroform; it crystallises in long, white needles, m. p. $91-92^\circ$, b. p. $163-165^\circ/12$ mm., and is not decomposed by water or alcohol; the corresponding bromide,

$C_9H_5O_2Br$, has m. p. $90-91^\circ$, b. p. $174-177^\circ/14$ mm., and is likewise not decomposed by water. The chloride or bromide, when treated with zinc dust and alcohol, yields coumarin.

The following compounds are prepared by heating benzotetronic acid, its chloride or bromide with the necessary amine: *benzotetronic anilide (4-anilinocoumarin)*, $C_{15}H_{11}O_2N$, glistening, yellow leaflets, m. p. $259-260^\circ$; the *o-toluidino*-compound, $C_{16}H_{13}O_2N$, pale yellow, prismatic plates, m. p. $214-216^\circ$; the *piperidino*-compound,

$C_{14}H_{15}O_2N$, white, flat, prismatic needles, m. p. $104-105^\circ$.

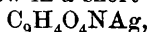
The action of phenylhydrazine on benzotetronic acid or its bromide leads to the formation of three substances: *benzotetronic acid phenylhydrazide (4-phenylhydrazinocoumarin)* (?), $C_{15}H_{12}O_2N_2$, white, glistening, prismatic needles, m. p. 201° ; a substance,



red needles, m. p. 186° ; a substance, $C_{15}H_{12}O_2N_2$, small, yellowish-red crystals, m. p. about 120° .

3-Oximinocoumarin, $C_6H_4 \begin{array}{c} \diagup CO:C:N\cdot OH \\ \diagdown O \text{---} CO \end{array}$, prepared by the action of nitrous acid on benzotetronic acid, crystallises in glistening, golden-yellow leaflets, m. p. 149° (decomp.); the solutions in aqueous alkalis

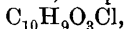
are first blue, but turn yellow in a short time; the *silver* salt,



is an emerald-green powder.

Benzotetronic acid, analogously to tetronic acid, condenses with formaldehyde, yielding 3-methylenebisbenzotetronic acid (3-methylenebis-4-hydroxycoumarin), $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{C}(\text{OH}) \cdot \text{C} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{C}(\text{OH}) \\ \text{O} \text{---} \text{CO} \quad \text{CO} \text{---} \text{O} \end{array} \right\rangle \text{C}_6\text{H}_4$, a white, crystalline substance, m. p. about 260° (decomp.), and with acetaldehyde forming the analogous *ethylidene* compound, $\text{C}_{20}\text{H}_{14}\text{O}_6$, m. p. 165° . Condensation products of benzotetronic acid with *n*-propaldehyde, *n*-butyraldehyde, and acetone could not be prepared.

[With JOSEPH WAGNER and PETER JUNKERSDORF.] II. Condensations with *Acetyl-m-cresotyl Chloride* (3-Acetoxy-*p*-toluyl Chloride). — *Acetyl-m-cresotic acid* [2-acetoxy-4-methylbenzoic acid], $\text{C}_{10}\text{H}_{10}\text{O}_4$, crystallises in small, white needles, m. p. 139° ; the *chloride*,



forms a white, crystalline mass, m. p. 15° , b. p. $141^\circ/10$ mm. (slight decomp.). 3-Carbethoxy-7-methylbenzotetronic acid (*ethyl 4-hydroxy-7-methylcoumarin-3-carboxylate*), $\text{CMe} \cdot \text{CH} \cdot \text{C} \begin{array}{c} \text{O} \text{---} \text{CO} \\ | \\ \text{CH} = \text{CH} \cdot \text{C} \cdot \text{C}(\text{OH}) \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array}$, prepared

by the interaction of the chloride just described with ethyl sodiummalonate, forms glistening, white leaflets, m. p. 140° ; the *sodium* salt, $\text{C}_{13}\text{H}_{11}\text{O}_5\text{Na}$; *ammonium* salt, small, white needles, m. p. $230\text{--}240^\circ$ (decomp.); *silver* salt, glistening white needles; and *acetate*, $\text{C}_{15}\text{H}_{14}\text{O}_6$, white crystals, m. p. 217° , were prepared.

The following compounds are obtained by treating the silver salt with the necessary alkyl iodide: *ethyl 4-methoxy-7-methylcoumarin-3-carboxylate*, $\text{C}_{14}\text{H}_{14}\text{O}_5$, forms small, white needles, m. p. 126° ; the analogous 4-*ethoxy*-derivative, $\text{C}_{15}\text{H}_{16}\text{O}_5$, forms pale yellow, transparent, monoclinic crystals, m. p. 104° ; the 4-*propoxy*-compound, $\text{C}_{16}\text{H}_{18}\text{O}_5$, forms pale yellow, transparent, monoclinic crystals, m. p. 112° . Attempts to prepare the isomeride of the ethoxy-compound having the

constitution $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{O} \text{---} \text{CO} \\ | \\ \text{CO} \cdot \text{CH} \text{Et} \cdot \text{CO}_2\text{Et} \end{array}$ by condensing ethyl sodiumethylmalonate with *acetyl-m-cresotyl chloride* were unsuccessful.

Ethyl 4-hydroxy-7-methylcoumarin-3-carboxylate is converted (1) by aniline at 175° into 7-methylbenzotetron-3-carboxylanilide (4-hydroxy-7-methylcoumarin-3-carboxylanilide), $\text{C}_{17}\text{H}_{13}\text{O}_4\text{N}$, a yellow substance, m. p. 202° ; (2) by phenetidine at 200° into the analogous *phenetidide*, $\text{C}_{19}\text{H}_{17}\text{O}_5\text{N}$, slender, very pale yellow needles, m. p. 218° ; (3) by an alcoholic 33% solution of ethylamine into the corresponding *ethylcarboxylamide*, $\text{C}_{13}\text{H}_{13}\text{O}_4\text{N}$, small, silvery crystals, m. p. 152° ; (4) by an alcoholic solution of phenylhydrazine into the *carboxylphenylhydrazide*, $\text{C}_{17}\text{H}_{14}\text{O}_4\text{N}_2$, small crystals, m. p. 232° ; the latter substance when heated with a solution of methyl iodide in methyl alcohol under pressure at $100\text{--}110^\circ$ yields the corresponding *carboxylphenylmethylhydrazide*, $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{O} \text{---} \text{CO} \\ | \\ \text{CO} \cdot \text{CH} \cdot \text{CO} \cdot \text{N}_2\text{HMePh} \end{array}$ (?), m. p. 207° .

The ester is converted by phosphorus pentachloride into *ethyl 4-chloro-7-methylcoumarin-3-carboxylate*, $\text{C}_{13}\text{H}_{11}\text{O}_4\text{Cl}$, a yellow substance.

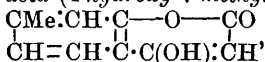
m. p. 109—110°, which, when treated with an alcoholic solution of aniline, yields *ethyl 4-anilino-7-methylcoumarin-3-carboxylate*,

$C_{17}H_{19}O_4N$,
m. p. 162°, and when heated with aniline at 184° yields *4-anilino-7-methylcoumarin-3-carboxylanilide*, $C_{23}H_{18}O_3N$, m. p. 220—222°.

3-Acetyl-7-methylbenzotetronic acid (*4-hydroxy-3-acetyl-7-methylcoumarin*), C_6H_3Me $\begin{array}{c} O \text{---} CO \\ \diagup \quad \diagdown \\ C(OH) : C \cdot AC \end{array}$, prepared by the action of an ethereal solution of acetyl-*m*-cresotyl chloride on ethyl sodioacetoacetate, crystallises in yellow needles, m. p. 136°; the *sodium*, *ammonium* (m. p. 198°), and *silver* salts were analysed; the *methyl* ether, $C_{13}H_{12}O_4$, forms pale yellow needles, m. p. 138°; the *ethyl* ether, $C_{14}H_{14}O_4$, crystallises in brownish-yellow needles, m. p. 133°; the *propyl* ether, $C_{15}H_{16}O_4$, forms dark yellow needles, m. p. 135°.

3-Cyano-7-methylbenzotetronic acid (*3-cyano-4-hydroxy-7-methylcoumarin*), C_6H_3Me $\begin{array}{c} C(OH) : C \cdot CN \\ O \text{---} CO \end{array}$, is prepared by the interaction of ethyl sodiocyanoacetate and acetyl-*m*-cresotyl chloride in ethereal solution; it is an amorphous powder, m. p. 250°; the *sodium* and *silver* salts were analysed; the *methyl* ether, $C_{12}H_9O_3N$, crystallises in small, yellow needles, m. p. 238°; the *ethyl* ether, $C_{13}H_{11}O_3N$, forms yellow needles, m. p. 218°; the *propyl* ether, $C_{14}H_{13}O_3N$, is a greyish-yellow substance, m. p. 223°.

7-Methylbenzotetronic acid (*4-hydroxy-7-methylcoumarin*),



is prepared by heating ethyl 4-hydroxy-7-methylcoumarin-3-carboxylate with a 10% aqueous solution of potassium hydroxide; it forms small, white needles, m. p. 217°; the *silver* salt is a white powder; the *methyl* ether, $C_{11}H_{10}O_3$, forms small needles, m. p. 162°; the *ethyl* ether, $C_{12}H_{12}O_3$, forms tufts of pale yellow needles, m. p. 144°; the *propyl* ether, $C_{13}H_{14}O_3$, has m. p. 148°; the *acetate*, $C_{12}H_{10}O_4$, crystallises in slender, white needles, m. p. 142°.

7-Methylbenzotetronyl bromide (*4-bromo-7-methylcoumarin*),

$C_{10}H_7O_2Br$,
forms yellowish-white needles, m. p. 149—150°, b. p. 185—195°/12 mm., and when treated with zinc dust and alcohol yields *7-methylcoumarin* (*m-cresocoumarin*), $CMe : CH \cdot C \text{---} O \text{---} CO$
 $CH = CH \cdot C \cdot CH : CH'$, a white substance,

m. p. 119—120°. From the bromide are obtained: *4-ethylamino-7-methylcoumarin*, $C_{12}H_{13}O_2N$, slightly yellow leaflets, m. p. 174°; *4-anilino-7-methylcoumarin*, $C_{16}H_{13}O_2N$, small crystals with a green shimmer, m. p. 247° (decomp.); *4-(p)-toluidino-7-methylcoumarin*, $C_{17}H_{15}O_2N$, has m. p. 252°.

The following compounds are prepared by condensing the acid with the necessary aldehyde: *methylenebis-4-hydroxy-7-methylcoumarin*,

C_6H_3Me $\begin{array}{c} O \text{---} CO \quad CO \text{---} O \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ C(OH) : C \cdot CH_2 : C : C(OH) \end{array}$ C_6H_3Me , long, white needles, m. p. 273—275°; *ethylidenebis-4-hydroxy-7-methylcoumarin*, $C_{22}H_{18}O_6$, m. p. 206°; *benzylidenebis-4-hydroxy-7-methylcoumarin*, $C_{27}H_{20}O_6$,

m. p. 230°. The acid does not yield a condensation product with propaldehyde.

[With JULIUS SIEBEN.]—III. *Condensations with Acetyl-p-cresotyl Chloride* (4-Acetoxy-m-toluyyl Chloride).—The compounds described later are obtained by methods similar to those already described.

Acetyl-p-cresotic acid (2-acetoxy-5-methylbenzoic acid), $C_{10}H_{10}O_4$, forms small, glistening needles, m. p. 142—143°; the *chloride* has m. p. 47°, b. p. 147°/12 mm. *Ethyl 4-hydroxy-6-methylcoumarin-3-carboxylate*, $C_{13}H_{12}O_5$, forms small, thin needles, m. p. 121—122°; the *sodium*, *ammonium*, and *silver* salts were prepared and analysed; the *ethyl* ether, $C_{15}H_{16}O_5$, forms small needles, m. p. 87°. *3-Cyano-4-hydroxy-6-methylbenzotetronic acid* (3-cyano-4-hydroxy-6-methylcoumarin), $C_{11}H_7O_3N$, has m. p. 248° (decomp.); the *sodium* and *silver* salts were analysed. *3-Acetyl-4-hydroxy-6-methylcoumarin*, $C_{12}H_{10}O_4$, forms pale yellow plates, m. p. 144—145°; the *sodium* and *silver* salts were analysed.

6-Methylbenzotetronic acid (4-hydroxy-6-methylcoumarin), $C_{10}H_8O_3$, crystallises in small, white needles, m. p. 241° (decomp.); the *ethyl* ether, $C_{12}H_{12}O_3$, forms small, white needles, m. p. 195°.

[With JOACHIM GRAFF.]—IV. *Condensations with 3-Acetoxy-2-naphthoic Acid*.—3-Acetoxy-2-naphthoyl chloride, $OAc \cdot C_{10}H_6 \cdot COCl$, forms white crystals, m. p. 89°; the *amide*, $OAc \cdot C_{10}H_6 \cdot CO \cdot NH_2$, is a yellowish-green, crystalline substance, m. p. 192°; the *anilide*, $C_{19}H_{15}O_3N$, crystallises in small, white needles, m. p. 152°. *3-Carboethoxy-(2:3)-naphthatetronic acid* [ethyl 4-hydroxy- $\beta\beta$ -naphthapyrone-3-carboxylate], $C_{10}H_6 \begin{smallmatrix} C(OH):C \cdot CO_2Et \\ \diagdown \quad \diagup \\ O \quad CO \end{smallmatrix}$, forms pale yellow, matted

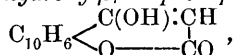
needles and slender leaflets, m. p. 182°; when treated with aqueous potassium hydroxide it yields 3-hydroxy-2-naphthoic acid and a yellow substance, $C_{12}H_{12}O_2$ or $C_{12}H_{10}O_2$, m. p. 115°. The *ammonium*, *sodium*, *silver*, and *copper* salts were analysed; the *methyl* ether, $C_{17}H_{14}O_5$, forms pale yellow crystals, m. p. 146°; the *acetate*, $C_{18}H_{14}O_6$, has m. p. 157°. The ester is converted by phenylhydrazine into the *phenylhydrazide*,

$C_{10}H_6 \begin{smallmatrix} CO \cdot CH \cdot CO \cdot NH \cdot NHPh \\ \diagdown \quad \diagup \\ O \quad CO \end{smallmatrix}$, small, reddish-yellow, felted needles, m. p. 245°. *Ethyl 3-acetoxy-2-naphthoylcynoacetate*,

$OAc \cdot C_{10}H_6 \cdot CO \cdot CH(CN) \cdot CO_2Et$, crystallises in red leaflets, m. p. 103°. *3-Cyano-(2:3)-naphthatetronic acid* [3-cyano-4-hydroxy- $\beta\beta$ -naphthapyrone], $C_{10}H_6 \begin{smallmatrix} C(OH):C \cdot CN \\ \diagdown \quad \diagup \\ O \quad CO \end{smallmatrix}$, is a yellow powder, m. p. 276°; the *sodium* and *copper* salts were analysed; the *acetate*, $C_{16}H_9O_4N$, forms brown crystals, m. p. 229°.

4-Hydroxy- $\beta\beta$ -naphthapyrone-3-carboxylamide, $C_{14}H_9O_4N$, forms yellow crystals, m. p. 256°. *4-Hydroxy-3-acetyl- $\beta\beta$ -naphthapyrone*,

$C_{10}H_6 \begin{smallmatrix} C(OH):C \cdot Ac \\ \diagdown \quad \diagup \\ O \quad CO \end{smallmatrix}$, crystallises in golden-yellow spangles, m. p. 239°; the *sodium*, *copper*, and *silver* salts were analysed. (2:3)-*Naphthatetronic acid* [4-hydroxy- $\beta\beta$ -naphthapyrone],



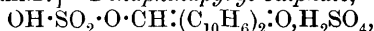
crystallise in small, white needles, m. p. 240°. 3:3-Methylenebis-4-

hydroxy-ββ-naphthapyrone, $C_{27}H_{16}O_6$, is a white substance, m. p. above 280° .

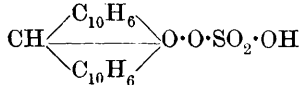
[With AUGUST NEFGEN.]—V. *Action of 5-Chloro-2-acetoxybenzoyl Chloride on Ethyl Sodiomalonnate*.—5-Chloro-2-acetoxybenzoic acid, $OAc \cdot C_6H_3Cl \cdot CO_2H$, has m. p. 148° . The chloride, $C_9H_6O_3Cl_2$, is a crystalline substance, m. p. 45° , and when treated with ethyl sodiomalonate yields 3-ethylcarboxy-6-chlorobenzotetronic acid (ethyl 6-chloro-4-hydroxycoumarin-3-carboxylate), $C_{12}H_9O_5Cl$, crystallising in silky, white needles, m. p. 175° .
W. H. G.

Pyryl Salts formed with Oxygen Acids. II. ROBERT FOSSE (*Bull. Soc. chim.*, 1909, [iv], 5, 787—790. Compare this vol., i, 599).—When a dilute acetic acid solution of dinaphthapyranol is treated with excess of a dilute acetic acid solution of picric acid, *dinaphthapyranol picrate*, $C_6H_2(NO_2)_3 \cdot O \cdot CH < \begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix} > O$, separates in brilliant, reddish-violet crystals, m. p. above 220° (decomp.), which detonate with difficulty when struck. The substance is a true salt analogous to potassium picrate, but not with the additive compounds which picric acid forms with hydrocarbons, etc. Dinaphthapyranol picrate oxidises boiling ethyl alcohol with the production of acetaldehyde and dinaphthaxanthone, thus: $C_2H_6O + C_6H_2(NO_2)_3 \cdot O \cdot CH : (C_{10}H_6)_2 : O = C_2H_4O + CH_2 : (C_{10}H_6)_2 : O + C_6H_2(NO_2)_3 \cdot OH$.

[With P. BERTRAND.]—*Dinaphthapyryl sulphate*,



obtained by dissolving the pyranol in hot dilute sulphuric acid and cooling, crystallises with a molecule of sulphuric acid in red crystals, which form several hydrates. The sulphate, like the picrate, oxidises alcohol to acetaldehyde; it reacts with potassium iodide solution, forming bisdinaphthapyryl, $C_{42}H_{26}O_3$, and *dinaphthapyryl tri-iodide*, $C_{21}H_{13}OI_3$, red crystals, having a green reflex. The oxidising properties of these salts tend to support Haller and Fosse's annexed formula, analogous to the peroxide formula, $HO \cdot O \cdot SO_2 \cdot OH$, of Caro's acid. The capacity of dinaphthapyryl sulphate to crystallise with sulphuric acid and with water is analogous to that of the alkali hydrogen sulphates.



Dinaphthapyryl chromate is a bright red precipitate, which separates when acetic acid solutions of the pyranol and chromic anhydride are mixed. *Dinaphthapyryl nitroprusside*, obtained by mixing acetic acid solutions of the pyryl bromide and sodium nitroprusside, forms beautiful cantharidin-green crystals. When dinaphthapyryl bromide is treated with potassium ferricyanide solution, a bright red precipitate containing iron and nitrogen is formed.
E. H.

Metallic Character of the Dinaphthapyryl Salts. III. Displacement of Hydrogen Chloride from the Pyryl Chloride by Hydrogen Bromide, and Conversely, of Hydrogen Bromide from the Pyryl Bromide by Hydrogen Chloride. **IV.** Displacement of the Acids from Pyryl Salts by Picric Acid.

V. Precipitation of the Dinaphthapyryl Salts as Sulphide by Hydrogen Sulphide. ROBERT FOSSE (*Bull. Soc. chim.*, 1909, [iv], 5, 790—797).—When dinaphthapyryl bromide is dissolved in hot hydrochloric acid and the solution cooled, red crystals separate, which, after recrystallisation from acetic acid, consist of pure dinaphthapyryl chloride with a molecule of acetic acid of crystallisation and quite free from bromine. Conversely, by dissolving dinaphthapyryl chloride in hot hydrobromic acid and cooling the solution, it is converted into the bromide, which, after recrystallisation from acetic acid, is free from chlorine. Addition of ferric bromide to the acetic acid solution of the pyryl bromide so prepared gives a crystalline precipitate of the double bromide of iron and dinaphthapyryl.

Addition of a slight excess of picric acid dissolved in 80% acetic acid to a solution of dinaphthapyryl bromide dissolved in the same solvent gives a precipitate of brilliant red crystals of dinaphthapyryl picrate (compare preceding abstract). This reaction is explained by the author by the partial hydrolysis (in aqueous acetic acid solution) of the bromide into hydrogen bromide and dinaphthapyranol, and consequent progressive transformation of the latter into picrate on addition of picric acid. By heating the pure picrate with hydrochloric acid until dissolved, it is converted into the chloride, which separates on cooling, and, after recrystallisation from hydrochloric acid, is free from picric acid.

When a current of hydrogen sulphide is passed through a solution of a dinaphthapyryl salt in a mineral or organic acid, the liquid is rapidly decolorised, and a greyish-rose precipitate of *dinaphthapyryl sulphide*, $S[\cdot CH:(C_{10}H_6)_2 \cdot O]_2$, is formed. The latter is deposited from benzene solution in brilliant white crystals, which redden superficially in the air and decompose at 275—280°, the temperature varying with the rate of heating. The action of hydrogen sulphide probably first produces the hydrosulphide, which is afterwards transformed into the neutral sulphide. Dinaphthapyryl sulphide when boiled with hydrochloric acid is converted into the chloride. E. H.

Electropositive Character of the Dinaphthapyryl Radicle. VI. Extremely Pronounced Aptitude of forming Insoluble or Sparingly Soluble Compounds. VII. Displacement of Potassium, Ammonium, and Alkylammonium Chlorides from their Platinichlorides by the Pyryl Chloride. VIII. Displacement of Potassium from Potassium Picrate by the Oxygenated Base Dinaphthapyranol. ROBERT FOSSE (*Bull. Soc. chim.*, 1909, [iv], 5, 797—800).—It has been shown previously (Abstr., 1901, i, 604) that chloro- and bromo-dinaphthaxanthone combine with the halide acids, platinic chloride, and mercuric chloride and bromide.

[With LESAGE.]—Dinaphthapyryl chloride and bromide are now found to form coloured and generally crystalline compounds with the halide salts of almost all the metals, except those of the alkalis and alkali earths. Halide double salts with platinum, palladium, gold, mercury, copper, lead, uranium, chromium, manganese, iron, cobalt, cadmium, zinc, tin, bismuth, antimony, and arsenic have been prepared. Moreover, in extension of a previous observation (*ibid.*, 1902,

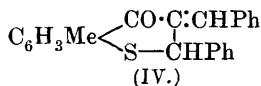
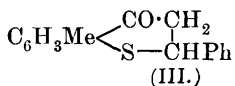
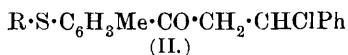
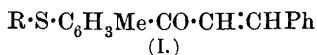
[iii], 27, 496) that several of the reagents for alkaloids precipitate the pyryl halides, it is now found that picric acid, tannin, chlorine, bromine, iodine, chromic anhydride, ammonium perchlorate, potassium iodide, potassium ferrocyanide, potassium ferricyanide, potassium nitroprusside, ammonium thiocyanate, ammonium molybdate, sodium phosphotungstate, and ammonium vanadate give coloured insoluble or sparingly soluble precipitates with the solutions of pyryl salts in dilute halide acids.

When a hydrochloric acid solution of potassium, ammonium, methylammonium, or trimethylammonium platinichloride is treated with a solution of dinaphthapyryl chloride in dilute hydrochloric acid, dinaphthapyryl platinichloride is deposited in red crystals having a golden reflex. These reactions are considered by the author to prove that potassium, ammonium, and alkyl ammonium platinichlorides are partly dissociated in hydrochloric acid solution.

When potassium picrate is treated with an acetic acid solution of dinaphthapyranol, potassium acetate and dinaphthapyryl picrate are formed, probably owing to the partial hydrolysis of the potassium picrate by the acetic acid, and the consequent progressive combination of the pyranol with the liberated picric acid. Conversely, dinaphthapyryl picrate is reconverted by potassium hydroxide solution into potassium picrate and dinaphthapyranol, the equilibrium between the picric acid and the pyranol thus depending on the acidity or alkalinity of the medium.

E. H.

Transformation of Thiophenol Ethers into Thioflavanone Derivatives. KARL AUWERS and F. ARNDT (*Ber.*, 1909, 42, 2706—2712).—In extension of their recent work (this vol., i, 175), the authors find that thiophenol ethers can be condensed with benzaldehyde with the formation of thioflavanone derivatives. The condensation is effected by means of dry hydrogen chloride, and, in the case of 6-methyl(or ethyl)-thiol-3-methylacetophenone, proceeds as follows: The benzylidene derivative (I) is first formed and combines with hydrogen chloride to give the compound (II), from which alkyl chloride is eliminated, and the resulting methylthioflavanone (III) condenses with a second molecule of benzaldehyde to yield benzylidene-methylthioflavanone (IV):



The analogous compounds containing oxygen cannot similarly be transformed into flavanone derivatives.

3-Benzylidene-6-methylthioflavanone forms short, stout, bright yellow, glistening prisms and pyramids, m. p. 109—110°, and gives an intense brown coloration with sulphuric acid. The bromide, $\text{C}_{23}\text{H}_{18}\text{OBr}_2\text{S}$, crystallises in pale yellow, glistening needles, m. p. 125°; and the hydroxylamine additive product, $\text{C}_{23}\text{H}_{21}\text{O}_2\text{NS}$ (no oxime is formed),

forms snow-white, glistening needles and plates, m. p. 174—176° (decomp.).

6-Methoxy-3-benzylideneflavanone, $\text{OMe} \cdot \text{C}_6\text{H}_3 < \begin{matrix} \text{CO} \cdot \text{C} \cdot \text{CHPh} \\ \text{O} - \text{CHPh} \end{matrix}$, prepared by condensing 6-methoxyflavanone (Abstr., 1904, i, 440) with benzaldehyde in the presence of hydrogen chloride, forms small, stout, glistening crystals, m. p. 118—119°; the hydrochloride crystallises in slender, felted needles, and has m. p. 189°, softening before this point. 3-Benzylidene-6-methylflavanone, similarly prepared from 6-methylflavanone, has m. p. 132—133°. 6-Ethylthiol-3-methylacetophenone, $\text{C}_{11}\text{H}_{14}\text{OS}$, prepared from *p*-ethylthioltoluene by the Friedel and Crafts' reaction, crystallises in long, glistening, white needles, m. p. 75.5°. *p*-isoPropylthioltoluene, $\text{C}_{10}\text{H}_{14}\text{S}$, prepared from *p*-methylthioltoluene, isopropyl bromide, and sodium, is a colourless oil having a terpene-like odour, b. p. 110°/14 mm., 228°/760 mm. J. C. C.

Aconitine. ERNST SCHMIDT [with ARTHUR SCHWANTKE and K. SCHWANTKE] (*Arch. Pharm.*, 1909, 247, 233—243).—Some derivatives of aconitine, m. p. 195—196°, obtained from the tubers of *Aconitum Napellus*, have been examined crystallographically. Aconitine, rhombic [$a : b : c = 0.54492 : 1 : 0.38917$]. Aconitine hydrochloride, rhombic [$a : b : c = 0.87488 : 1 : 1.3040$]. Aconitine hydrobromide, rhombic [$a : b : c = 0.86455 : 1 : 1.3095$]. Ethylpicraconitine, rhombic [$a : b : c = 0.97952 : 1 : 1.2700$]. Aconine hydrochloride, monoclinic, hemimorphous [$a : b : c = 0.63461 : 1 : 1.0374$; $\beta = 90^\circ$].

Pseudoaconitine, m. p. 201—202°, from *Aconitum ferox*, must be purified by the repeated crystallisation of its nitrate in order that the regenerated base may separate from dilute methyl alcohol in well-formed, colourless needles.

Japaconitine, from the tubers of *Aconitum Fischeri*, is identical with commercial japaconitine, and different from the alkaloid obtained from *Aconitum Napellus*; it separates from 90% alcohol in crystals identical with those measured by Pope (*Trans.*, 1900, 76, 49). It is remarkable that the hydrochlorides and hydrobromides of japaconitine and aconitine are almost identical, although the two alkaloids are widely different crystallographically (following abstract). C. S.

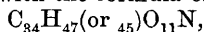
The Aconitines from Japanese Aconite Tubers. KOJIRO MAKOSHI (*Arch. Pharm.*, 1909, 247, 243—282).—Since 1877 japaconitine, the alkaloid prepared from Kusauzu tuber-roots obtained in Japan from varieties of the *Aconitum* family, has been examined by several investigators without concordant results. The author gives a full account of the aconitum tubers, of Japanese and Chinese origin, used commercially, and is of opinion that these discordant results are not to be attributed to the different sources from which the japaconitine has been obtained, but, in view of the ready decomposition of the aconite alkaloids, may be due to differences in the methods of isolation and purification of the alkaloid. This view is supported by the m. p.'s of aconitine and japaconitine given by different observers, which, varying between 183° and 204.5°, lead to the conclusion that chemically individual substances have hitherto not been employed.

Two varieties of Kusauzu tubers are recognised: Bushi tubers, obtained from the *Aconitum Fischeri*, grown in Hokkaido (Jeso), and the Kusauzu tubers obtained from a variety of this shrub grown in Hondo. The author commences his attempt to elucidate the mystery of the nature of aconitine (which is asserted by some chemists, and denied by others, to be identical with japaconitine) by a thorough examination of the alkaloid, called jesaconitine, obtained from the Bushi tubers, and japaconitine, prepared from the Kusauzu tubers of Hondo.

A detailed account of the isolation of jesaconitine from Bushi tubers (yield 0.54%) is given. Briefly, the main portion of the alkaloid is obtained by evaporating under 50 mm. pressure to a thin syrup the solution obtained by thrice extracting the coarsely-powdered roots with 96% alcohol for ten days at the ordinary temperature; the syrup is mixed with water, and the bulk of the crude alkaloid precipitated by concentrated sodium carbonate solution. Attempts to obtain the base or its salts in a crystalline form have failed. Jesaconitine must be regarded as benzoylanisoylaconine, since its hydrolysis by water under 8—9 atmospheres yields benzoic and anisic, but not acetic, acids and aconine, the identity of the last, isolated as the hydrochloride, m. p. 175—176°, with the aconine hydrochloride obtained from aconitine being proved by the mixed m. p., by crystallographic examination, and by the formation of tetra-acetylaconine. In four weeks at the ordinary temperature acetyl chloride and jesaconitine yield an *acetyl* derivative, $C_{40}H_{48}O_{12}NaC_3 \cdot 2H_2O$ (?), m. p. 213—213.5°, which separates from ether in slender needles.

Although more poisonous, jesaconitine is closely related to aconitine (Merck's *aconitine pur. amorph.*) in toxic properties. Its physiological action on dogs and frogs causes the typical paralysis produced by aconitine, but a difference is noticeable in that jesaconitine does not cause mydriasis and salivation in dogs; the local action of the hydrochlorides of the two alkaloids is practically identical.

The extraction of japaconitine from Hondo Kusauzu tubers is very similar to that of jesaconitine from the Bushi tubers. The alkaloid precipitated by sodium carbonate is recrystallised from ether, and finally purified either by repeated crystallisation from methyl alcohol or by the crystallisation of the hydrochloride or hydrobromide. The alkaloid crystallises in needles or small plates, and has m. p. 202.5—203.5°, the same as that of commercial japaconitine purified by the preceding process. The mean value of nine analyses of japaconitine corresponds with the formula of aconitine,



but the two alkaloids are undoubtedly different. The hemihedral crystals of japaconitine hydrochloride, or hydrobromide, have the same angles as the holohedral crystals of the corresponding salts of aconitine. The author confirms in the main the observations of Dunstan and Read (Trans., 1900, 77, 45) on the triacetyl derivative (m. p. 189°, not 166°) and the salts of japaconitine, on pyrojapaconitine, japbenzaconine, and japaconine. The different natures of japaconine and aconine are evident; the former does not form crystallisable salts, and yields a *tetra-acetyl* derivative, $C_{25}H_{37}(\text{or } ^{35}_{35})O_9NaC_4$,

m. p. 236—237°, the aurichloride of which, m. p. 253°, crystallises in yellow plates; aconine forms easily crystallisable salts and a tetra-acetyl derivative, m. p. 231—232°, the aurichloride of which is uncrystallisable.

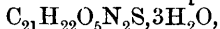
The chief result of the paper is the proof that japaconitine is different from aconitine and from jesaconitine. C. S.

A New Base Isolated from Ergot of Rye, Ergothionine. CHARLES TANRET (*Compt. rend.*, 1909, 149, 222—224 *).—A description of the preparation and properties of a new sulphur-containing base occurring to the extent of 0.1% in ergot of rye. *Ergothionine*, $C_9H_{15}O_2N_3S \cdot 2H_2O$, crystallises in colourless, clinorhombic lamellæ, m. p. 290° (decomp.), on the Maquenne block; $[\alpha]_D + 110^\circ$. It is soluble in 8.6 parts of water at 20°, and insoluble in absolute alcohol or ether. Ergothionine is a feeble base, and forms well defined salts, which in aqueous solution give precipitates with mercuric chloride, potassium mercuric iodide, and platinic chloride in excess, but not with picric or tannic acids.

The hydrochloride, $C_9H_{15}O_2N_3S \cdot HCl \cdot 2H_2O$, occurs in orthorhombic crystals, $[\alpha]_D + 88.5^\circ$; the anhydrous salt has m. p. 250°; its solution gives with silver nitrate a curdy precipitate having the composition $[(C_9H_{15}O_2N_3S)_2Ag_2O](AgCl)_2$. The sulphate, $(C_9H_{15}O_2N_3S)_2 \cdot H_2SO_4 \cdot 2H_2O$, has $[\alpha]_D + 87.4^\circ$. The phosphate, $C_9H_{15}O_2N_3S \cdot H_3PO_4$, has $[\alpha]_D + 83.8^\circ$. The mercurichloride, $C_9H_{15}O_2N_3S \cdot HgCl_2 \cdot HCl$, is crystalline.

W. O. W.

Strychnine Alkaloids. V. Isomeric Strychninesulphonic Acids. HERMANN LEUCHS and WILHELM SCHNEIDER (*Ber.*, 1909, 42, 2681—2685. Compare *Abstr.*, 1908, i, 563; this vol., i, 120, 253, 602).—An aqueous solution of strychnine, containing sulphur dioxide, is treated at 40—50° with precipitated manganese dioxide until the latter has dissolved. By cooling to 20°, acicular crystals of the strychninesulphonic acid already described (this vol., ii, 120) are obtained. By keeping the mother liquor overnight at 0°, a second *strychninesulphonic acid*, $C_{21}H_{22}O_5N_2S \cdot 2H_2O$, is obtained in stout prisms, which darkens at 300°, has m. p. 370° (decomp.), and has $[\alpha]_D^{20} - 138^\circ$ in aqueous solution. From the concentrated filtrate, after removal of the manganese and acids of sulphur, a third acid,



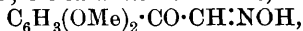
is obtained, which crystallises from boiling water in brilliant, flattened polyhedra or quadratic plates, has m. p. 276° (decomp. corr.), and $[\alpha]_D^{20} 163.3^\circ$ in aqueous solution.

In the authors' opinion four isomeric strychninesulphonic acids should exist, of which two are stereoisomerides. C. S.

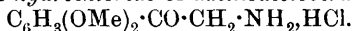
Synthesis of Papaverine. AMÉ PICTET and A. GAMS (*Compt. rend.*, 1909, 149, 210—212. Compare this vol., i, 323).—Attempts to prepare papaverine by dehydration of a compound containing 2H less than homoveratroylhomoveratrylamine were unsuccessful, owing to the instability of the parent base, $C_6H_3(OMe)_7 \cdot CH:CH \cdot NH_2$. The synthesis has been accomplished, however, as follows: veratrole is

* and *J. Pharm. Chim.*, 1909, [vi], 30, 145—153.

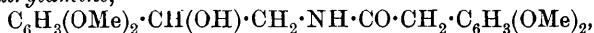
treated with acetyl chloride and aluminium chloride, whereby aceto-veratrone is produced; its *oximino*-derivative,



has m. p. 131°. On reduction with stannous chloride and hydrochloric acid, this yields the *hydrochloride* of *aminoacetoveratrone*,



The free base is unstable. The hydrochloride is shaken with homoveratroyl chloride and aqueous sodium hydroxide, when *homoveratroyl-aminoacetylveratrone*, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_3(\text{OMe})_2$, is obtained in brilliant spangles, m. p. 142°. On reduction with sodium amalgam in alcoholic solution, it furnishes *homoveratroylhydroxy-homoveratrylamine*,

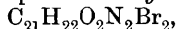


colourless needles, m. p. 124°. When this is boiled in xylene with anhydrous phosphoric acid, $2\text{H}_2\text{O}$ is eliminated and a substance formed which is identical with natural papaverine. This synthesis completely establishes the annexed constitution for the alkaloid.

W. O. W.

Bromination of Strychnine, Brucine, and other Alkaloids.

JÓZEF BURACZEWSKI and M. DZIURZYŃSKI (*Bull. Acad. sci. Cracow*, 1909, 632—641).—When bromine dissolved in carbon disulphide is added slowly to a cold saturated alcoholic solution of strychnine, a sparingly soluble yellow precipitate of *strychnine dibromide*,

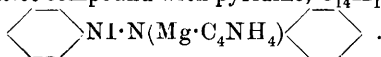


is obtained, which carbonises when heated, loses its colour in boiling alcohol, and dissolves incompletely in hot water. The addition of alkali to the aqueous filtrate precipitates a colourless, soluble basic *bromide*, $\text{C}_{21}\text{H}_{21}\text{O}_2\text{N}_2\text{Br}$, m. p. 250°, which, in alcoholic solution, yields with bromine in carbon disulphide solution a yellow *substance*, which appears to be a mixture of tri- and tetra-bromostychnine.

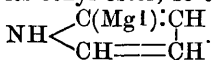
By the action of bromine in carbon disulphide on alcoholic brucine, a white, gelatinous precipitate is first formed, which redissolves by the further addition of bromine, the solution yielding a dark yellow precipitate. The white substance is a *bromobrucine*, $\text{C}_{23}\text{H}_{25}\text{O}_4\text{N}_2\text{Br}$, which differs from Laurent's bromobrucine in colour and in being reddened by mineral acids. The yellow precipitate is a non-hygroscopic *bromobrucine dibromide* (?), $\text{C}_{23}\text{H}_{25}\text{O}_4\text{N}_2\text{Br}_2$, different, therefore, from Beckurt's brucine tribromide.

C. S.

Magnesium Pyrrol Iodide and its Use in the Synthesis of Pyrrole Derivatives. BERNARDO ODDO (*Gazzetta*, 1909, 39, i, 649—659).—The action of pyrrole on magnesium methyl iodide in ethereal solution yields magnesium pyrrol iodide, which was separated in the form of its *additive* compound with pyridine, $\text{C}_{14}\text{H}_{14}\text{N}_3\text{IMg}$ or



The action of carbon dioxide or ethyl chlorocarbonate on magnesium pyrrol iodide in ethereal solution yields pyrrole-2-carboxylic acid or its ethyl ester, so that magnesium pyrrol iodide has the constitution



T. H. P.

Action of Potassium Hydroxide on Acetyl- ψ -isatindioxime.

JEAN KOZAK (*Bull. Acad. sci. Cracow*, 1909, 628—632).—Acetyl- ψ -isatindioxime is hydrolysed by 15% potassium hydroxide in two to three weeks at the ordinary temperature and in thirty minutes by heating, and yields the monoxime, not the expected dioxime. C. S.

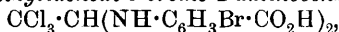
Quinaldyl Chloride. EMIL BESTHORN (*Ber.*, 1909, 42, 2697—2698).

—A final reply to Meyer and Turnau (this vol., i, 419). C. S.

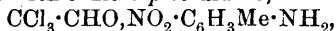
Condensation of Chloral with Primary Aromatic Amines.

III. ALVIN S. WHEELER and STROUD JORDAN (*J. Amer. Chem. Soc.*, 1909, 31, 937—943).—In earlier papers (*Abstr.*, 1903, i, 246; 1908, i, 392), descriptions have been given of the condensation products of chloral with several primary arylamines. The work has been continued, and the following compounds are described.

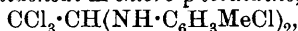
Trichloroethylidenedi-m-bromoaniline, $\text{CCl}_3 \cdot \text{CH}(\text{NH} \cdot \text{C}_6\text{H}_4\text{Br})_2$, m. p. 115—116°, crystallises in colourless, rhombic bi-pyramids. *Trichloroethylidenedi-p-aminobenzoic acid*, $\text{CCl}_3 \cdot \text{CH}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2$, m. p. 215—220° (decomp.), forms colourless crystals. *Trichloroethylidenedi-m-aminobenzoic acid*, m. p. 240° (decomp.), also forms colourless crystals. *Trichloroethylidenedi-5-bromo-2-aminobenzoic acid*,



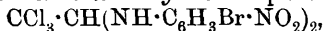
m. p. 174—175°, crystallises in clusters of needles. *Trichloroethylidenedi-o-nitro-p-toluidine*, $\text{CCl}_3 \cdot \text{CH}(\text{NH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NO}_2)_2$, m. p. 108—109°, forms a bright yellow, crystalline powder. An additive compound of chloral with *o*-nitro-*p*-toluidine,



m. p. 187—188°, has been obtained in the form of yellow needles. *Trichloroethylidenedi-p-nitro-o-toluidine*, m. p. 142—143°, forms long, golden-yellow needles. *Trichloroethylidenedi-m-nitro-p-toluidine*, m. p. 165—136°, crystallises in yellow needles, and is decomposed by boiling water. *Trichloroethylidenedi-m-chloro-p-toluidine*,

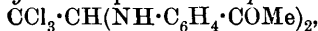


m. p. 110°, forms slender, white needles. The additive product of chloral with *m*-chloro-*p*-toluidine, m. p. 182—183°, crystallises in long, silvery white needles. *Trichloroethylidenedi-p-bromo-o-nitroaniline*,



m. p. 190—191°, forms small, lemon-yellow needles, and reacts with bromine to form a yellow, crystalline compound, m. p. 130—131°; the additive compound, $\text{CCl}_3 \cdot \text{CHO} \cdot \text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{NH}_2$, m. p. 232—233° (decomp.), crystallises in yellow needles. *Trichloroethylidenedi-p-bromo-m-nitroaniline*, m. p. 147—148°, also forms yellow needles. *Trichloroethylidenedi-p-iodoaniline*, $\text{CCl}_3 \cdot \text{CH}(\text{NH} \cdot \text{C}_6\text{H}_4\text{I})_2$, m. p. 123°, forms a

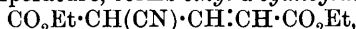
mass of steel-grey, branching needles. *Trichloroethylidenedi-4-bromo-1-naphthylamine*, $\text{CCl}_3 \cdot \text{CH}(\text{NH} \cdot \text{C}_{10}\text{H}_6\text{Br})_2$, crystallises with one mol. of toluene. *Trichloroethylidenedi-p-aminoacetophenone*,



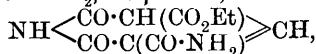
m. p. 162° , forms colourless plates.

Each of these condensation products is decomposed by strong mineral acids with regeneration of the amine. When the compounds are treated with a solution of bromine in glacial acetic acid, chloral is produced, together with the hydrobromide of the original amine or a bromoamine. E. G.

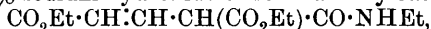
Constitution of the Imino-compounds from Ethyl Ethoxycoumalindicarboxylate and Ammonia or Alkylamines. MAX GUTHZEIT and HERMANN EYSEN (*J. pr. Chem.*, 1909, [ii], 80, 34—68).—The compound, m. p. 178° , obtained by the action of dry ammonia on a 5% benzene solution of ethyl 6-ethoxycoumalin-3:5-dicarboxylate, and formerly regarded as ethyl 2-hydroxy-5:6-dihydro-6-pyridone-3:5-dicarboxylate—easily changing to ethyl 2:6-dihydroxypyridine-3:5-dicarboxylate, m. p. 199° (Guthzeit, Abstr., 1894, i, 71)—is now regarded, in consequence of the present work, as ethyl 6-imino-5:6-dihydrocoumalin-3:5-dicarboxylate, a constitution first suggested by Errera (Abstr., 1902, i, 115) by reason of the analogous behaviour of ethyl 6-imino-5:6-dihydrocoumalin-3:4:5-tricarboxylate, which readily changes to the dihydroxypyridinetricarboxylate. Similar constitutions are assigned to the compounds obtained by the action of ethylamine or aniline on ethyl 6-ethoxycoumalin-3:5-dicarboxylate, m. p. 123° and 147° respectively (Guthzeit, Haussmann, and Band, Abstr., 1895, i, 557, 560). The evidence for this change of opinion is mainly the action of sodium hydroxide, ammonium hydroxide, and ethylamine on the three compounds. 2*N*-Ammonium hydroxide, 0.5% sodium hydroxide, or 2% ethylamine, acting on the first-mentioned compound, m. p. 178° , at the ordinary temperature, forms *ethyl- α -cyanoglutaconate*,



a viscous, yellow oil with a bitter taste, which gives a red coloration with ferric chloride and forms a *sodium* derivative, $\text{C}_{10}\text{H}_{12}\text{O}_4\text{NNa}$, and an *ethyl* derivative, $\text{C}_{12}\text{H}_{17}\text{O}_4\text{N}$, m. p. 79° . The same compound, m. p. 178° , reacts with 2.5% alcoholic ammonia to form the *amides*, $\text{NH}_2 \cdot \text{CH} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{NH}_2$, m. p. 170° , and



which decomposes at 259° , and reacts with ethereal 2.5% ethylamine to form the *substances*, $\text{NHEt} \cdot \text{CH} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{NH}_2$, m. p. 102° , and $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHEt}$, an oil which readily yields diethylmalonamide, and with aniline to form compounds already described (Guthzeit, Band, *loc. cit.*). The compound $\text{C}_{13}\text{H}_{17}\text{O}_6\text{N}$, m. p. 123° , obtained by the action of ethylamine on ethyl 6-ethoxycoumalin-3:5-dicarboxylate, reacts with 0.5% sodium hydroxide to form an oily *substance*,



and with 2.5% alcoholic ammonia to form Ruhemann and Morrell's amide, $\text{NH}_2 \cdot \text{CH} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{NH}_2$ (Trans., 1891, 59, 743), a pyridine

derivative, $\text{NEt} \begin{array}{c} \text{CO} \cdot \text{CH} (\text{CO}_2\text{Et}) \\ \text{CO} \cdot \text{C} (\text{CO} \cdot \text{NH}_2) \end{array} \text{CH}$, m. p. 204° , and an oil which is probably $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{Et}$. The compound $\text{C}_{17}\text{H}_{17}\text{O}_6\text{N}$, m. p. 147° , obtained by the action of aniline on ethyl 6-ethoxycoumalin-3 : 5-dicarboxylate, reacts with 0.5% sodium hydroxide to form the *anilide*, $\text{CO}_2\text{Et} \cdot \text{C} (\text{CO}_2\text{Na}) : \text{CH} \cdot \text{CH} (\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{NHPh}$, from which the original compound is obtained by acidification, with dilute ammonium hydroxide to form an analogous ammonium salt, $\text{C}_{17}\text{H}_{22}\text{O}_7\text{N}_2$, with 2.5% alcoholic ammonia to form malonanilide and the pyridine

derivative, $\text{NPh} \begin{array}{c} \text{CO} \cdot \text{CH} (\text{CO}_2\text{Et}) \\ \text{CO} \cdot \text{C} (\text{CO} \cdot \text{NH}_2) \end{array} \text{CH}$, m. p. 271° , and with ethereal 2.5% ethylamine to form diethylmalonamide, $\text{CH}_2(\text{CO} \cdot \text{NH} \cdot \text{Et})_2$, and the *anilide*, $\text{NH} \cdot \text{Et} : \text{CH} : \text{C} (\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{NHPh}$, m. p. 84° .

The formation of the preceding substances is explained by assigning to the compounds, m. p. 178° , 123° , and 147° , the constitution $\text{O} \begin{array}{c} \text{CO} \text{---} \text{C} (\text{CO}_2\text{Et}) \\ \text{C} (\text{NR}) \cdot \text{CH} (\text{CO}_2\text{Et}) \end{array} \text{CH}$, where R is H, Et, and Ph respectively.

C. S.

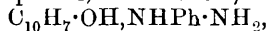
Action of Phenylhydrazine on Formaldehyde. LEO F. ILJIN (*Ber.*, 1909, 42, 2886—2889).—By adding phenylhydrazine dissolved in acetic acid to an aqueous suspension of paraformaldehyde and warming the thoroughly stirred mixture for a short time on a water-bath, a yellow, crystalline solid, $\text{C}_{21}\text{H}_{24}\text{N}_6$, was obtained, which, after purification, separated from chloroform in colourless, mother-of-pearl, glistening scales; this substance darkens at 115° , and has m. p. 170 — 180° . The alcoholic mother liquors yielded a second compound, $\text{C}_{30}\text{H}_{32}\text{N}_8$, which crystallises in slender, colourless needles darkening at 160° , m. p. 180 — 185° . P. H.

Compounds of Phenylhydrazine with Phenols. ROBERTO CIUSA and A. BERNARDI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 690—694).—The freezing-point curve of mixtures of phenol and phenylhydrazine exhibits (1) a minimum at 18.06° , which is the eutectic point for the system comprising phenol and the compound of phenol with phenylhydrazine, and (2) a maximum at about 42° , corresponding with the compound containing 1 mol. of phenol and 1 mol. of phenylhydrazine.

This compound, $\text{Ph} \cdot \text{OH} \cdot \text{NHPh} \cdot \text{NH}_2$, which may be prepared by mixing the fused constituents, crystallises from light petroleum in white needles, m. p. 42° , and when dissolved in benzene is largely dissociated into its components.

The compound, $\text{C}_6\text{H}_4\text{Me} \cdot \text{OH} \cdot \text{NHPh} \cdot \text{NH}_2$, prepared from *m*-cresol and phenylhydrazine, crystallises from light petroleum in slender, white needles, m. p. 36 — 37° , and is strongly dissociated by benzene. The corresponding *p*-cresol compound, $\text{C}_6\text{H}_4\text{Me} \cdot \text{OH} \cdot \text{NHPh} \cdot \text{NH}_2$, crystallises from light petroleum in white needles, m. p. 26° . *o*-Cresol also combines with phenylhydrazine, but the mixture remains superfused.

With α -naphthol, phenylhydrazine gives an unstable compound, m. p. 26° , and with β -naphthol, a stable compound,



which crystallises from a mixture of benzene and light petroleum in white scales, m. p. 62—63°, and undergoes considerable dissociation when dissolved in benzene.

The compound, $C_6H_4(OH)_2 \cdot 2NHPh \cdot NH_2$, formed from catechol and phenylhydrazine, crystallises from benzene in white, silky needles, m. p. 63°. T. H. P.

Phototropy of Certain Phenylhydrazones. MAURICE PADOA (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 694—699. Compare Stobbe, *Abstr.*, 1908, ii, 339).—In order to throw light on the changes occurring in phototropic compounds under the influence of light, the author has studied the behaviour of crystalline mixtures composed of a phototropic substance and of a non-phototropic one capable of forming solid solutions with the former. In all the cases examined, such solid solutions exhibit behaviour differing from that of the pure phototropic substances.

In freezing benzaldehydephenylhydrazone—the molecular depression of freezing point of which is found to have the mean value $K = 112.9$ —benzylidenebenzylamine has the mol. wt. 214.2—218.2, instead of 195. The pure phenylhydrazone colours rapidly in sunlight, and becomes decolorised only slowly in the dark, this latter change being favoured by heating. A mixture containing 4.6% of benzylidenebenzylamine becomes red in sunlight, but turns colourless again after an hour in the dark. With only 1% of the amine, the decoloration is almost complete in twenty-four hours. The pure phenylhydrazone, when heated slowly in diffused light, is completely decolorised at 115—120°, mixtures containing 1% and 3% of the amine at 95—100° and 80—85° respectively.

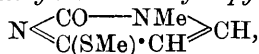
Mixed crystals of benzaldehydephenylhydrazone and diazoaminobenzene, containing 4.92% of the latter, are absolutely insensitive to light. A mixture containing 1.57% of the diazo-compound has its colour slightly intensified by the action of light, the reverse change being complete after twenty-four hours; if the action of light is repeated, the darkening is less than at first, and the decoloration correspondingly more rapid.

Anisaldehydephenylhydrazone becomes violet when exposed to light, but, if left exposed for a long time, again turns white, and does not again assume its property of colouring in the light even if kept for several days in the dark; its m. p. remains unchanged even after prolonged exposure. A mixture of this phenylhydrazone with anisylidenebenzylamine, containing 1% of the latter, when exposed to light, colours more intensely and more rapidly than the pure phenylhydrazone, and exhibits the same behaviour as the latter when the exposure is prolonged. The phenomena observed when the phenylhydrazone and mixtures of it with anisylidenebenzylamine are heated are similar to those shown by benzaldehydephenylhydrazone and its mixtures with benzylidenebenzylamine. A small proportion of benzaldehydephenylhydrazone is incapable of imparting phototropic properties to benzylidenebenzylamine. If compounds which do not form solid solutions with phototropic substances are fused with these, they exert no influence on the behaviour towards light.

Anisylidenebenzylamine, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{CH}_2\text{Ph}$, prepared by mixing anisaldehyde (1 mol.) and benzylamine (1 mol.), separates from light petroleum in white crystals, m. p. 33° . T. H. P.

Pyrimidines. XLIII. Preparation of 3-Methyl- and 3-Benzyl-uracil. HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1909, 42, 30—37).—In earlier papers (Abstr., 1907, i, 728; 1908, i, 692, 835, 1018; this vol., i, 59) accounts have been given of a study of the alkylation of 2-thiol-6-pyrimidones. Some irregularity has been observed in these reactions, analogous salts giving different results with the same halide, whilst with different halides the salt may be attacked in different positions. It has been considered of interest, therefore, to study the alkylation of some isomeric 6-thiol-2-pyrimidones. When 6-methylthiol-2-pyrimidone is treated with methyl iodide or benzyl chloride in presence of potassium hydroxide, 3 alkyl derivatives are produced; if isomeric products are formed in these reactions, the quantity is extremely small. The 6-thiol, like the 2-thiol, compounds are decomposed by hot hydrochloric acid, with formation of mercaptan and uracil derivatives. 3-Methyluracil has been thus obtained, and completes the series of the possible methyluracils.

6-Methylthiol-2-pyrimidone, $\text{N} \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{C}(\text{SMe}) \cdot \text{CH} \end{smallmatrix} \text{CH}$, m. p. 205° , obtained by the action of methyl iodide on 6-thiouracil (Wheeler and Liddle, this vol., i, 61) in presence of sodium methoxide, forms long, slender needles or prisms. 6-Methylthiol-3-methyl-2-pyrimidone,



m. p. 124° , crystallises in needles.

3-Methyluracil, $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{NMe} \\ \text{CO} \text{---} \text{CH} \end{smallmatrix} \text{CH}$, m. p. 232° , crystallises in prisms; it dissolves in alkali hydroxide, and is reprecipitated on the addition of dilute hydrochloric acid. This compound does not colour a solution of diazobenzenesulphonic acid in sodium hydroxide, whereas 1-methyluracil gives a red coloration.

6-Methylthiol-3-benzyl-2-pyrimidone, $\text{N} \begin{smallmatrix} \text{CO} \cdot \text{N}(\text{CH}_2\text{Ph}) \\ \text{C}(\text{SMe}) \text{---} \text{CH} \end{smallmatrix} \text{CH}$, m. p. $148\text{--}149^\circ$, crystallises in prisms, and when boiled with hydrochloric acid is converted quantitatively into 3-benzyluracil (Johnson and Derby, Abstr., 1908, i, 1018).

A further study of the action of methyl iodide on the potassium salt of 2-ethylthiol-6-pyrimidone (Johnson and Heyl, Abstr., 1907, i, 728) has shown that both the 1- and 3-methyl derivatives are formed, whereas in the earlier work only the 1-methyl derivative was isolated.

E. G.

Pyrimidines. XLIV. Preparation of 1:4-Dimethyluracil and of the Monobenzyl Derivatives of 4-Methyluracil. HENRY L. WHEELER and DAVID F. MCFARLAND (*Amer. Chem. J.*, 1909, 42, 101—115).—An exceedingly convenient method for the preparation of 1:4-dimethyluracil is the following. Ethyl acetoacetate, thio-

By experiments on benzeneazo- β -naphthyl benzoate, β -benzeneazo- α -naphthyl benzoate, and benzeneazo-*p*-tolyl benzoate, the authors show that reduction proceeds mainly in direction (I) in alcoholic solution, and in direction (II) in acetic acid. Evidence is obtained in all cases that the reductive fission of the hydrazo-compound proceeds in a third direction, yielding an aminophenol (or naphthol), aniline, and benzoic acid.

C. S.

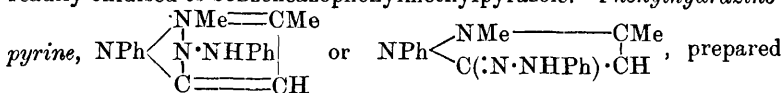
Quinazolines. XXII. 3-Amino-2-methyl-4-quinazalone and Certain of its Derivatives. MARSTON TAYLOR BOGERT and ROSS A. GORTNER (*J. Amer. Chem. Soc.*, 1909, 31, 943—947).—In earlier papers (Abstr., 1906, i, 712, 988; 1908, i, 466) a description has been given of 5-, 6-, and 7-nitro-derivatives of 3-amino-2-methyl-4-quinazalone. The present communication deals with the preparation and properties of the parent substance.

When acetylanthranil is treated with hydrazine hydrate (50% solution), 3-amino-2-methyl-4-quinazalone, $C_6H_4 \begin{smallmatrix} N=CMe \\ | \\ CO-N \cdot NH_2 \end{smallmatrix} \cdot H_2O$, is produced, which forms long, colourless needles, and, on heating at 110° , loses its water of crystallisation; the anhydrous compound melts at 152° (corr.). It does not yield azo-derivatives with aromatic nitroso-compounds, and is not oxidised by mercuric oxide. It condenses with ethyl diacetylsuccinate to form a pyrrole derivative. It gives a phenylcarbamino-compound with phenylcarbimide, and does not condense with ketones. When the quinazalone is treated with nitrous acid, it does not undergo diazotisation, but the amino-group is replaced by hydrogen. It is evident that an intermediate substance is produced, however, since, if after the addition of the nitrous acid the mixture is immediately poured into an alkaline solution of β -naphthol, a compound, $C_{41}H_{32}O_8N_5$, is produced, which forms bright red needles, darkens at 200 — 230° , decomposes at 266° (corr.), and possesses high tinctorial power. If α -naphthol is used instead of β -naphthol, a similar compound, m. p. 245° (decomp.), is produced. In one experiment with β -naphthol, however, the dye was not produced, but an additive compound, $C_9H_8ON_3 \cdot C_{10}H_8O$, m. p. 144 — 145° (corr.), was obtained, which formed bright orange needles and did not exhibit tinctorial properties.

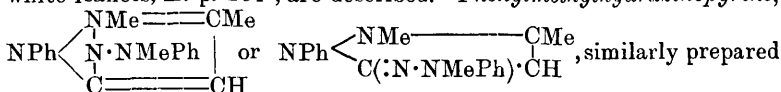
3-Amino-2-methyl-4-quinazalone hydrochloride, m. p. 206.9° (corr.), forms long, colourless needles. The picrate blackens at 187° (corr.). The formyl derivative softens at 185° and melts at 203 — 204° (corr.). The acetyl derivative melts at 176.5° (corr.). 3-Phenylcarbamido-2-methyl-4-quinazalone, $C_6H_4 \begin{smallmatrix} N=CMe \\ | \\ CO-N \cdot NH \cdot CO \cdot NPh \end{smallmatrix}$, does not melt below 300° . 3-Benzylideneamino-2-methyl-4-quinazalone, $C_{16}H_{13}ON_3$, forms stellate groups of needles, m. p. 183° (corr.).

When acetylanthranil is warmed with *as*-phenylmethylhydrazine, a compound, m. p. 106° (uncorr.), is produced, which contains 9.90% of nitrogen. Hydrazine hydrate reacts with *m*-nitrobenzoylanthranil with formation of a compound, m. p. 196 — 197° (decomp.). E. G.

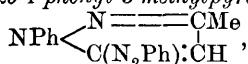
Phenylhydrazinopyrine and 5-Benzeneazo-1-phenyl-3-methylpyrazole. AUGUST MICHAELIS and KARL KOBERT (*Ber.*, 1909, 42, 2765—2770).—The authors find that phenylhydrazine condenses with antipyrine chloride to form the phenylhydrazino-derivative, which is readily oxidised to benzeneazophenylmethylpyrazole. *Phenylhydrazino-*



by heating phenylhydrazine and antipyrine chloride for some hours on the water-bath, is a yellow, viscid oil, which becomes black on exposure to the air; the *hydriodide* crystallises in yellow leaflets, m. p. 175°, and the *hydrochloride*, *platinichloride*, m. p. 161°, *ferrocyanide*, and *methiodide*, white leaflets, m. p. 201°, are described. *Phenylmethylhydrazinopyrine*,

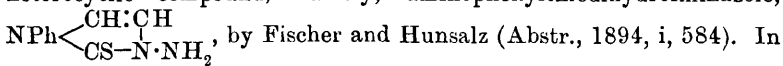


from phenylmethylhydrazine and antipyrine chloride, forms large, yellow crystals, m. p. 128°; the *platinichloride*, *picate*, small, yellow leaflets, m. p. 114°, *ferrocyanide*, *chromate*, *methiodide*, white leaflets, m. p. 191°, *ethiodide*, white leaflets, m. p. 130°, and benzoyl chloride additive compound, are described. *Phenylethylhydrazinopyrine*, $\text{C}_{19}\text{H}_{22}\text{N}_4$, forms stumpy, yellow crystals, m. p. 78°; the *alkyliodides* are mentioned. *5-Benzeneazo-1-phenyl-3-methylpyrazole*,

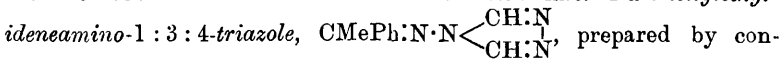


prepared by oxidising phenylhydrazinopyrine with yellow mercuric oxide, crystallises in yellowish-red needles, m. p. 62°; the *methochloride* was isolated as its *platinichloride*, m. p. 206—207°, and the *methiodide* crystallises in slender, yellow needles, m. p. 194°. J. C. C.

The Amino-group of 1-Amino-1:3:4-triazole. CARL BÜLOW (*Ber.*, 1909, 42, 2715—2721).—The author has already shown that 1-amino-1:3:4-triazole undergoes the three typical reactions for heterocyclic *N*-amino-substituted compounds, namely, that (1) the amino-group is displaced by hydrogen by the action of nitrous acid; (2) the basic character is greatly diminished as the salts are completely hydrolytically dissociated by water, and (3) with benzaldehyde a benzylidene derivative is obtained; these reactions were first shown to be applicable to the instance of an *N*-amino-substituted heterocyclic compound, namely, aminophenylthiodihydroiminazole,

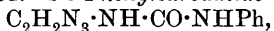


the present paper, further reactions are described which show that 1-amino-1:3:4-triazole behaves like an aromatic amine. *1-α-Phenylethyl-*

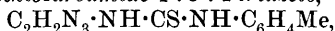


densing 1-amino-1:3:4-triazole with acetophenone in alcoholic solution with the addition of a few drops of pyridine, forms yellow needles, m. p. 119°. *1-Formylamino-1:3:4-triazole*, $\text{C}_2\text{H}_2\text{N}_3 \cdot \text{NH} \cdot \text{CHO}$,

prepared from the amine and formic acid, forms transparent, blunt crystals, m. p. 117° ; the silver, copper, mercurous, and mercuric compounds are described. s-1-Phenylcarbamido-1:3:4-triazole,



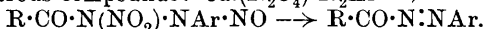
prepared from the base and phenylcarbimide, crystallises in small, slender, white needles, m. p. 222° ; when boiled with ferric chloride, a brown coloration is produced, and silver nitrate gives a milky turbidity. s-1-Tolylthiocarbamido-1:3:4-triazole,



prepared from the base and tolylthiocarbimide, forms white needles, m. p. 156° , then becoming solid, and again melting at $194-196^{\circ}$; when boiled with ferric chloride, a brownish-yellow coloration is produced, and it is desulphurised by heating with silver nitrate.

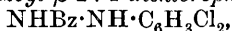
s-1-Naphthylcarbamido-1:3:4-triazole, $\text{C}_2\text{H}_2\text{N}_3\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, similarly prepared, crystallises in soft, white, silky needles, m. p. 240° ; when boiled with ferric chloride, a yellowish-brown coloration is obtained, and silver nitrate gives a white precipitate. J. C. C.

New Method of Preparing Acylazoaryl Compounds. GIACOMO PONZIO (*Gazzetta*, 1909, 39, i, 661—666. Compare this vol., i, 443).—Acylazoaryl compounds may be prepared by treating the potassium salt of a primary dinitrohydrocarbon with the acetate of a diazo-compound, and, when a para-substituted diazo-derivative is employed, by dissolving the compound, $\text{CR}(\text{N}_2\text{O}_4)\cdot\text{N}_2\text{Ar}$, thus obtained in moist ether and removing the solvent by evaporation after nitrous fumes cease to be evolved. The diazo-salt of the dinitrohydrocarbon thus undergoes isomeric change into the corresponding acylarylnitro-nitrosohydrazine, which then loses 2 atoms of nitrogen and 3 of oxygen as nitrous compounds: $\text{CR}(\text{N}_2\text{O}_4)\cdot\text{N}_2\text{Ar} \rightarrow$



In the case when moist ether transforms the diazo-salt into the isomeric stable azodinitrohydrocarbon, $\text{CR}(\text{NO}_2)_2\cdot\text{N}\cdot\text{NAr}$, it is necessary first to prepare, by means of anhydrous benzene, the nitro-nitrosohydrazine and subject this to the action of the ether.

Benzoylazo-2:4-dichlorobenzene, $\text{NBz}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Cl}_2$, prepared from 2:4-dichlorodiazobenzene acetate and the potassium derivative of ω -dinitrotoluene, crystallises from light petroleum in flattened, brown needles, m. p. 101° , and is rapidly reduced by phenylhydrazine in ethereal solution to α -benzoyl- β -2:4-dichlorophenylhydrazine,



which crystallises from benzene in yellow needles, m. p. 166° .

Bisbenzoylazodiphenyl, $\text{NBz}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NBz}$, prepared from benzidine, crystallises from benzene in shining, yellowish-brown laminæ, m. p. $186-187^{\circ}$. When reduced with phenylhydrazine in benzene solution, it is converted into *dibenzoyldiphenyldihydrazine*, $\text{NHBz}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NHBz}$, m. p. 245° . T. H. P.

Transformations of Azo-compounds by means of Hydrogen Chloride in Alcoholic Solution. PAUL JACOBSON (*Annalen*, 1909, 367, 304—331).—An investigation on the nature of the changes which azo-compounds undergo when treated with hydrogen chloride in methyl alcohol.

[With C. BARTSCH and A. STEINBRECK.]—*Azobenzene and Hydrogen Chloride in Methyl Alcohol*.—Azobenzene is destroyed completely when its methyl-alcoholic solution is saturated with hydrogen chloride, kept for about twelve hours at the ordinary temperature, and subsequently boiled. The product of the reaction consists chiefly of benzidine, aniline, and *p*-chloroaniline, together with about 7—8% of a chlorinated amine, $C_{12}H_8Cl_4N_2$. The latter substance is 2:3:5:4'-tetrachloro-4-aminodiphenylamine, since it is produced by the chlorination of 4'-chloro-4-aminodiphenylamine, which is formed during the reaction; it is also formed by the action of hydrogen chloride on a solution of *o*-benzeneazotoluene in methyl alcohol; further, when oxidised it yields a tetrachlorobenzoquinonophenylimine, which is converted by sulphuric acid into *p*-chloroaniline and trichlorobenzoquinone.

The formation of the above compounds from azobenzene probably takes place through the following series of changes: (a) $NPh:NPh + 2HCl = NPh \cdot NPh + Cl_2$. (b) $NPh:NPh + 4HCl = 2NH_2Ph + 2Cl_2$. The hydrazobenzene passes into benzidine, whilst part of the aniline undergoes chlorination, yielding *p*-chloroaniline. (c) $NPh:NPh + HCl = NPh \cdot NPhCl \rightarrow NPh \cdot NH \cdot C_6H_4Cl$. The *p*-chlorohydrazobenzene thus formed is converted by the combined action of the hydrogen chloride and of the chlorine liberated according to (a) and (b) into 2:3:5:4'-tetrachloro-4-aminodiphenylamine, most probably through the intermediate formation of 4'-chloro-4-aminodiphenylamine.

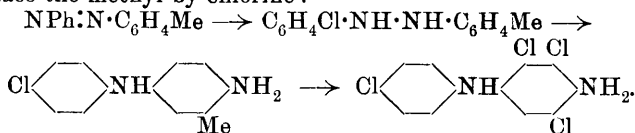
2:3:5:4'-Tetrachloro-4-aminodiphenylamine, $C_{12}H_8N_2Cl_4$, forms white, silky needles, m. p. 150—151°; the *o*-hydroxybenzylidene derivative, $C_{19}H_{12}ON_2Cl_4$, forms yellow crystals, m. p. 153—154°. The base is oxidised by chromic acid, yielding 2:3:5-trichlorobenzoquinone-*p*-chlorophenylimine, $C_6H_4Cl \cdot N:Cl < \begin{smallmatrix} CH=CCl \\ CCl:CCl \end{smallmatrix} > CO$, which crystallises in red needles, m. p. 153°, and is reduced by zinc dust and acetic acid to 2:3:5:4'-tetrachloro-4-hydroxydiphenylamine, $C_{12}H_7ONCl_4$, crystallising in rosettes of colourless needles, m. p. 128°.

[With A. LOEB.]—*p*-Chloroazobenzene, *p*-Chlorohydrazobenzene, and Hydrogen Chloride in Methyl Alcohol.—The reactions which occur when *p*-chloroazobenzene is treated in the same manner as azobenzene are analogous to those already described, the products formed being aniline, *p*-chloroaniline, and 2:3:5:4'-tetrachloro-4-aminodiphenylamine; since other chlorinated bases are not formed, however, it shows that a reaction analogous to (c) does not take place in this case. In two experiments, a substance, $C_{12}H_{10}N_2Cl_2$, either a dichlorodiaminodiphenyl or dichloroaminodiphenylamine, was isolated, but the conditions governing its formation could not be determined; it crystallises in slender, brown leaflets, m. p. 182—183°.

p-Chlorohydrazobenzene is converted by a cold saturated solution of hydrogen chloride in methyl alcohol into *p*-chloroazobenzene (37.5%), aniline and *p*-chloroaniline (15%), 5-chloro-2:4'-diaminodiphenyl (17.5%), 4-chloro-4'-aminodiphenylamine (2.5%), benzidine (0.5%), and 4-chloro-2'-aminodiphenylamine. In this case it is seen that an orthosemidine is formed together with the parasemidine, but chlorination does not enter into the various changes. The

same products, and to roughly the same extent, are formed by the action of a solution of sulphuric acid in methyl alcohol on *p*-chloro-hydrazobenzene.

[With C. BARTSCH.]—*Methylazobenzenes and Hydrogen Chloride in Methyl Alcohol*.—*m*-Benzeneazotoluene undergoes transformation with the same ease as azobenzene, but the ortho- and para-isomerides are far more stable. An exact separation of the compounds formed during the reaction has been effected only in the case of *o*-benzeneazotoluene; here, in addition to *o*-methylbenzidine, *o*-toluidine, and volatile chlorinated amines, the same tetrachloro-*p*-aminodiphenylamine was obtained as from azobenzene. Its formation shows that the chlorinating action of the hydrogen chloride which appears during the reaction is sufficient to replace the methyl by chlorine:



[With A. STEINBRECK.]—*Azobenzenecarboxylic Acids and Hydrogen Chloride in Methyl Alcohol*.—Azobenzene-*o*-carboxylic acid yields methyl benzidine-3-carboxylate, *p*-chloroaniline, and small quantities of other bases.

Azobenzene-m-carboxylic acid, $\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_2$, prepared by oxidising *m*-benzeneazotoluene with sodium dichromate and glacial acetic acid, crystallises in pale red leaflets, m. p. 166–167°; the *silver* salt was analysed; the *methyl* ester, prepared from the silver salt and methyl iodide, forms yellow leaflets, m. p. 57–58°. The acid is converted by a methyl-alcoholic solution of hydrogen chloride into *p*-chloroaniline and a *substance*, which is probably a methyl ester of a chlorinated benzidinecarboxylic acid.

Azobenzene-*p*-carboxylic acid yields *p*-chloroaniline, and probably a methyl chloroazobenzenecarboxylate and a methyl azobenzenecarboxylate.

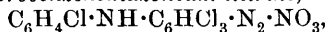
W. H. G.

Diazonium Salts of Highly Halogenated Parasemidines and Certain other Highly Halogenated Bases. PAUL JACOBSON (*Annalen*, 1909, 367, 332–347).—The polyhalogen derivatives of *p*-aminodiphenylamine when treated with sulphuric acid (50%) and excess of sodium nitrite do not yield diazonium sulphates, but diazonium nitrates, probably because the latter salts are soluble only with great difficulty. The diazonium nitrates are very stable towards mineral acids, and may be crystallised from hot concentrated nitric acid; on the other hand, they are decomposed by alcohol with great ease, the diazo-group being replaced by hydrogen.

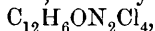
[With C. BARTSCH, A. LOEB, and A. STEINBRECK.]—*p*-Aminodiphenylamine is converted by a solution of bromine in glacial acetic acid at 0° into a *tribromo*-derivative, $\text{C}_{12}\text{H}_9\text{N}_2\text{Br}_3$, which crystallises in pale violet needles, m. p. 137–138°. A *pentabromo*-derivative, $\text{C}_{12}\text{H}_7\text{N}_2\text{Br}_5$, is formed by adding a solution of the base in glacial acetic acid to a solution of bromine in the same solvent at 80°; it forms bright red needles, m. p. 229–230°, and is converted by

sulphuric acid (50%) and sodium nitrite into the *diazonium nitrate*, $C_{12}H_5NBr_5 \cdot N_2 \cdot NO_3 \cdot H_2O$, crystallising in small, slender, yellow needles, m. p. 140—160° (decomp.). The latter substance, when boiled with alcohol, yields *pentabromodiphenylamine*, $C_{12}H_6NBr_5$, which crystallises in slender, white needles, m. p. 194—195°.

2 : 3 : 5 : 4'-Tetrachloro-4-aminodiphenylamine (compare preceding abstract), when diazotised in the same manner, yields 4-(p)-chloro-anilino-2 : 3 : 6-trichlorobenzenediazonium nitrate,



which crystallises in yellow needles, and with alcohol yields 2 : 3 : 5 : 4'-tetrachlorodiphenylamine, $C_{12}H_4NCl_4$, small, colourless crystals, m. p. 107—108°; when decomposed by a smaller quantity of alcohol in the presence of potassium carbonate, it also yields a substance,



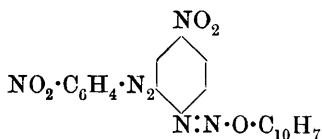
which crystallises in tufts of red needles, m. p. 176°, and is probably a nitroso-derivative of 2 : 3 : 5 : 4'-tetrachlorodiphenylamine.

Pentabromobenzenediazonium nitrate, $C_6O_3N_3Br_5$, prepared by diazotising pentabromoaniline in the presence of a large excess of sulphuric acid (50%), crystallises in white leaflets. Attempts to prepare a diazonium salt from tetrabromobenzidine by similar means were unsuccessful; when an alcoholic solution of the base is treated with gaseous nitrous acid, however, it yields *tetrabromodiphenylbis-diazonium hydrogen sulphate*, $[C_6H_2Br_2 \cdot N_2 \cdot SO_4H]_2$, which forms rod-like crystals, and is converted by alcohol into tetrabromodiphenyl
W. H. G.

Formation of p-Nitroaniline-Red. MAURICE PRUD'HOMME and A. COLIN (*Bull. Soc. chim.*, 1909, [iv], 5, 779—785).—Cotton tissue when immersed first in a solution containing 25 grams of β -naphthol and 25 grams of sodium hydroxide solution (40°B) per litre, and then in a diazo-solution composed of 0.1 gram-molecule of *p*-nitroaniline, 0.1 gram-molecule of sodium nitrite, and 0.3 gram-molecule of hydrogen chloride per litre, is not coloured until washed in water, when it becomes orange-brown. If, however, the diazo-solution contains 0.2 gram-molecule of sodium acetate in addition to the above, thirty seconds' immersion of the cotton followed by immediate washing produces a good red colour, whilst with 0.5 gram-molecule of sodium acetate the cotton dyes a more bluish and intense red.

These differences, which are attributed by Goldschmidt, Lichtenstein, and others to differences in the concentration of the hydrogen ion, are considered by the authors to be due to the action of the ionised hydrogen chloride on the diazonium chloride, giving the two new electrolytes: $(R \cdot NH^+ \cdot NCl) \cdot Cl^-$ and $[R(NCl)_2] \cdot H^+$ (R representing the $NO_2 \cdot C_6H_4 \cdot$ group). These electrolytes are supposed to regenerate the diazonium chloride when the solution is diluted by the washing, and the naphthol then being in excess, produces a very pale red colour. Acetic acid being almost non-ionised, does not have this effect. The complex ions in the two electrolytes could be well expected to form foreign colouring matters with β -naphthol, and, in fact, the first of the above diazo-solutions when diluted and treated with sodium naphth-

oxide couples very slowly, giving first a brown precipitate and then an orange, insoluble colouring matter.



When the first diazo-solution is treated with increasing quantities (0.1, 0.2, and 0.3 gram-molecule) of sodium hydroxide, the red colour produced on cotton diminishes in intensity and disappears. If, however, the β -naphthol is previously precipitated on the cotton, the diazo-solution (containing 0.3 gram-molecule NaOH) gives an orange colour, possibly explained by the formation of the croceine-like compound (annexed formula).

E. H.

Constitution of Protein. EDUARD PFLÜGER (*Pflüger's Archiv*, 1909, 129, 99—102).—It is doubted whether the work of Fischer, Abderhalden, and others brings us much nearer to a solution of the question of the constitution of protein. In their work a large portion of the molecule is still unaccounted for. The only certain test for a protein is its capacity to maintain life and enter into the composition of protoplasm. If this definition is accepted, gelatin, protamines, and polypeptides are not proteins.

W. D. H.

Hydrolysis of Proteins by Hydrogen Fluoride: New Results. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1909, 149, 41—43. Compare Abstr., 1908, i, 706; this vol., i, 195).—Fifteen % aqueous hydrogen fluoride brings about complete hydrolysis of gelatin. The 20—30% acid gives amino-acids accompanied by dipeptides and tripeptides, whilst the 35% acid gives more complex polypeptides, one of which, on further hydrolysis, has yielded arginine, lysine, alanine, phenylalanine, and glycine. Acid containing 45% hydrogen fluoride furnishes the diamines only. The peptides obtained by means of this reagent are not of synthetic origin, since it is found that no condensation takes place when free amino-acids are heated alone with hydrogen fluoride. It follows, therefore, that the breakdown products of gelatin represent pre-existing natural complexes.

W. O. W.

Casein and Paracasein. T. KIKKOJI (*Zeitsch. physiol. Chem.*, 1909, 61, 139—146).—Lœwenhardt's hypothesis that casein and paracasein (or, to adopt English nomenclature, caseinogen and casein) are identical is not confirmed. Their solubilities are different, and the latter substance is not coagulable by rennet.

W. D. H.

Action of Rennet or Calcium Paracaseinate. M. VAN DAM (*Zeitsch. physiol. Chem.*, 1909, 61, 147—163).—The digestion of paracasein (casein in English nomenclature) by rennet is accelerated by the number of hydrogen ions in solution. Petry's supposition that there is in rennet a special proteolytic enzyme acting only on casein was not confirmed. The peptic and rennetic activities of preparations of rennet run parallel, and this is in favour of the identity of pepsin

and rennet. Sodium chloride hastens both actions. The action of the enzyme plays a part in the ripening of cheese. W. D. H.

Yeast Nucleic Acid. II. PHCEBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1909, 42, 2703—2706).—The hydrolysis of yeast nucleic acid under carefully defined conditions (this vol., i, 620) yields a number of nucleosides (that is, complexes of a base and a carbohydrate), of which one, guanosin, has been already isolated. The mother liquor is treated with 25% lead acetate, and, after filtration, the soluble lead compounds of the nucleosides are precipitated by ammonium hydroxide. The precipitate is suspended in water, freed from lead by hydrogen sulphide, and the solution, after being evaporated to a syrup, is treated with a hot saturated solution of picric acid, whereby *adenosin picrate*, $C_{10}H_{13}O_4N_5 \cdot C_6H_3O_7N_3$, is obtained. It crystallises in glistening leaflets, and shrivels at 185° (corr.). *Adenosin*, $C_{10}H_{13}O_4N_5$, m. p. 229° (corr.), separates from hot water in long needles containing $1\frac{1}{2}H_2O$, has $[\alpha]_D -67.30^\circ$ in *N*/10-sodium hydroxide, and yields adenine and *d*-ribose on hydrolysis with hot dilute sulphuric acid.

C. S.

The Pentose from Inosic Acid and from the Pancreas. CARL NEUBERG (*Ber.*, 1909, 42, 2806—2809).—The author recounts the different views as to the constitution of the pentose obtained from inosic acid, which has been identified as *d*-lyxose by Haiser and Wenzel (this vol., i, 540), and claimed as *d*-ribose by Levene and Jacobs (this vol., i, 541), identical with the pentose obtained from the guanylic acid of the pancreas (this vol., i, 620).

C. S.

Systematic Investigation of the Oxydases. III. OCTAVE DONY-HÉNAULT (*Bull. Acad. roy. Belg.*, 1909, 342—409. Compare Abstr., 1907, i, 1100; 1908, i, 588).—The doubtful nature of the guaiacum reaction as a test for the oxydases has been pointed out by Pighini (*Arch. Fisiol.*, [iv], 1, 57), Lesser (Abstr., 1907, ii, 827), and Fouard (Abstr., 1906, i, 421). Experiments described in the paper show that freshly prepared tincture of guaiacum is extremely sensitive to alkali, being coloured yellow or green by quantities too small to be detected by the usual indicators. Tincture of guaiacum, when treated with small quantities of manganous acetate and then with traces of alkali, gives the characteristic blue colour. This reaction is prevented by small quantities of acid. An artificial laccase, obtained by precipitating with alcohol a mixture of gum arabic, sodium carbonate, and manganous formate, is only slightly active towards guaiacum, but if Rochelle salt (which acts by preventing the precipitation of the manganese by the alkali) is added before precipitation, a laccase as active as that from Japanese lac is obtained. These observations indicate that the guaiacum reaction, like the oxidation of quinol, is not characteristic of the oxydases. Since guaiacum is coloured blue by acid ferric chloride solution (although excess of the acid retards the reaction), it seems that the oxidation of this substance can be effected in both alkaline and acid solution.

In the previous paper it was stated that the oxidation of guaiacol is

not to be explained by the activity of the alkaline or the manganous elements of laccase. It is now shown that, although the coloration of guaiacol by ferric chloride is evanescent, addition of a very small quantity of alkali causes a red coloration, followed by a precipitate of tetraguaiacoquinone, the phenomena being in every way analogous to those observed by Bertrand with laccase (Abstr., 1904, i, 157). Moreover, the presence of manganese salts has no similar effect. The presence of acid renders the ferric chloride quite inactive, whilst the second coloration (with alkali), but not the first (evanescent), is only produced in the presence of oxygen. Some specimens of guaiacol do not give the reaction either with ferric chloride and alkali or with Bertrand's laccase. The conclusion is drawn that the guaiacol reaction, also, must be rejected as a test for oxydases. The coloration of guaiacol solution in the presence of hydrogen peroxide by milk, hitherto attributed to oxidising enzymes in the latter, is probably to be explained by the action of traces of iron and alkali in the milk.

Bertrand's laccase, although considerably more stable towards heat than the hydrolytic enzymes (invertase, pepsin, etc.), is rendered inactive by prolonged boiling. This can be completely explained by the production of a trace of acid during boiling, and experiments are described showing that, although the simple synthetic laccase obtained by alcoholic precipitation of a mixture of gum, manganous salt, and alkali is insensitive to heat, synthetic laccases containing ammonium chloride, the copper salt of asparagine, egg-albumin, or serum-albumin are rendered very much less active by boiling.

The inhibition by acid of both the guaiacum and the guaiacol reactions with artificial laccase indicates that the sensitiveness of Bertrand's laccase towards acids is to be explained simply by the neutralising action of the latter.

Thus all the typical properties of laccase can be reproduced by the catalytic association of manganous and ferric molecules with free alkali. Bertrand's view that laccase is an easily hydrolysed compound of a manganous base with a weak acid is shown to be erroneous. Laccase probably does not exist in the latex of the lac tree, but is formed during the alcoholic precipitation.

In the second part of the paper the author puts forward the view that none of the oxydases are truly enzymic in character, but are inorganic catalysts in a colloidal substratum. It is suggested also that the activity of the hydrolytic enzymes bears a similar explanation, the accelerating influence of traces of acid on invertase, Hanriot's work showing the activity of iron in lipase (Abstr., 1901, ii, 562), and that of Tribot and Chrétien (this vol., i, 73, 346) attributing a similar rôle to magnesium in invertase, being cited in support of this view.

[With EDOUARD LEROY.]—Euler and Bolin's (Abstr., 1908, ii, 1021) observations concerning the oxidation of quinol by the catalyst ($\text{Mn} \times \text{OH}$) confirm those of the author, but the statement that this oxidation can be effected in acid solution is erroneous, the mistake arising from the fact that phenolphthalein was used as indicator, of which the sensitiveness to alkalis is known to be small. The lucerne laccase prepared by Euler and Bolin is quite dissimilar from Bertrand's laccase, being inactive towards quinol until treated with manganous

salt, and the quantity of acid added to it by them, whilst making it acid to phenolphthalein, leaves it still alkaline to Förster's reagent. Euler and Bolin find that the addition of citrates, tartrates, gluconates, etc., to laccase accelerates its action on quinol, and seem to attribute this action to the formation of complex ions containing manganese. The present authors, however, consider the activity of these salts to be due partly to the alkali produced by their hydrolysis and partly to their rendering manganous hydrate soluble. It is shown experimentally that the activating effect of sodium citrate decreases with its alkalinity, and disappears at the point of true neutrality. Only the trisodium citrate is at all active. In the absence of manganous salt, salts such as Rochelle salt (which, although neutral to phenolphthalein, is alkaline to Förster's reagent) increase the oxidation of quinol by alkali.

The oxidising activity of a manganous salt plus a citrate is greater than the sum of the activities of the two separately, and since the co-operative effect is greatest for the ratio $12\text{Mn} : 1$ citrate molecule, it cannot be due to the formation of a complex manganese citrate. Moreover, the co-operative effect of manganous salt + citrate being nearly the same as that of manganous salt + alkali indicates that the two actions are of the same kind. E. H.

Malt Catalase and the Mineral Catalysts. HENRI VAN LAER (*Bull. Soc. chim. Belg.*, 1909, 23, 293—296).—The catalytic power of malt (as measured by the volume of oxygen liberated from hydrogen peroxide during the first minute of the action) is increased by alkali, reaching a maximum when the liquid is neutral to phenolphthalein. If the alkalinity is reduced by making the solution neutral to methyl-orange, the catalytic power diminishes. Ground dry malt retains a certain amount of activity even after heating for two hours at 125° , and must be heated at 200° in order to destroy its activity towards hydrogen peroxide. The volume of oxygen evolved by the action of malt on hydrogen peroxide is reduced by the addition of an equal weight of the same malt previously heated, indicating that heating liberates a trace of acid. The reduction of the catalytic power of one malt by addition of another is probably due to extra acidity in the latter, whilst the progressive increase in the catalytic power of a barley during germination and its decrease on kilning are also to be explained by changes in the reaction of the medium surrounding the catalase rather than to a change in the quantity of the latter.

Magnesium salts have no effect on hydrogen peroxide until partly transformed into hydroxide by addition of alkali.

The activity of blood-charcoal, animal-charcoal, and spongy platinum is affected by traces of alkali and acid similarly to that of malt catalase. The only fundamental differences between the latter and mineral catalysts are that malt catalase is used up in the reaction and that it is destroyed by heat. E. H.

Organic Chemistry.

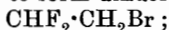
A Mode of Production of Iodoform. A. LABAT (*J. Pharm. Chim.*, 1909, [vi], 30, 107—109).—The supposed formation of iodoform from carbon dioxide recorded by Guérin (this vol., i, 126) depends on the ammonia employed, and does not occur with all specimens. It appears to be due to a ketonic impurity, probably acetone, which can be separated from the ammonia by neutralisation and distillation. The distillate gives the iodoform reaction, and forms an immediate white precipitate with Denigés' solution of mercuric sulphate. The samples of ammonia examined could not have contained more than 0.01% of the suspected impurity.

W. O. W.

Preparation of Tetranitromethane. R. SCHENCK (D.R.-P. 211198 and 211199).—Tetranitromethane was previously prepared by Pictet and Genequand (*Abstr.*, 1903, i, 305, 596) by the action of acetic anhydride on diacetylorthonitric acid at 60°; the yield was 10% of the theory, and the action dangerously violent. It has now been found that a satisfactory yield can be obtained by slowly dropping acetic anhydride (120 parts) into a mixture of nitrogen pentoxide (155 parts) and nitrogen peroxide (75 parts) at a temperature below 40°.

F. M. G. M.

Fluorodibromoethane and *as*-Fluorobromoethylene. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1909, 728—743. Compare *Abstr.*, 1898, i, 457; 1899, i, 254; 1902, i, 129).—It has been shown previously that antimony trifluoride condenses with tribromoethane in presence of bromine at 100° to form difluorobromoethane,



at higher temperatures some α -fluoro- $\alpha\beta$ -dibromoethane, $\text{CH}_2\text{Br} \cdot \text{CHBrF}$, is also formed (*Abstr.*, 1902, i, 129), and at 180° the amount of the latter obtained is twice as great as of the former. Further, at 180° a minute quantity of the isomeric α -fluoro- $\beta\beta$ -dibromoethane, $\text{CHBr}_2 \cdot \text{CH}_2\text{F}$, is also produced. It follows from these observations that substitution of fluorine for bromine in the chain $\cdot\text{CH}_2\text{Br}$ only occurs at the higher temperature.

Fluorobromoethylene reacts with hydrobromic acid (D 1.78) at 100° to form α -fluoro- $\alpha\beta$ -dibromoethane, a small quantity of fluorotribromoethane being also produced, due probably to free bromine contained in the acid used.

α -Fluoro- $\alpha\beta$ -dibromoethane, on treatment with potassium hydroxide in alcohol, yields a mixture of two fluorobromoethylenes (compare *Abstr.*, 1902, i, 129). The *s*-isomeride, $\text{CHF} \cdot \text{CHBr}$, b. p. 36°, is stable in air and does not polymerise. The *as*-isomeride, $\text{CBrF} \cdot \text{CH}_2$, b. p. 12.5°, oxidises rapidly in air, forming ethylene oxide, although the greater part of it polymerises spontaneously. It absorbs bromine

readily, yielding α -fluoro- $\alpha\alpha\beta$ -tribromoethane, b. p. 163° , which can also be prepared by the substitution of fluorine in tetrabromoethane.

T. A. H.

The Isolation of Aliphatic Alcohols. CARL NEUBERG and E. KANSKY (*Biochem. Zeitsch.*, 1909, 20, 445—449).— α -Naphthylcarbimide is heated with an equimolecular proportion of the dry alcohol, and the resulting α -naphthylcarbamate separated from a little dinaphthylcarbamide by extraction with light petroleum, from which the carbamate crystallises on cooling. α -Naphthylcarbamates of the following alcohols were prepared: *n-propyl*, m. p. 80° ; *isopropyl*, m. p. 105 — 106° ; *n-butyl*, m. p. 71 — 72° ; *isobutyl*, m. p. 103 — 105° ; *sec-butyl*, m. p. 97 — 98° ; *tert-butyl*, m. p. 100 — 101° ; *isoamyl*, m. p. 67 — 68° ; optically active *amyl*, m. p. 82° ; *sec-amyl*, m. p. 76 — 79° ; *tert-amyl*, m. p. 71 — 72° ; *n-heptyl*, m. p. 62° ; *n-octyl*, m. p. 66° ; *cetyl*, m. p. 81 — 82° ; *allyl*, m. p. 109° . G. B.

Condensation of isoPropyl Alcohol with its Sodium Derivative. Formation of Methylisobutylcarbinol and of $\delta\zeta$ -Dimethylheptan- β -ol. MARCEL GUERBET (*Compt. rend.*, 1909, 149, 129—132; *J. Pharm. Chim.*, 1909, [vi], 30, 153—161. Compare Abstr., 1902, i, 130, 583, 657; 1908, i, 162, 635).—The study of the reaction between alcohols and their sodium derivatives has now been extended to secondary aliphatic alcohols. When sodium is heated with excess of *isopropyl* alcohol for twenty-four hours at 200° , *methylisobutylcarbinol* is formed, together with $\delta\zeta$ -*dimethylheptan- β -ol*, $\text{CH}_2\text{Pr}^\beta\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$. This substance, which arises from the condensation of sodium *isopropoxide* with *methylisobutylcarbinol*, is a liquid with a rose-like odour, b. p. 194 — 195° (corr.), D 0.8787; the *acetyl* derivative has b. p. 201 — 202° (corr.). Oxidation with chromic acid mixture furnishes $\delta\zeta$ -*dimethylheptan- β -one*, $\text{CH}_2\text{Pr}^\beta\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$,

b. p. 190 — 191° , D 0.9024; the *semicarbazone* has m. p. 210° . Oxidation of the ketone leads to formation of acetic acid and $\alpha\gamma$ -*dimethylvaleric acid*, together with a little carbon dioxide and an acid, $\text{C}_9\text{H}_{18}\text{O}_2$. W. O. W.

Action of Active Copper on Linalool. C. J. ENKLAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 104—108).—When linalool, $\alpha_D - 17.14'$, is passed at 135° over active copper, prepared by the reduction of the oxide at 200° , it is largely decomposed into hydrocarbon and water. By distillation, finally over sodium, the product yielded four fractions, three of which, b. p./12 mm. 67.5 — 68.5° , 68.5 — 69° , and 69 — 70° , assumed to be a single substance, $\text{C}_{10}\text{H}_{16}$, have been examined. The molecular refraction lies between those calculated for a monocyclic and an aliphatic terpene, whilst the molecular dispersion exceeds those of both. The substance rapidly absorbs two atoms of bromine, and a third very slowly with evolution of hydrogen bromide. Hydrogen at 180° , with nickel as catalyst, converts the substance into a product which yields a main fraction, $\text{C}_{10}\text{H}_{18}$, b. p. 164 — 166° , D 15 0.787, which is stable towards potassium

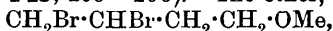
permanganate, but is attacked rapidly by bromine at the ordinary temperature. This behaviour is exhibited by the hydrocarbons, $C_{10}H_{18}$, obtained by the hydrogenation of dicyclic terpenes. The substance $C_{10}H_{18}$ is oxidised by potassium permanganate to a glycol, probably $C_{10}H_{18}O_2$, and various acids, among which a butyric acid is present, and also a non-volatile acid, which is oxidised to a hydroxy-acid by hydrogen peroxide.

It appears, therefore, that linalool is dehydrated by active copper with closure of the ring.

Another method, in which closure of the ring is avoided as much as possible, consists in heating linalool and phenylcarbimide (2 mols.) at $140-150^\circ$. Carbon dioxide is evolved, *s*-diphenylcarbamide crystallises out, whilst a hydrocarbon is obtained by distillation, which has $D_0 0.810$, and resembles myrcene in its odour and in its reduction by sodium and alcohol to a hydrocarbon having the b. p. of dihydro-myrcene.

C. S.

Some Derivatives of $\alpha\beta\delta$ -Trihydroxybutane. PARISELLE (*Compt. rend.*, 1909, 149, 295—298).—The ether,



prepared by Lespieau (*Abstr.*, 1907, i, 580), has b. p. $96^\circ/16$ mm., n_D^{20} 1.5158. When boiled with water and the resultant syrup fractionally distilled in a vacuum, two compounds are obtained: (1)

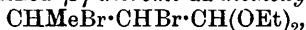
3-hydroxytetrahydrofuran, $O \begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{OH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$, b. p. $81-82^\circ/13$ mm.,

or 181° under ordinary pressure; its *phenylurethane* has m. p. 120° ; (2) *$\alpha\beta$ -dihydroxy- δ -methoxybutane*, $OH \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot OMe$, b. p. $121^\circ/12$ mm., D 1.11, n_D^{20} 1.448; its *diphenylurethane* has m. p. $111-112^\circ$. When saturated with hydrogen bromide at $110-115^\circ$, it yields *$\alpha\delta$ -dibromo- β -hydroxybutane*, $CH_2Br \cdot CH(OH) \cdot CH_2 \cdot CH_2Br$, b. p. $114-115^\circ/13$ mm., D 2.023, n_D^{20} 1.544. When this is treated with potassium hydroxide in dry ether, it forms *α -bromo- $\Delta\gamma$ -butylene oxide*,

$\begin{array}{c} CH_2 \\ \diagup \quad \diagdown \\ O \end{array} \text{CH} \cdot CH_2 \cdot CH_2Br$, b. p. $58^\circ/14$ mm., 160° under ordinary pressure, D 1.59, n_D^{20} 1.478; on boiling with water containing a little sulphuric acid the expected monobromohydrin was not formed, hydroxytetrahydrofuran being produced, together with some *$\alpha\delta$ -dibromo- β -hydroxybutane*, arising from fixation of hydrogen bromide by the unhydrolysed oxide.

W. O. W.

Ethyl Acetal of Tetrolaldehyde [Diethoxybutinene]. P. L. VIGUIER (*Compt. rend.*, 1909, 149, 403—405).—The following compounds were obtained in an unsuccessful attempt to prepare tetrolaldehyde from crotonaldehyde. The latter compound was converted into *$\alpha\beta$ -dibromobutaldehyde*, which, on treatment by Claisen's method, readily furnished *$\beta\gamma$ -dibromo- $\alpha\alpha$ -diethoxybutane*,



b. p. $113-114^\circ/13$ mm. On treatment with alcoholic sodium ethoxide this yielded *bromo- $\alpha\alpha$ -diethoxybutinene*, $C_8H_4Br \cdot CH(OEt)_2$, b. p. $86^\circ/15$ mm., D_0 1.247, D^{21} 1.2255, n_D^{21} 1.4565. Acid hydrolysis converted it into *bromocrotonaldehyde*, $C_5H_4Br \cdot CHO$, a pale yellow liquid, b. p.

63—64°/14 mm., having a penetrating odour, and forming crystalline derivatives with hydroxylamine and semicarbazide.

When bromo-*aa*-diethoxybutinene is distilled with potassium hydroxide, a small quantity of *diethoxybutinene*, $\text{CMe}:\text{C}\cdot\text{CH}(\text{OEt})_2$, is obtained as an agreeably-smelling liquid, b. p. 62—65°/15 mm., 163—166° under ordinary pressure, D_0^{20} 0.915, D_D^{23} 0.8945, n_D^{23} 1.437.

Attempts to obtain definite products by hydrolysis with acids were unsuccessful. W. O. W.

Preparation of Mixed Glycerol Esters. VEZIO VENDER (D.R.-P. 209943).—Glycerol was heated at 150° with anhydrous oxalic acid, and the resulting mixture of glycerol and monoformin treated with nitrosulphuric acid. The resulting mixture of nitroglycerol (67%) and *dinitroformin* (33%) is a pale yellow oil, D^{15} 1.57.

Nitroacetin, prepared from acetin by the same method, is a pale yellow oil, D_{15} 1.45, insoluble in water, benzene, or carbon disulphide, but soluble in alcohol or acetone; it contains 12.5% of nitrogen.

F. M. G. M.

Alcoholysis of Lecithin. ADOLF ROLLETT (*Zeitsch. physiol. Chem.*, 1909, 61, 210—214).—The difficulties arising from oxidation during the alcoholysis of oils containing unsaturated acids (compare Haller, Abstr., 1908, i, 123) may be obviated by the addition of tin or zinc to the mixture of oil and alcoholic solution of hydrogen chloride. Naturally the same device may be employed with advantage in the esterification of acids which readily undergo oxidation.

Lecithin from egg having the iodine value 69 (Hübl), when treated with a 2.5 *N*-solution of hydrogen chloride in methyl alcohol, yields an ester, b. p. 218—250°/32 mm., having the iodine value 86.7 (Hübl). This increase in the iodine value, which was observed in most experiments, is not so great as is required by the formula generally assigned to lecithin. It is probable, therefore, that some part of the molecule, other than the unsaturated fatty acids, is concerned in the absorption of iodine by lecithin.

W. H. G.

Action of Finely-divided Metals on the Aliphatic Acid Anhydrides. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1909, [iv], 5, 814—819. Compare this vol., i, 452).—When acetic anhydride vapour is passed over commercial zinc dust heated in a tube at 230—240°, zinc acetate is formed on the upper wall of the tube, a mixture of almost equal parts of acetone and acetaldehyde distils, the gases evolved consist of rather more than two volumes of carbon dioxide to one of hydrogen, and carbon is deposited on the zinc. These results are to be explained by (1) the action of zinc oxide, thus: $\text{O}(\text{CMe})_2 + \text{ZnO} = \text{Zn}(\text{CO}_2\text{Me})_2$, and (2) the catalytic action of the metallic zinc decomposing one part of the anhydride into acetone and carbon dioxide, thus: $\text{O}(\text{CMe})_2 = \text{CO}_2 + \text{CMe}_2$ (*a*), and another part into the two residues $\text{CH}_3\cdot\text{CO}\cdot$ and $\text{CH}_3\cdot\text{CO}_2\cdot$, the latter of which decomposes into carbon dioxide, carbon, and hydrogen, part of the hydrogen reducing the acetyl to acetaldehyde, thus: $\text{O}(\text{CMe})_2 = \text{CO}_2 + \text{H}_2 + \text{C} + \text{CH}_3\cdot\text{CHO}$ (*b*). The slight excess of carbon dioxide is

explained by the partial decomposition of the zinc acetate into carbon dioxide, acetone, and zinc oxide.

Propionic anhydride is decomposed by zinc dust at 240° , giving carbon, carbon dioxide, hydrogen, propaldehyde, diethyl ketone, and zinc propionate, the decomposition proceeding according to reactions analogous to (a) and (b) above. Butyric, isobutyric, and isovaleric anhydrides behave quite similarly.

The above five anhydrides are decomposed by finely-divided cadmium (produced by reducing the oxide with hydrogen) into the corresponding symmetrical ketone and carbon dioxide, no secondary reactions being observed.

The vapour of acetic anhydride when passed over finely-divided nickel heated at $200-220^{\circ}$ is decomposed into a mixture of carbon, carbon monoxide, hydrogen, and acetic acid, the latter containing traces of acetaldehyde. Evidently the anhydride is catalytically decomposed into the two groups $\text{CH}_3\cdot\text{CO}_2\cdot$ and $\text{CH}_3\cdot\text{CO}\cdot$, the latter of which decomposes into carbon monoxide, hydrogen, and carbon, whilst part of the hydrogen combines with the $\text{CH}_3\cdot\text{CO}_2\cdot$ group to form acetic acid: $(\text{COMe})_2\text{O} = \text{C}_2\text{H}_4\text{O}_2 + \text{CO} + \text{H}_2 + \text{C}$.

The behaviour of propionic, butyric, isobutyric, and isovaleric anhydrides is quite analogous, the corresponding olefine being formed in place of hydrogen. At a higher temperature ($280-290^{\circ}$) the carbon monoxide is converted into carbon dioxide and carbon.

Finely-divided copper is much less active. A temperature of $290-300^{\circ}$ is required to effect decomposition, and the products in all cases are hydrogen, carbon monoxide, a little carbon dioxide, carbon, the aliphatic acid, traces of the corresponding aldehyde and ketone, and unattacked anhydride. The main reaction is the same as that produced by nickel.

Porphyrised iron at 300° decomposes the acid anhydrides, forming carbon, carbon dioxide, hydrogen, and considerable quantities of the aldehyde and ketone. No carbon monoxide is produced. The decomposition of acetic anhydride is expressed by the equations $\text{O}(\text{COMe})_2 = \text{COMe}_2 + \text{CO}_2$ and $\text{O}(\text{COMe})_2 = \text{CH}_3\cdot\text{CHO} + \text{H}_2 + \text{CO}_2 + \text{C}$.

E. H.

Preparation of Acid Chlorides and Anhydrides. FARBWERKE VORM MEISTER LUCIUS and BRÜNING (D.R.-P. 210805).—Acid anhydrides can be conveniently prepared by the action of sulphur dioxide (either in gas or liquid form) on the dry salts of the required acids; and by subsequent treatment with chlorine the acid chlorides are formed. A detailed account of the preparation of acetic anhydride, acetyl chloride, and of benzoyl chloride is given. F. M. G. M.

Preparation of Formic Acid. DAVID STRAUZ (D.R.-P. 209418).—Sodium formate in aqueous solution is treated with hydrofluoric acid (80%) and the free formic acid distilled off. The residual sodium fluoride is treated with lime, and the hydrofluoric acid recovered as its insoluble calcium salt. The substitution of hydrofluoric for sulphuric acid precludes the destructive action of the latter on the formic acid.

F. M. G. M.

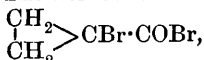
Replacement of Formic Acid by its Esters, especially as Concerns its Behaviour towards Bicarbonate Solutions. O. MAKOWKA (*Zeitsch. angew. Chem.*, 1909, 22, 1601—1602).—For the decomposition of bicarbonate solutions formic acid may be replaced by such of its esters that are readily hydrolysed. Methyl and ethyl formates are not suitable. Glycol mono- and di-formates, as also mono-, di-, and tri-formin, react readily, but they possess the drawback that they are liquids. The mono- and di-formates of erythritol and mannitol, which are solids, are found to be satisfactory. It was not found possible to produce stable formates of mannitol of higher complexity than the diformate. It is probable that these higher formates are formed when mannitol is heated with excess of oxalic acid, but they immediately decompose with the formation of the diformate and formic acid; by distillation of the mixture under diminished pressure, concentrated and crystallisable formic acid is readily obtained.
T. S. P.

Production of Alkyl Chloroacetates from Dihalogenated Vinyl Ethers. GEORGES IMBERT UND CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 210502. Compare this vol., i, 453).—It has previously been shown that concentrated hydrochloric acid produces this change. The reaction is now regarded as taking place in two phases, an additive product being first formed, which then decomposes as follows:

- (1) $C_2HCl_2 \cdot OEt + HCl = C_2H_2Cl_3 \cdot OEt$.
- (2) $C_2H_2Cl_3 \cdot OEt + H_2O = CH_2Cl \cdot CO_2Et + 2HCl$.

F. M. G. M.

Bromination of cycloPropanecarboxylic Acid. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 659—664).—The action of bromine on cyclopropanecarboxylic acid or its chloroanhydride leads to the formation of the bromoanhydride or chloroanhydride of α -dibromobutyric acid. The normal bromination product,



is probably formed first, the action of the liberated hydrogen bromide on this compound resulting in the rupture of the cyclopropane ring.

Ethyl α -dibromobutyrate, $CH_2Br \cdot CH_2 \cdot CHBr \cdot CO_2Et$, prepared by treating the chloro- or bromo-anhydride with alcohol in ethereal solution, is a heavy liquid with a fruity odour, b. p. 149—150°/52 mm., D_4^{20} 1.6871.

The action of zinc and alcohol on this ester does not yield ethyl cyclopropanecarboxylate, but results in reduction and hydrolysis of the ester, the main product of the reaction being zinc *n*-butyrate.

T. H. P.

Electrolytic Preparation of Glyoxylic Acid. KINZLBERGER & Co. (D.R.-P. 210693).—The electrolysis of ethyl oxanilate (5 parts) in 80% sulphuric acid (100 parts) with a mercury cathode leads to the formation of phenylglycine. At 5°, and employing a lead anode, the electrolysis of oxalic acid yields glyoxylic acid. F. M. G. M.

White and Yellow Silver Lævulates. MARGARETE FURCHT and ADOLF LIEBEN (*Monatsh.*, 1909, 30, 555—634).—A white and a yellow modification of silver lævulate have long been known. In addition to Tollens' method, the white salt is obtained conveniently by adding to a solution of lævulic acid (1 part) in boiling water (200 parts) less than one equivalent of silver oxide, heating for the shortest time required for the solution of the oxide, and evaporating the filtered solution in a vacuum. The yellow salt is obtained by boiling 10 grams of lævulic acid in 600 grams of water with $1\frac{1}{2}$ equivalents of silver oxide for six hours and cooling the hot filtered solution, whereby the nodular crystals of the yellow salt separate. When a moderately concentrated solution of the yellow salt is kept in a warm place for three months, it is decolorised, and the filtered solution yields by distillation in a vacuum a white salt, which, however, retains the crystalline appearance and shows the characteristic decomposition of the original yellow salt.

White silver lævulate is converted into the yellow form by prolonged heating with water, more rapidly in the presence of silver oxide. The yellow modification is changed into the white, with great loss of material, by heating its solution with animal charcoal at 70° for fifteen minutes, keeping overnight at the ordinary temperature, and evaporating the colourless filtered solution in a vacuum.

When the white salt is boiled with water, a portion is changed into the yellow salt and a portion undergoes decomposition, yielding silver, lævulic acid, and smaller quantities of carbon dioxide and a strongly odourous oil, which consists of, or contains, diacetyl, since it forms diacetyl dioxime with hydroxylamine. The boiling solution of the yellow salt decomposes more rapidly than that of the white salt, and yields the same products.

The decomposition of the white and the yellow salts by water increases with the temperature and with the time of heating. The rate of decomposition is greater the more finely divided the salt and the greater the surface of contact between the salt and the water, is increased by the presence of silver oxide, and is diminished by the presence of lævulic or succinic acid, sodium sulphate, or sodium nitrate.

A characteristic difference between the two salts is the following. Experiments on solutions containing from 20 to 1000 parts of water to 1 part of salt show that the decomposition of the white salt, effected by twenty-four hours' heating on a water-bath, is smaller the greater the quantity of water present, and that the deposited silver is always granular. Under similar conditions the decomposition of the yellow salt in solutions containing from 20 to 200 parts of water to 1 part of salt is more pronounced, but is again smaller the greater the amount of water present, and the deposit of silver is granular. When, however, a solution of 1 part of the yellow salt in 300—1000 parts of water is heated under the same conditions, an extraordinarily pronounced decomposition occurs, greater even than that of a solution of 1 part of salt in 20 parts of water, and the silver is obtained in colloidal suspension. The great decomposition in this case is due very probably to the large surface exposed by the colloidal silver.

Since white and yellow silver l  vulates give the same products of decomposition, are interconvertible, form the same methyl l  vulate with methyl iodide, and have the same solubility either separately or mixed, it appears very probable that they are one and the same substance, the colour and the characteristic properties of the yellow salt being due to a small amount of impurity. Attempts to isolate the impurity by extraction with various solvents have failed, but its presence has been proved by the following. A solution of the yellow salt is treated with the equivalent amount of hydrochloric acid, and the filtered solution, after being evaporated to a small bulk, is treated with ether, whereby the l  vulic acid is extracted, leaving a small residue of an amorphous, brown substance, which is soluble in water (only sparingly soluble after being dried at 100  ) and, when added to a solution of the white silver l  vulate, causes the salt to be deposited, after evaporation, in yellow, nodular crystals, and also increases very considerably its rate of decomposition by boiling water, the silver being obtained in a colloidal form if the solution is sufficiently dilute. The amorphous substance, which has reducing properties, does not exist apparently as such in the yellow salt, but is continually destroyed during the decomposition of the salt, yielding the odorous oil mentioned previously, and is continually being regenerated at the expense of the l  vulic acid. At the ordinary temperature, daylight exerts on a solution of the white or yellow salt a decomposing influence very similar to that of heat, but in a very much smaller degree. There is a great difference, however, between the actions of light and heat. The former causes a deposition of silver from a solution of the yellow salt, but the salt remaining in solution becomes more stable, just as though the amorphous impurity, originally existent in the yellow salt, has been destroyed and is not being regenerated.

The decomposition of the white and yellow salts by boiling water under otherwise equal conditions is greater in a horizontal sealed glass tube than in a vertical sealed glass tube or in a sealed glass flask. The white and the yellow salts decompose to the extent of 19–23% and 41% respectively when a solution of one part of the salt in 20 parts of water is heated in a horizontal tube for twenty-four hours in boiling water. C. S.

Preparation of Magnesium Phosphotartrate. KARL SORGER (D.R.-P. 210857).—*Magnesium phosphotartrate*, colourless powder or crystalline nodules, is obtained by the action of (1) magnesium hydrogen tartrate on magnesium phosphate; (2) magnesium hydrogen phosphate on neutral magnesium tartrate; or (3) the decomposition of sodium hydrogen phosphotartrate with magnesium oxide. It is not easily soluble in water or acids, but dissolves in ammonium hydroxide or dilute alkalis; it is decomposed by warm concentrated sulphuric acid with evolution of the oxides of carbon. Being tasteless, this salt should be of therapeutic value. F. M. G. M.

Preparation of an Allophanic Ester of Castor Oil. VEREINIGTE CHININFABRIKEN ZIMMER & CO. (D.R.-P. 211197).—The *allophanic acid* ester, $C_3H_5O_3(CO \cdot C_{17}H_{32} \cdot O \cdot C_2O_2N_2H_3)_3$, colourless, tasteless,

odourless powder, m. p. 61—62°, is produced on adding carbamide hydrochloride to a solution of castor oil in benzene and boiling during one hour; it dissolves sparingly in cold, but readily in hot, alcohol, and is insoluble in water.

F. M. G. M.

Oxidation of Phoronic Acid by Nitric Acid. RICHARD ANSCHÜTZ and PAUL WALTER (*Annalen*, 1909, 368, 95—100. Compare Anschütz, Abstr., 1893, i, 304).—When phoronic acid is heated with 50% nitric acid at 90° for about ten hours, it is converted into a mixture of approximately equal quantities of dimethylmalonic acid and *as*-dimethylsuccinic acid, the amount of these acids actually obtained being about 77% of that required by the equation:

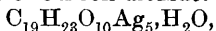
$[\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}_2]_2\text{CO} \rightarrow \text{CMe}_2(\text{CO}_2\text{H})_2 + \text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$.
The formula assigned previously (*loc. cit.*) to phoronic acid and given in the preceding equation is thus definitely established.

Attempts to prepare the substance $\text{CO} \begin{smallmatrix} \text{CH}_2\cdot\text{CMe}_2 \\ \text{CH}_2\cdot\text{CMe}_2 \end{smallmatrix} \text{CO}$ by the dry distillation of calcium phoronate were unsuccessful. W. H. G.

Degradation of Cholic Acid. I. Fusion of Bilianic Acid with Potassium Hydroxide. OTTO VON FÜRTH and ERNST JERUSALEM (*Biochem. Zeitsch.*, 1909, 20, 375—383).—The only product which could be isolated after fusion with potassium hydroxide at 220° was a minute quantity of unchanged bilianic acid. G. B.

Degradation of Cholic Acid by Oxidation. E. LETSCHE (*Zeitsch. physiol. Chem.*, 1909, 61, 215—239. Compare this vol., i, 587).—The formula assigned by Panzer to cholic acid (this vol., i, 586) is criticised adversely. The formation of bilianic acid from dehydrocholic acid points to the presence of an ethylene linking in the latter compound, and consequently also in cholic acid. Further, it is to be expected that the molecule of cholic acid having Panzer's formula would readily decompose into two roughly equal parts at the secondary alcohol group after its conversion into the ketonic group, but bilianic acid is very stable and yields cilianic acid when oxidised.

Cholic acid when acted on by a mixture of equal volumes of nitric acid (D 1·38) and sulphuric acid (D 1·84) yields a pentabasic acid, $\text{C}_{19}\text{H}_{28}\text{O}_{10}$, crystallising in slender prisms, m. p. 226° (decomp.), $[\alpha]_D^{25} + 12\cdot3^\circ$ (in 96% alcohol); it behaves as a saturated compound towards bromine and potassium permanganate, and when heated above its m. p. liberates 2 mols. of carbon dioxide. The silver,



barium, $(\text{C}_{19}\text{H}_{25}\text{O}_{10})_2\text{Ba}_3$, and copper, $(\text{C}_{19}\text{H}_{28}\text{O}_{10})_2\text{Cu}_5$, salts are amorphous powders; other complex copper salts were also prepared and analysed. The diethyl ester, $\text{C}_{23}\text{H}_{36}\text{O}_{10}$, crystallises in very slender needles, m. p. 195—196°, $[\alpha]_D^{20} + 11\cdot39^\circ$ (in absolute alcohol); it loses carbon dioxide when heated above its m. p., and when boiled for one hour with a *N*/2-potassium hydroxide solution yields the double compound, $\text{C}_{19}\text{H}_{28}\text{O}_{10}\cdot\text{C}_{21}\text{H}_{32}\text{O}_{10}$, crystallising in stellate aggregates of slender needles, m. p. 207—208°, $[\alpha]_D^{25} + 10\cdot2^\circ$. The following salts of the latter substance were analysed: silver, $\text{C}_{40}\text{H}_{52}\text{O}_{20}\text{Ag}_8\cdot 2\text{H}_2\text{O}$; copper, $\text{C}_{40}\text{H}_{52}\text{O}_{20}\text{Cu}_4\cdot 4\text{H}_2\text{O}$; iron, $\text{C}_{19}\text{H}_{25}\text{O}_{10}\text{Fe}_2\cdot\text{C}_{21}\text{H}_{29}\text{O}_{10}$.

The diethyl ester, $C_{23}H_{36}O_{10}$, when boiled with a $N/2$ -potassium hydroxide for longer than one hour, yields an *acid*, $C_{19}H_{32}O_{12}$, crystallising in rhombic plates; it softens and froths up at about 140° , subsequently becomes solid, and then has m. p. $230-231^{\circ}$; when heated at 115° it loses $2H_2O$, and at about 125° loses $2\frac{1}{2}H_2O$, yielding the *anhydride*, $(C_{18}H_{27}O_8 \cdot CO)_2O$, a white substance, m. p. $230-231^{\circ}$; the *ammonium*, $C_{19}H_{29}O_{12}(NH_4)_3$, and *silver*, $C_{19}H_{28}O_{12}Ag_4$, salts were analysed. A tetrabasic *acid*, $C_{18}H_{28}O_8$, was sometimes obtained by boiling the ester, $C_{23}H_{36}O_{10}$, with N -potassium hydroxide solution; it crystallises in slender needles, commences to char at 273° , and is brownish-black at 280° ; the *diethyl ester*, $C_{22}H_{36}O_8$, forms stellate aggregates of lamellæ, m. p. 248° .

A *substance*, $C_{48}H_{76}O_{10}$, is formed together with the ester, $C_{23}H_{36}O_{10}$, during the esterification of the acid, $C_{19}H_{28}O_{10}$; it forms spherical aggregates of slender crystals, m. p. $183-184^{\circ}$. W. H. G.

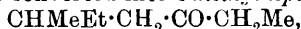
Action of Iron and Cyanides on the Spontaneous Oxidation of Cystine. Action of Metals and Strong Salt Solutions on the Spontaneous Oxidation of Cysteine. ALBERT P. MATHEWS and SYDNEY WALKER (*J. Biol. Chem.*, 1909, 6, 289-298, 299-312).—Spontaneous oxidation of cystine occurs in alkaline solutions; the rate of this is increased by the addition of a mixture of ferric chloride and potassium cyanide, although neither reagent alone has any action. The products of oxidation and the mechanism of its acceleration are unknown.

The spontaneous oxidation of cystine to cystine is accelerated by a small amount of iron; some metals act in the same way, but others retard, and others again have no effect on the oxidation. An explanation, based on "solution tension," is given of the actions of different metals and their salts. W. D. H.

A New Isomeride of Pinacolin. F. CLAESSENS (*Bull. Soc. chim.*, 1909, [iv], 5, 809-812).—When pinacolyl bromide, $CMe_3 \cdot CHMeBr$, is boiled with powdered potassium hydroxide in a reflux apparatus for three hours and the fraction of the product b. p. $57-65^{\circ}$ treated with iodine and mercuric oxide in the manner described previously (this vol., i, 127), an iodohydrin is formed, which, on pouring its ethereal solution on to an excess of solid potassium hydroxide, is transformed into a new *oxide*. This forms a colourless, agreeably smelling liquid, b. p. $100.7-101.4^{\circ}$, $D_0^{20} 0.8413$, which combines energetically with hydrogen chloride and bromide. When treated with an equal volume of water, the two liquids form a homogeneous product after several weeks, but with nine volumes of water, the oxide, although diminishing considerably in volume, does not disappear. A 10% solution of potassium hydroxide has apparently no action. If treated with an equal volume of water containing a trace of acid, the oxide diminishes in volume and thickens considerably. It is not reduced by sodium in moist ether. E. H.

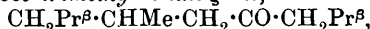
Synthesis of Unsaturated Aliphatic Ketones. F. BODROUX and FELIX TABOURY (*Compt. rend.*, 1909, 149, 422-423. Compare Abstr., 1908, i, 854).—Propanone reacts energetically with calcium

carbide, forming mesityl oxide, isophorone, xylitone, and more complex compounds. Under the special conditions already described, mesityl oxide is the sole product. The ketone obtained previously by the action of calcium carbide on butanone is now shown to be ϵ -methyl- Δ^8 -hepten- γ -one, $\text{CH}_3\text{Me}\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2\text{Me}$; it forms a semicarbazone, m. p. 114—115°, and on hydrogenation at 180° by Sabatier and Senderens' method is converted into ϵ -methylheptan- γ -one,



an agreeably smelling liquid, b. p. 153—155°/760 mm., D^{24}_D 0.820; the semicarbazone has m. p. 102°.

Calcium carbide acts on β -methylpentan- δ -one, furnishing $\beta\delta\theta$ -trimethyl- Δ^8 -nonen- ζ -one, $\text{CH}_2\text{Pr}^\beta\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\text{Pr}^\beta$, b. p. 217—219°/760 mm., D^{18}_D 0.838, n^{18}_D 1.4491; the oxime is a viscous liquid, b. p. 143—145°/17 mm. On catalytic hydrogenation at 280°, the ketone yields $\beta\delta\theta$ -trimethylnonan- ζ -one,



b. p. 210—212°/760 mm., D^{18}_D 0.820, n^{18}_D 1.4262; the oxime has b. p. 138—140°/15 mm.

Mesityl oxide is attacked by calcium carbide with formation of a liquid, $\text{C}_{12}\text{H}_{18}\text{O}_2$, b. p. 238—242°/741 mm., D^{17}_D 0.937, having a penetrating odour. This probably consists of a mixture of ketones, since it gives two semicarbazones, one of which is gummy, whilst the other crystallises in prisms, m. p. 165—166°. On hydrogenation, it yields a liquid from which no definite compounds have been isolated.

W. O. W.

Preparation of Ketonesulphoxylates. FARBWERKE VORM. MEISTER, LUCIUS and BRÜNING (D.R.-P. 210467. Compare this vol., i, 455).—Zinc sulphite (145 parts) is suspended in water (1000 parts) and treated with acetone (65 parts) and zinc dust (120 parts), the whole being stirred during twenty hours at a temperature of 50—55°. The zinc is precipitated with sodium carbonate, and the filtrate consists of a solution of sodium acetonesulphoxylate.

The acetone may be replaced by methyl ethyl ketone, and the zinc sulphite by ammonium sulphite, when the reaction is complete in ten hours.

F. M. G. M.

"Solubilisation" of Colloidal Starch by the Action of Alkalis. EUGÈNE FOUARD (*Bull. Soc. chim.*, 1909, [iv], 5, 828—834).—The addition of alkalis to solutions of the various polysaccharides causes a progressive alteration in their optical rotatory power, usually explained by the gradual neutralisation of their acid groups, since definite chemical compounds are precipitated by addition of a large excess of alcohol. It has already been shown (this vol., i, 209) that the progressive "solubilisation" of colloidal starch by alkalis is accompanied by a corresponding change in the rotatory power of the solution.

The composition of the precipitates formed when mixtures of 20 c.c. of a clear solution of starch containing 25.79 grams per litre with 5 c.c. of solutions of potassium hydroxide, ammonia, or piperidine, of varying strength, are added to 250 c.c. of absolute alcohol, has been studied.

The precipitates obtained in the presence of potassium hydroxide continued to give up alkali when washed with alcohol, even when the washing had been prolonged over some months, and the amount of alkali precipitated with the starch was, therefore, determined indirectly by estimating that left in solution. The results of the experiments with potassium hydroxide show that as the amount of alkali present decreases from 3.287 grams to 0.0147 gram, that precipitated with the starch decreases from 0.169 gram to 0.0091 gram or from 0.946 to 0.0512 gram-molecule per gram-molecule of starch. By plotting the amounts of alkali fixed by 1 gram-molecule of starch (as ordinates) against the total numbers of gram-molecules of potassium hydroxide present (as abscissæ), a hyperbolic curve is obtained, showing that the absorption of alkali varies in a continuous manner. It is therefore proved that no chemical compound of starch and potassium hydroxide is formed.

If a colloidal starch solution is used in place of the clear solution, an analogous series of numbers is obtained, but for a given concentration of alkali, the amount carried down from the colloidal is invariably less than that from the clear starch solution.

The experiments with ammonia and piperidine give similar results, but the proportion of alkali absorbed by the starch is less in the case of ammonia than in the presence of potassium hydroxide, and still less with piperidine.

Observations of the conductivity of solutions of potassium hydroxide, ammonia, and piperidine, alone and after adding a clear starch solution, show that in all three cases ionisation is diminished by addition of the starch solution, whereas if compounds with the alkali were formed, it would be increased in the case of ammonia and piperidine.

The conclusion is drawn that the action of alkalis on starch in solution is one of "solubilisation," that is, of subdividing the granules of the colloid to a high degree, at the same time modifying them (by altering the optical rotatory power) and being fixed by them in a variable proportion. This extremely complex phenomenon is neither purely chemical nor purely physical, but is an intramolecular change.

E. H.

Electric Transport of Glycogen and Starch. FILIPPO BORTAZZI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 87—90).—The results of the author's experiments are not in accord with those of Hardy (Abstr., 1906, i, 121), according to whom glycogen and starch are relatively isoelectric hydrosols.

When solutions of glycogen and starch are subjected to a field of about 5 volts per cm. (0.1 milliampere), both the glycogen and starch move towards the anode, only traces migrating towards the cathode. In the presence of small proportions of mineral acids, alkalis, or neutral salts, glycogen loses its electronegative character and undergoes no migration in either direction. Starch, however, behaves like protein or gelatin; in acid solution it migrates towards the cathode and in alkaline solution towards the anode, whilst in presence of neutral salts no migration is observed.

Hardy's results (*loc. cit.*) were probably obtained with glycogen less

pure than that employed by the author, a trace of an electrolyte being sufficient to prevent transport. T. H. P.

Lecithin-glucoses and Jecorin. A. BASKOFF (*Zeitsch. physiol. Chem.*, 1909, 61, 426—453).—The lecithin-glucoses, which can be separated from one another by their solubilities, are unions (or only mixtures) of glucose with the cleavage products of lecithin, and are of very variable composition. Drechsel's jecorin is regarded as a similar material obtained from lecithin or other phosphatides. W. D. H.

Etherifying Action of Organic Bases. THÉODORE VAN HOVE (*Bull. Acad. roy. Belg.*, 1909, 759—772).—The author has shown that when a solution of quinoline hydrochloride in an alcohol is heated in a closed vessel, the corresponding alkyl ether is formed, and that the action is due to the hydrogen chloride liberated by the dissociation of the amine hydrochloride (Abstr., 1907, i, 173). Since the amount of dissociation in any given case must be proportional to the strength of the base, he has endeavoured to apply this method to the determination of the relative strengths of organic bases.

A semi-normal solution of the amine hydrochloride in sufficient 98.5% alcohol to form 20 c.c. was heated at 180° during two hours. From the resulting product 15 c.c. were distilled off with suitable precautions to avoid loss of ether, and the distillate was agitated with three times its volume of glycerol, & known and sufficient volume of ether being added to cause complete separation of the ether formed, from the alcohol-glycerol mixture. The separated ether was then measured. The results are not strictly quantitative, but afford qualitative indications of the relative strengths of bases.

The action of triamylamine hydrochloride on ethyl alcohol was examined in detail, with a view to determine the nature of the secondary reactions. The volatile products consisted of ethyl chloride, ethyl ether, and ethyl *iso*amyl ether, the first and third being formed only in small quantities. From the saline residue, ethyldi*iso*amylamine and diethyl*iso*amylamine were obtained. T. A. H.

Preparation of Guanidine. CELSO ULPANI (D.R.-P. 209431).—When dicyanodiamide is treated with aqua regia, a quantitative yield of guanidine nitrate is obtained. One hundred grams of dicyanodiamide are dissolved in 500 c.c. of warm water and treated with 500 c.c. of concentrated hydrochloric acid and 200 c.c. of nitric acid (D 1.38). The mixture is evaporated at 60—65° to about one-fifth of its volume, when guanidine nitrate crystallises out in a pure condition. F. M. G. M.

Production of Putrefaction Bases. GEORGE BARGER (*Zeitsch. physiol. Chem.*, 1909, 61, 188).—The putrefactive formation of *p*-hydroxyphenylethylamine from tyrosine, which is suggested by Ackermann (this vol., i, 619), has already been proved by Barger and Walpole (this vol., ii, 416). The non-putrefactive formation of putrescine and cadaverine in ergot, observed by Rieländer, is similar to the occurrence of *iso*amylamine and *p*-hydroxyphenylethylamine in the

same fungus, observed by Barger and Dale (this vol., ii, 689). It is suggested that putrine, $C_{11}H_{26}O_3N_2$ (Ackermann, Abstr., 1908, i, 10), is derived from Fischer and Abderhalden's diaminotrihydroxydodecanoic acid, $C_{12}H_{26}O_5N_2$, by a similar loss of carbon dioxide. G. B.

Reduction of Amino-acids to Amino-aldehydes. CARL NEUBERG and E. KANSKY (*Biochem. Zeitsch.*, 1909, 20, 450—462. Compare Neuberg, Abstr., 1908, i, 322; Fischer, *ibid.*, i, 323).—The hydrochlorides of the esters of the amino-acids were reduced in acid solution with sodium amalgam, and the amino-aldehydes isolated as phenyl-osazones and *p*-nitrophenylosazones; some were oxidised with mercuric chloride to pyrazines. The following new substances were prepared: benzoyl derivatives of aminoacetaldehyde and α -aminopropionaldehyde, syrups, not analysed; *polymeric aminoacetaldehyde*, formed by sodium hydroxide, $(NH_2 \cdot CH_2 \cdot CHO)_x$; *pyrazine aurichloride*, $C_4H_4N_2 \cdot AuCl_3$, m. p. 202° ; *p*-nitrophenylosazone of α -aminopropionaldehyde,

$C_{15}H_{14}O_4N_6$
(from alanine), m. p. 277° ; 2:5-dimethylpyrazine aurichloride,
 $C_6H_8N_2 \cdot AuCl_3$,
m. p. 153° ; *p*-nitrophenylosazone of α -aminoisovaleraldehyde,

$C_{18}H_{20}O_4N_6$
m. p. 256 — 257° . The reduction of *isoserine* ester probably yielded aminolactaldehyde, but no derivatives of this could be isolated. After treatment with nitrous acid, glyceraldehyde could, however, be isolated as the *p*-nitrophenylosazone. G. B.

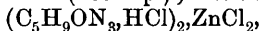
The Next Homologues of Sarcosine and Creatine. EMIL GANSSER (*Zeitsch. physiol. Chem.*, 1909, 61, 16—68).—In order to facilitate the detection and isolation of the homologues of sarcosine and creatine, which may possibly be present among the products of the hydrolysis of proteins, the preparation and properties of these substances have been investigated.

α -Methylaminopropionic acid crystallises with $\frac{1}{2}H_2O$ in slender, monoclinic prisms, sinters at 280° , and partly sublimes above 292° (compare Lindenberg, this Journ., 1876, i, 700); the *sulphate* is a hygroscopic, crystalline substance, m. p. 130 — 135° ; the *hydrochloride*, $C_4H_9O_2N \cdot HCl$, forms crystalline nodules; the *platinichloride* ($2H_2O$) crystallises in yellow prisms, m. p. 202° (decomp.); the *copper* salt crystallises with $2H_2O$; the *ethyl* ester, $C_6H_{13}O_2N$, is a colourless oil, b. p. 42 — $43^\circ/7$ mm., D_4^{20} 0.9502. α -Methylaminopropionmethylamide, $NHMe \cdot CHMe \cdot CO \cdot NHMe$, obtained by the action of methylamine on ethyl α -bromopropionate, is a hygroscopic, crystalline mass, which solidifies at 43.2° , b. p. $110^\circ/8$ mm.; the *platinichloride*, orange-yellow crystals, m. p. 201° (decomp.), and *aurichloride*, lemon-yellow prisms, m. p. 159 — 165° , were analysed. Contrary to Lindenberg's statement (*loc. cit.*), the action of cyanamide on α -methylaminopropionic acid in ammoniacal solution leads to the formation of α -methylguaninopropionic acid lactam (2-imino-5-keto-3:4-dimethyltetrahydroglyoxaline),

$$\begin{array}{c} CO-NH \\ | \\ CHMe \cdot NMe \end{array} > C:NH, \text{ which forms colourless crystals, sinters at about } 270^\circ, \text{ m. p. } 280^\circ \text{ (decomp.)}; \text{ the crystalline hydrochloride, } C_5H_9ON_3 \cdot HCl,$$

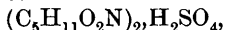
has m. p. 207° ; the *sulphate*, $(C_5H_9ON_3)_2 \cdot H_2SO_4$, forms tufts of light downy needles, m. p. 232° (decomp.); the *platinichloride* $(1H_2O)$ crystallises in small, orange-red, prismatic plates, m. p. $182-183^{\circ}$ (decomp.).

β -Methylaminopropionic acid, $NHMe \cdot CH_2 \cdot CH_2 \cdot CO_2H$, prepared by the action of a 33% solution of methylamine on β -iodopropionic acid at 120° under pressure, crystallises with $1H_2O$ in colourless plates, sinters at 72° , m. p. $99-100^{\circ}$; the *sulphate*, prismatic needles, m. p. 130° , *hydrochloride*, colourless, prismatic needles, m. p. 105° , and *platinichloride*, orange-yellow crystals, m. p. 196° (decomp.), were analysed; the *copper salt*, $(C_4H_8O_2N)_2Cu \cdot 6H_2O$, crystallises in dark blue prisms; the *ethyl ester*, $C_6H_{13}O_2N$, is a colourless oil, b. p. $58^{\circ}/8$ mm., D^{20}_4 0.9669. The acid interacts with cyanamide, yielding β -methylguaninopropionic acid, $NH:C(NH_2) \cdot NMe \cdot CH_2 \cdot CH_2 \cdot CO_2H$, which crystallises with $1H_2O$ in colourless, compact prisms, m. p. $201-202^{\circ}$ (decomp.); the *sulphate*, tufts of needles decomposing at 145° , *hydrochloride*, colourless flakes, m. p. 160° , and *platinichloride*, small, quadratic prisms, m. p. 195° (decomp.), were analysed. The corresponding lactam could not be isolated, but was obtained in the form of salts; the *hydrochloride*, $C_5H_9ON_3 \cdot HCl$, has m. p. 228° ; the *platinichloride*, $(C_5H_9ON_3)_2 \cdot H_2PtCl_6 \cdot 2H_2O$, forms long, orange, prismatic needles, m. p. 203° (decomp.); the *salt*,

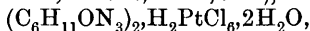


crystallises in white needles, m. p. $199-200^{\circ}$.

α -Methylaminobutyric acid crystallises with $1H_2O$ in tufts of colourless prisms, and commences to sublime at 280° (compare Duvillier, Abstr., 1881, 87); the *mercury salt*, $(C_5H_{10}O_2N)_2Hg$, forms crusts of colourless crystals and does not melt below 260° ; the *sulphate*,



crystallises in slender needles, m. p. $199-200^{\circ}$; the *platinichloride* $(4H_2O)$ crystallises in long, orange-yellow prisms, sinters at $65-70^{\circ}$, m. p. 72° ; the *anhydrous salt* sinters at 141° , m. p. 150° , and decomposes at 210° ; the *ethyl ester*, $C_7H_{15}O_2N$, is a liquid, b. p. $51-52^{\circ}/8$ mm., D^{20}_{18} 0.9348. The *platinichloride* of α -methylguaninobutyric acid lactam (compare Duvillier, Abstr., 1883, 220),



forms dark orange-yellow crystals, m. p. $186-187^{\circ}$ (decomp.).

γ -Methylaminobutyric acid may be prepared by the action of anhydrous methylamine on ethyl γ -chlorobutyrate (compare Tafel and Wassmuth, Abstr., 1907, i, 719); the *hydrochloride* forms thin plates, m. p. 125° ; the *platinichloride* $(2H_2O)$ forms orange-red prisms, m. p. $85-90^{\circ}$; the *anhydrous salt* softens at 150° , sinters at 157° , m. p. 160° , and decomposes at 202° ; the *sulphate*, $(C_5H_{11}O_2N)_2 \cdot H_2SO_4 \cdot 2H_2O$, crystallises in colourless plates, and passes at 110° after several hours into the *hydrogen sulphate*, $C_5H_{11}O_2N \cdot H_2SO_4$, a viscid, hygroscopic mass. Attempts to isolate the ethyl ester were unsuccessful, since it readily dissociates into ethyl alcohol and 1-methylpyrrolidone (compare Tafel and Wassmuth, loc. cit.); the *platinichloride* of the latter substance, $(C_5H_9ON)_2 \cdot H_2PtCl_6 \cdot 2H_2O$, is a pale yellow, crystalline substance.

γ -Methylguaninobutyric acid, $NH:C(NH_2) \cdot NMe \cdot [CH_2]_3 \cdot CO_2H$, prepared by the action of cyanamide on γ -methylaminobutyric acid,

crystallises in crusts of small, colourless prisms, m. p. 307° ; the crystalline *hydrochloride*, m. p. $117-126^{\circ}$, *sulphate*, colourless prisms, m. p. $245-246^{\circ}$ (decomp.), *nitrate*, colourless crystals, m. p. 133° , and *platinichloride*, reddish-brown crystals, m. p. $190-191^{\circ}$, were analysed. All attempts to prepare the corresponding lactam were unsuccessful. W. H. G.

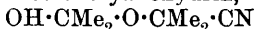
Preparation of Alkyleneiminosulphonates. CHEMISCHE FABRIK VON HEYDEN AKT.-GES. (D.R.-P. 209502).—The interaction of aldehydes and aminosulphonic acids furnishes compounds having the general formula $\text{CHR}:\text{N}\cdot\text{SO}_3\text{R}_1$, where R represents hydrogen or a carbon residue and R_1 a metal or salt-forming group.

Sodium methyleneiminosulphonate, $\text{CH}_2:\text{N}\cdot\text{SO}_3\text{Na}$, a crystalline powder, m. p. 125° , charring at 230° , prepared from sodium aminosulphonate and formaldehyde, is readily soluble in water. *Barium ethylideneiminosulphonate*, prepared by the action of acetaldehyde on barium aminosulphonate, forms crystalline leaflets. *Ammonium methyleneiminosulphonate*, $\text{CH}_2:\text{N}\cdot\text{SO}_3\cdot\text{NH}_4$, m. p. 185° , is decomposed if heated above 50° in aqueous solution. These compounds are of therapeutic value. F. M. G. M.

Cyanohydrins. II. and III. A. J. ULTÈE (*Rec. trav. chim.*, 1909, 28, 248—256, 257—260. Compare this vol., i, 293).—The cyanohydrins derived from aldehydes are, in general, very little dissociated at the ordinary temperature.

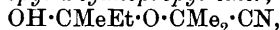
Cyanomethyl alcohol, first prepared by Henry (Abstr., 1890, 739), has D^{19} 1.1039, n_D^{19} 1.41168. If during its preparation the water is expelled by evaporation on a water-bath at atmospheric pressure, it is very liable to polymerise, becoming dark brown. Cyanomethyl alcohol polymerises very readily in the presence of a trace of alkali. α -Cyanoethyl alcohol (Gautier, *Ann. Chim. Phys.*, 1869, [iv], 17, 148) has b. p. $90^{\circ}/17$ mm., D^{14} 0.9959, n_D^{14} 1.40644; at 25° in the presence of a trace of alkali, acetaldehyde and hydrogen cyanide combine to the extent of 99.55%. α -Cyano-*n*-propyl alcohol has b. p. $102-103^{\circ}/23$ mm., D^{15} 0.9690, n_D^{15} 1.41745; combination between aldehyde and hydrogen cyanide at 25° occurs to the extent of 99.54%. α -Cyano-*n*-butyl alcohol (Justin, Abstr., 1885, 137) has b. p. $110.5-111^{\circ}/20.5$ mm., $D^{15.5}$ 0.9434, $n_D^{15.5}$ 1.42285; combination at equilibrium at 25° amounts to 99.69%. α -Cyanoisobutyl alcohol (Lipp, Abstr., 1881, 84) has b. p. $106-106.5^{\circ}/22$ mm., D^{16} 0.9453, n_D^{16} 1.42215; combination at equilibrium at 25° amounts to 99.69%. α -Cyano-*n*-heptyl alcohol (Gautier, *loc. cit.*) has m. p. -10° , b. p. $143.5-144^{\circ}/19$ mm., $D^{14.5}$ 0.9099, $n_D^{14.5}$ 1.43787; the extent of combination at equilibrium at 25° is 99.69%. Benzaldehydecyanohydrin cannot be purified by distillation under reduced pressure, but by fractional crystallisation the author has raised the m. p. to $21.5-22^{\circ}$; at 25° combination at equilibrium amounts to 95.87%. In the presence of a trace of alkali a small quantity is converted into the acetal, $\text{CHPh}(\text{O}\cdot\text{CHPh}\cdot\text{CN})_2$, described by Stollé (Abstr., 1902, i, 468). The cyanohydrin derived from furfuraldehyde could not be obtained, but the *anilino*-derivative, $\text{C}_4\text{H}_5\text{O}\cdot\text{CH}(\text{NHPh})\cdot\text{CN}$, was prepared in crystals, m. p. 74° , which readily become rose-coloured.

When a mixture of equimolecular quantities of acetone and acetonecyanohydrin [α -cyanoisopropyl alcohol] are submitted to a current of dry hydrogen chloride and heated in a reflux apparatus for several hours, Urech's diacetonecyanohydrin,



(Abstr., 1873, 59), is formed; it crystallises in needles, m. p. 162—163°.

α -Hydroxy- α -methylpropyl α -cyanopropyl ether,



long needles, m. p. 116—117°, is prepared similarly.

Dicyclohexanonecyanohydrin, $\text{OH} \cdot \text{C}_6\text{H}_{10} \cdot \text{O} \cdot \text{C}_6\text{H}_{10} \cdot \text{CN}$, has m. p. 194°.

E. H.

Prussian Blue and Turnbull's Blue. II. ERICH MÜLLER and THEOPHIL STANISCH (*J. pr. Chem.*, 1909, [ii], 80, 153—170. Compare this vol., i, 142).—Solutions of ferric chloride and potassium ferrocyanide, of the same concentrations as before, have been mixed in proportions varying between 9 : 1 and 1 : 9, and the resulting precipitates have been examined *in situ* by the methods previously described, the results being checked by an estimation, as sulphate, of the potassium remaining in the solution. The results, which are expressed graphically, lead to the following conclusions. When x , denoting $\text{FeCl}_3/\text{K}_4\text{Fe}(\text{CN})_6$, > 1.33 , the precipitate consists entirely of insoluble Prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, which is unaffected by the excess of ferric chloride. When x lies between 1.33 and 1.0, the solution does not contain any iron, and the precipitate consists of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ and $\text{KFe}'''[\text{Fe}(\text{CN})_6]$, containing only the latter when $x = 1$. Hence

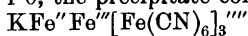
is changed to $\text{KFe}'''[\text{Fe}(\text{CN})_6]$ by $\text{Fe}(\text{CN})_6$ ions. When $x < 1.0$, the ratio of the non-ionisable to the ionisable iron in the precipitate is always unity, but that of the ferrous to the ferric iron increases with the amount of potassium ferrocyanide. The precipitate consists of $\text{KFe}'''[\text{Fe}(\text{CN})_6]$ and $\text{K}_2\text{Fe}''[\text{Fe}(\text{CN})_6]$, and the reactions which occur are (i) $\text{FeCl}_3 + \text{K}_4\text{Fe}(\text{CN})_6 = \text{KFe}'''[\text{Fe}(\text{CN})_6] + 3\text{KCl}$ and (ii) $\text{FeCl}_3 + 2\text{K}_4\text{Fe}(\text{CN})_6 = \text{K}_2\text{Fe}''[\text{Fe}(\text{CN})_6] + \text{K}_3\text{Fe}(\text{CN})_6 + 3\text{KCl}$. Hence

$\text{KFe}'''[\text{Fe}(\text{CN})_6]$ is reduced by $\text{Fe}(\text{CN})_6$ ions, and the reaction $\text{KFe}'''[\text{Fe}(\text{CN})_6] + \text{K}_4\text{Fe}(\text{CN})_6 \rightleftharpoons \text{K}_2\text{Fe}''[\text{Fe}(\text{CN})_6] + \text{K}_3\text{Fe}(\text{CN})_6$ must be reversible, since the solution still contains $\text{Fe}(\text{CN})_6$ ions when $x = 0.5$. It should be noted that the precipitate does or does not contain potassium according as $x < \text{or} > 1.33$, and also that ionisable ferrous iron is present or not in the precipitate according as $x < \text{or} > 1.0$.

The results are almost the same when the precipitations are effected in 0.1*N*-hydrochloric acid.

Exactly similar experiments have been performed with solutions of ferrous chloride and potassium ferricyanide. It has been shown previously (*loc. cit.*) that the precipitates are always ferrocyanides. When y , denoting $\text{FeCl}_2/\text{K}_3\text{Fe}(\text{CN})_6$, > 1.33 , the ratio of ferrous to ferric iron in the precipitate is always 1.33, and that of the non-ionisable to the ionisable iron is 0.75. Hence the reaction is: $3\text{K}_3\text{Fe}(\text{CN})_6 + 4\text{FeCl}_2 = \text{KFe}'''\text{Fe}_3'''[\text{Fe}(\text{CN})_6]_3 + 8\text{KCl}$, and the precipitate of insoluble

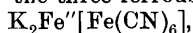
Turnbull's blue is unaffected by the excess of ferrous chloride. When y lies between 1.33 and 1.0, the precipitate contains



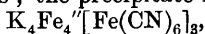
and $KFe'''[Fe(CN)_6]_3'''$, and consists of the latter alone when $y = 1$. When $y < 1$, the precipitate always consists of $KFe'''[Fe(CN)_6]_3'''$, which is therefore unchanged by an excess of potassium ferricyanide. All Turnbull's blues, the precipitates obtained from ferrous salts and potassium ferricyanide, contain potassium.

The authors' and Hofmann's experiments (this vol., i, 637) are not comparable, since the latter deal with precipitates after atmospheric oxidation. C. S.

Ferrous Ferrocyanides. ERICH MÜLLER and W. TREADWELL (*J. pr. Chem.*, 1909, [ii], 80, 170—182. Compare preceding abstract).—The effects of the reactions of aqueous solutions of ferrous chloride and potassium or hydrogen ferrocyanide, of heating potassium ferrocyanide and dilute sulphuric acid, and of heating an aqueous solution of hydrogen ferrocyanide, all in an atmosphere of hydrogen or carbon dioxide, have been examined and the precipitates analysed *in situ* by the methods already described. The results are not conclusive, but it appears probable that only the three ferrous ferrocyanides,



$K_4Fe_4''[Fe(CN)_6]_3$, and $Fe_2''[Fe(CN)_6]$, can exist. The last is formed when an aqueous solution of hydrogen ferrocyanide is heated until hydrogen cyanide ceases to be evolved. The two compounds containing potassium are precipitated from solutions containing potassium, ferrocyanogen, and ferrous ions; the precipitate is mainly



when potassium ferrocyanide reacts with a large excess of ferrous chloride, whilst $K_2Fe''[Fe(CN)_6]$ is the chief product under the converse conditions or when potassium ferrocyanide is heated with 0.5*N*-sulphuric acid. C. S.

[Stable Soluble Compounds of Organic Substances and Silver Double Salts.] ALBERT BUSCH (D.R.-P. 209345. Compare Abstr., 1907, i, 370).—The compound of hexamethylenetetramine with silver carbonate, $5C_6H_{12}N_4 \cdot 3Ag_2CO_3 \cdot 15H_2O$, can be rendered soluble and stable by digestion with albumen, after which hydrogen sulphide, ammonium sulphide, or dilute sodium chloride solutions give no precipitate of silver salts.

Albumen (70 parts) is dissolved in 200 parts of water and heated to 40—50°, the double carbonate (30 parts) is added, and the heating continued at a lower temperature and evaporated, preferably in a vacuum. The product contains 7.5% of silver. F. M. G. M.

Preparation of 2:6-Dichloro- and 2:3:6-Trichloro-toluene-4-sulphonyl Chlorides. ANILINFARBEN UND EXTRAKT-FABRIKEN VORM. J. R. GEIGY IN BASEL (D.R.-P. 210856).—*p*-Toluenesulphonyl chloride is treated at 70—75° with sufficient antimony pentachloride to furnish 2—3 atoms of chlorine. When cool, the mass is hydrolysed with alkali to a mixture of the corresponding acids, or the acyl group

can be completely removed and the resulting mixture of 2:6-di- and 2:3:6-tri-chlorotoluenes separated by fractional distillation.

F. M. G. M.

Sulphonation of Naphthalene. Quantitative Examination. P. C. J. EUWES (*Rec. trav. chim.*, 1909, 28, 298—338).—When equimolecular quantities of naphthalene and 100% sulphuric acid are heated for eight hours, the product at 80° consists almost wholly of the α -sulphonic acid. As the temperature employed rises, the proportion of β -acid formed increases, reaching a maximum between 150° and 160°, above which temperature considerable quantities of sulphone and disulphonic acid are produced. The amount of naphthalene remaining unattacked diminishes from 27% at 80° to 6% at 161°.

Experiments in which the duration of heating was varied show that the primary product of sulphonation is the α -acid, which is gradually transformed into the β -isomeride. Thus after thirty-five minutes at 129° the product contains 79.1% of the α -acid, whilst after six hours the proportion is reduced to 45.1%. At 143° and 158°, however, conditions of equilibrium are attained, and may be reached either by sulphonating naphthalene or by heating lead naphthalene- β -sulphonate with equivalent weights of sulphuric acid and water.

The author accepts the explanation offered by Merz and Weith (*Ber.*, 1870, 3, 195) and by Friedländer and Lucht (*Abstr.*, 1894, i, 138), that the transformation is due to the hydrolysis of the two acids into naphthalene and sulphuric acid, and subsequent resulphonation, the α -acid being more stable at low, and the β -acid at high, temperatures. This view is supported by the observations that, when either acid is heated in a medium containing water, naphthalene is formed, and that the β -acid is not converted into its isomeride when heated with fuming sulphuric acid at 129°.

At 129° the product of heating the β -sulphonic acid with sulphuric acid has not the same composition as the product of sulphonating naphthalene at this temperature. In explanation of this, the author suggests that at 129° the above hydrolysis is largely replaced by an irreversible intramolecular change of the α - into the β -acid, the change being effected catalytically by sulphuric acid, but inhibited when the latter contains a certain amount of water or the reaction product.

The presence of water in the sulphuric acid used for sulphonating naphthalene diminishes the amount of hydrocarbon attacked, and largely accelerates the transformation of the α -acid, equilibrium being reached with 96% sulphuric acid in two hours instead of the six hours required with 100% acid. Addition of sulphur trioxide largely increases the amount of sulphone formed, whilst phosphoric oxide causes the production of much disulphonic acid.

Lead and mercuric sulphates have practically no effect on the reaction.

E. H.

Action of Bromine on β -Methylnaphthalene in the Presence of Aluminium Bromide. F. BODROUX and FELIX TABOURY (*Bull. Soc. chim.*, 1909, [iv], 5, 826—827).—In the presence of aluminium bromide, bromine reacts with β -methylnaphthalene, furnishing penta-

bromo-β-methylnaphthalene, $C_{10}H_7MeBr$, which forms slender, white needles, m. p. 285—286°. E. H.

Doubly Linked Carbon Atoms and the Carbon Nitrogen Linking. HERMANN EMDE (*Arch. Pharm.*, 1909, 247, 314—332).—It is well known that the single linking between the carbon and the nitrogen atoms is frequently easily ruptured when the group C·N is in the neighbourhood of an olefinic linking. The author quotes numerous examples from the literature to illustrate in what circumstances such is the case, and the conclusions are drawn that in the combination C:C·N a loosening of the union between carbon and nitrogen is effected by an olefinic linking, but not by the benzene double linking (centric linking), and also that a similar loosening in the combination C:C·C·N is caused by olefinic or centric linkings, but in the former case only when the olefinic linking is present in a large group, such as cinnamyl, not in a smaller radicle, such as allyl. As typical examples, neurine in aqueous solution readily loses trimethylamine, aniline is a stable substance, cinnamyltrimethylammonium chloride and sodium amalgam yield phenylpropylene and trimethylamine, whilst trimethylallylammonium chloride is unaffected by nascent hydrogen in either acid or alkaline solution. C. S.

Doubly Linked Carbon Atoms and the Carbon Nitrogen Linking. II. Cinnamylamino-compounds. HERMANN EMDE and MAX FRANKE (*Arch. Pharm.*, 1909, 247, 333—350. Compare this vol., i, 565 and following abstracts).—Cinnamyl chloride and 10% alcoholic ammonia in eight days at the ordinary temperature yield mono- and di-cinnamylamine, whilst at 100° in three days, according to Posner, the secondary and tertiary bases are the chief products. The authors now find that the number of hydrogen atoms in ammonia replaced by the cinnamyl group increases with the concentration of the ammonia. When cinnamyl chloride, concentrated methyl alcoholic ammonia, and ether are kept for fourteen days, the chief product is a crystalline *chloride*, m. p. 189° (*nitrate*, m. p. 201°; *iodide*, m. p. 176°), which is also obtained by heating cinnamyl chloride and tricinnamylamine at 100° for thirty minutes; although the analytical data point to the composition $C_{72}H_{73}N_3Cl_2$, the authors provisionally regard the substance as tetracinnamylammonium chloride, since it is converted by sodium amalgam into tricinnamylamine and phenylpropylene.

The remainder of the paper is a description of the behaviour of cinnamyl chloride with different amines. With cold 33% alcoholic dimethylamine it yields dimethylamine hydrochloride, *cinnamyl dimethylamine hydrochloride*, m. p. 188° (*platinichloride*, $C_{22}H_{30}N_2 \cdot H_2PtCl_6$, m. p. 140°), and *dicinnamyl dimethylammonium chloride* [*platinichloride*, $(C_{20}H_{24}N)_2PtCl_6$, m. p. 192°; *cadmichloride*, $(C_{20}H_{24}N)_2CdCl_4$, m. p. 161°]. With ethereal ethylamine at 0°, it yields ethylamine hydrochloride and *tricinnamylethylammonium chloride*, m. p. 188° [*platinichloride*, $(C_{20}H_{32}N)_2PtCl_6$, m. p. 184°]. With triethylamine in five days it yields *cinnamyl triethylammonium chloride* [*platinichloride*, $(C_{15}H_{24}N)_2PtCl_6$, m. p. 180°; *aurichloride*, $(C_{15}H_{24}N)AuCl_4$, m. p. 107°]. With ethereal

propylamine it yields *dicinnamylpropylamine hydrochloride*, m. p. 167° [*platinichloride*, $(C_{21}H_{24}N)_2, H_2PtCl_6$, m. p. 122°]. With tripropylamine it yields *cinnamyltripropylammonium chloride* [*platinichloride*,

$(C_{18}H_{30}N)_2PtCl_6$, m. p. 197° ; *aurichloride*, m. p. 96°]. With ethereal aniline it yields *dicinnamylaniline*, m. p. 88° [*platinichloride*, $(C_{24}H_{23}N)_2, H_2PtCl_6$, m. p. 173° decomp.]. With methylaniline, it yields a red oil, which appears to be *phenyldicinnamylmethylammonium chloride* [unstable *platinichloride*, $(C_{25}H_{26}N)_2PtCl_4$, m. p. 117° decomp.]. With dimethylaniline in fourteen days, it yields *phenylcinnamyl dimethylammonium chloride* [*platinichloride*, $(C_{17}H_{20}N)_2PtCl_6$, m. p. 177° decomp.; *cadmichloride*,

$(C_{17}H_{20}N)_2CdCl_4$, m. p. 141°]. With quinoline in three days it yields *cinnamylquinolinium chloride* [*platinichloride*, $(C_{18}H_{16}N)_2PtCl_6$, m. p. 202° ; *aurichloride*, m. p. 228°]. C. S.

Doubly Linked Carbon Atoms and the Carbon Nitrogen Linking. III. Methylated Benzylamines. HERMANN EMDE (*Arch. Pharm.*, 1909, 247, 351—368).—The reaction between methyl iodide, benzylamine, and methyl alcohol is not a convenient method for the preparation of methylated benzylamines, since the crystalline product is a difficultly separable mixture of iodides of constant m. p., 133.5° . Dibenzylamine, methyl alcohol, and methyl iodide (1 mol.) react to form dibenzylamine hydriodide, *dibenzyl dimethylammonium iodide*, m. p. 191° (*platinichloride*, m. p. 208° decomp.), and a *periodide* of dibenzylmethylamine, $C_{35}H_{54}N_3I_4$, m. p. 155° .

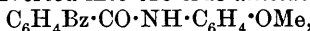
Methylated benzylamines are conveniently obtained by the interaction of benzyl chloride and the methylamines. The action of benzyl chloride on trimethylamine has been examined by Collie and Schryver (*Trans.*, 1890, 57, 778), and on dimethylamine by Jackson and Wing (*Abstr.*, 1887, 721). Benzyl chloride and 33% alcoholic methylamine (>2 mol.) react at 0° to form methylamine hydrochloride, benzylmethylamine, and *dibenzylmethylamine*, b. p. $304-305^{\circ}$ (corr.), which forms a *platinichloride*, m. p. 192° (decomp.), and two *aurichlorides*, $C_{15}H_{17}N, HAuCl_4$, m. p. 135° , and $C_{30}H_{36}N_2Cl_5Au$, m. p. $134-136^{\circ}$, the former being obtained by adding a concentrated solution of the hydrochloride to an excess of 10% gold chloride, and the latter by adding 10% gold chloride to a dilute solution of the hydrochloride.

C. S.

Doubly Linked Carbon Atoms and the Carbon-Nitrogen Linking. IV. Behaviour of Quaternary Ammonium Compounds towards Nascent Hydrogen. HERMANN EMDE (*Arch. Pharm.*, 1909, 247, 369—391. Compare this vol., i, 565 and preceding abstracts).—The comparative stability of the systems $C:C:N$ and $C:C:C:N$ has been examined during the continuation of previous work. In addition to the results previously recorded, the author finds that aqueous or dilute alcoholic solutions of cinnamyltriethylammonium chloride, cinnamyltripropylammonium chloride, *dicinnamyl dimethylammonium chloride*, phenyldicinnamylmethylammonium chloride and tricinnamylethylammonium chloride suffer reductive

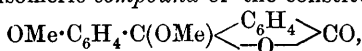
fission by treatment with 5% sodium amalgam, yielding phenylpropylene and the tertiary amine, whilst benzyltrimethylammonium chloride in a similar manner yields trimethylamine and toluene. Cinnamylpyridinium chloride, cinnamylquinolinium chloride, trimethylallylammonium iodide, and phenyltrimethylammonium iodide do not behave in a similar way by treatment with sodium amalgam. The preceding reductive fissions are not effected by nascent hydrogen in acid solution. C. S.

Anilides and Anisidides of Aromatic Ketonic and Aldehydic Acids. HANS MEYER and RICHARD TURNAU (*Monatsh.*, 1909, 30, 481—496. Compare Abstr., 1908, i, 25).—Equal weights of *p*-anisidine and *o*-benzoylbenzoic acid, when heated together over an oil-bath and subsequently over a water-bath, yielded a *ψ*-anisidide, $C_{21}H_{17}O_3N$, which crystallises in colourless needles, m. p. 198°; this substance can be titrated directly with 10% potassium hydroxide, and when treated with phenylhydrazine its anisidine residue is replaced by the phenylhydrazine with the formation of the phenylhydrazone of *o*-benzoylbenzoic acid, m. p. 168° (compare Abstr., 1885, 797, 1905, i, 133). The *ψ*-anisidide is converted into the true *anisidide*,



by gently boiling for twenty minutes with twenty times its weight of acetic anhydride; this substance crystallises in colourless needles, m. p. 204°; it is neutral to potassium hydroxide, and no longer reacts with phenylhydrazine.

A 70% yield of *p*-methoxybenzoylbenzoic acid was obtained by heating a solution of phthalic anhydride and anisole in nitrobenzene with aluminium chloride; its m. p., 148°, is rather higher than that quoted by Nourisson (Abstr., 1886, 1029). It yields two isomeric methyl derivatives; the *methyl ester*, $CO_2Me \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot OMe$, m. p. 63°, is obtained by the action of methyl sulphate on *p*-hydroxybenzoylbenzoic acid; the isomeric *compound* of the constitution



obtained by the action of thionyl chloride on *p*-methoxybenzoylbenzoic acid, has m. p. 84°. The study of the reaction between anisidine and anisoylbenzoic acid was commenced, but has not yet been brought to a satisfactory conclusion.

The *ψ*-anilide of opianic acid described by Liebermann is converted into the true *anilide*, $C_{16}H_{15}O_4N$, by boiling with excess of acetic anhydride; it crystallises in leaflets, m. p. 179°; when heated with phenylhydrazine it is converted into the *hydrazone* of opianic acid, $C_{22}H_{21}O_3N_3$, pale yellow needles, m. p. 204°. The *ψ*-anilide of opianic acid is reduced by zinc and acetic acid to a compound, $C_{16}H_{15}O_3N$, which forms slender needles, m. p. 141°.

Meconine and aniline heated together in presence of aniline hydrochloride do not yield the *ψ*-anilide of opianic acid, but give instead *methylnormeconineanilide*, $C_{16}H_{16}O_4N$, which contains one methyl group less, and has the constitution

$$\begin{matrix} CH & \text{---} & CH : C \cdot CH_2 \\ | & & | \\ C(OMe) \cdot C(OH) : C & \text{---} & CO \end{matrix} > NPh ; \text{ it forms}$$

colourless, glistening leaflets, m. p. 164° ; its *acetyl* derivative forms slender needles, m. p. 161° .

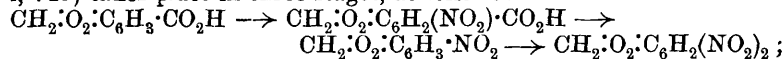
The anilide of meconine, when heated with aniline and aniline hydrochloride, also yields methyl*norme*conine anilide; the latter compound does not react with methyl sulphate. P. H.

Preparation of Nitro-1 : 8-naphthasultamsulphonic Acid and 2 : 4-Dinitro-1 : 8-naphthasultam. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 210222).—When 1 : 8-naphthasultam-2 : 4-disulphonic acid is treated at $75-80^{\circ}$ with nitric acid (D 1·2), either one or both the sulphonic groups are replaced by a nitro-group. In the presence of 50% sulphuric acid, the mono- or di-nitro-compound is formed, according to the amount of nitric acid employed; whilst in the absence of sulphuric acid, but with a greatly increased quantity of nitric acid, the dinitro-compound alone is obtained.

Sodium nitro-1 : 8-naphthasultamsulphonate is a crystalline, yellow powder, which dyes wool a yellow colour. 2 : 4-Dinitro-1 : 8-naphthasultam, m. p. 262° (with decomp.), is a deep yellow powder, which forms a salt when dissolved in sodium carbonate or hydroxide; it also dissolves readily in hot alcohol, but only sparingly in the cold solvent or in water. F. M. G. M.

4 : 5-Dinitro-1 : 2-catechol Methylene Ether. [4 : 5-Dinitro-1 : 2-methylenedioxybenzene.] EFISIO MAMELI (*Gazzetta*, 1909, 39, ii, 172—186).—The author describes the methods by which he has established the constitution of dinitromethylenedioxybenzene (compare Abstr., 1906, i, 743), which is of especial interest as it forms the final product of the energetic nitration of compounds containing the methylenedioxybenzene grouping, even when the positions occupied by the nitro-groups are previously filled by carboxyl groups, or by lateral chains. The formation of this dinitro-compound hence serves as a test for such grouping, which occurs in many natural products.

The formation of dinitromethylenedioxybenzene from piperonylic acid (compare Jobst and Hesse, Abstr., 1878, 733; Mameli, 1904, i, 743) takes place in three stages, as follows:



each of these stages has been realised by the author.

That one of the nitro-groups in dinitromethylenedioxybenzene occupies the 4-position with respect to the methylenedioxy-group is shown by the formation of this compound from nitropiperonylic acid and nitromethylenedioxybenzene. That the second nitro-group is in the *o*-position to the first is shown by the formation from an alcoholic solution of dinitromethylenedioxybenzene, by the action of gaseous ammonia, of a nitroaminomethylenedioxybenzene, which, by reduction with zinc and acetic acid and condensation of the reduction product with phenanthraquinone, yields the corresponding phenazine. That this second nitro-group occupies the 5- and not the 3-position is shown by diazotising the nitroaminomethylenedioxybenzene and replacing the diazo-group by cyanogen, the compound thus obtained being identical with that obtained by dehydrating the oxime of 2-nitro-4 : 5-

methylenedioxybenzaldehyde. The two nitro-groups in dinitromethylenedioxybenzene are hence in the 4- and 5-positions with respect to the methylenedioxy-group.

4 - Nitro - 5 - aminomethylenedioxybenzene, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_2(\text{NO}_2)\cdot\text{NH}_2$, crystallises in shining, red laminae, or tufts of acicular crystals, m. p. 199° . The phenazine obtained from the corresponding diamino-compound, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_2\text{:N}_2(\text{C}_{14}\text{H}_8)$, forms a dark yellow, crystalline powder, m. p. 305° , which sublimes in slender, golden-yellow needles, and dissolves in sulphuric acid, giving a reddish-violet coloration.

T. H. P.

Preparation of Phthalimidocatechol Ethers. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 209962).—*Phthalimidoacetylveratrole*, m. p. 202° , white powder insoluble in alcohol, is obtained by heating together on the water-bath equal weights of veratrole, phthalylglycyl chloride, and aluminium chloride. The mixture is treated successively with water and dilute hydrochloric acid, the unchanged veratrole removed in a current of steam, and the residue purified by extraction with alcohol.

α -*Phthalimidopropionyl chloride*, white crystals, m. p. 71° , is produced by treating dry α -phthalimidopropionic acid, m. p. 160° (phthalyl- α -alanin), with phosphorus pentachloride on the water-bath until a solution is obtained; the phosphoryl chloride is distilled off in a vacuum, and the product crystallised from petroleum. The foregoing acid chloride is fused on the water-bath with an equal weight of veratrole, and, after cooling, the same quantity of aluminium chloride introduced.

α -*Phthalimidopropionylveratrole*, white powder, m. p. 212° , is isolated in a manner similar to that employed for its lower homologue.

β -*Phthalimidopropionylveratrole*, colourless needles, m. p. 175° , is prepared in the same way from β -phthalimidopropionyl chloride.

F. M. G. M.

Homocatechol and its Methyl Ethers. O. DE VRIES (*Rec. trav. chim.*, 1909, 28, 276—297).—Homocatechol, prepared from creosol by Stoermer's method (Abstr., 1908, i, 190), has m. p. 65° (Béhal and Desvignes give 51° , Abstr., 1892, 1312; Cousin gives 49 — 50° , Abstr., 1899, i, 346), $D_{25}^{73.6}$ 1.1567, $D_4^{73.6}$ 1.1287, $n_D^{73.6}$ 1.5373, $n_D^{73.6}$ 1.5425, $n_F^{73.6}$ 1.5560, n_G 1.5678.

By cooling in liquid air, creosol has been solidified in large, colourless prisms, m. p. 5.5° (thermometer in liquid). At the ordinary temperature it is a colourless oil, D_{25}^{25} 1.0951 (Perkin, Trans., 1896, 69, 1185, gives 1.0886), $D_{38.6}^{38.6}$ 1.0867, D_4^{25} 1.0919, $D_4^{38.6}$ 1.0789, n_C^{25} 1.5303, n_D^{25} 1.5353, n_F^{25} 1.5483, n_G^{25} 1.5596, $n_C^{38.6}$ 1.5237, $n_D^{38.6}$ 1.5288, $n_F^{38.6}$ 1.5418, $n_G^{38.6}$ 1.5530.

Creosol picrate forms orange-yellow needles, m. p. 112° (corr.) (Goedike, Abstr., 1894, i, 119, and Bamberger and Vischner, Abstr., 1901, i, 220, give m. p. 96°).

For *m*-nitro-*p*-cresol, an intermediate compound in the synthesis of isocresol by Brasch and Freyss' method (Abstr., 1891, 1231), the author finds m. p. 32.5° (corr.), b. p. $114.5^\circ/7.5$ mm.,

125°/22 mm., whilst Hofmann and Miller (Abstr., 1881, 592) gave m. p. 33°, Noelting and Wild (Abstr., 1885, 973) 33·5°, Brasch and Freyss 36·5° (non-corr.) and Upson (Abstr., 1904, i, 734) 34°. The author's specimen was purified through the sodium salt, which was recrystallised from alcohol. The substance has $D_{38}^{38\cdot6}$ 1·2489, $D_4^{38\cdot6}$ 1·2399, n_C^{25} 1·5720, n_D^{25} 1·5828, $n_G^{38\cdot6}$ 1·5657, $n_D^{38\cdot6}$ 1·5763.

The methyl ether, hitherto only obtained as an oil, forms beautiful large crystals, m. p. 8·5° (corr. thermometer in substance), b. p. 159°/15 mm, D_{25}^{25} 1·2059, D_4^{25} 1·2025, n_C^{25} 1·5458, n_D^{25} 1·5536, n_F^{25} 1·5737. The observed m. p. of *isocreosol* is 35·5° (corr.), whilst Perkin gave 37—39° (*loc. cit.*). *isoCreosol* has $D_{38}^{38\cdot6}$ 1·0820, $D_4^{38\cdot6}$ 1·0742, $n_C^{38\cdot6}$ 1·5219, $n_D^{38\cdot6}$ 1·5269, $n_F^{38\cdot6}$ 1·5396, $n_G^{38\cdot6}$ 1·5504. *isoCreosol* picrate forms crystals, m. p. 87·5°.

Homoveratrole, hitherto obtained only as an oil, forms large, colourless prisms, m. p. 21° (corr. thermometer in substance), D_{25}^{25} 1·0540 (Perkin gave 1·0525), D_4^{25} 1·0509, n_C^{25} 1·5209, n_D^{25} 1·5257, n_F^{25} 1·5383, n_G^{25} 1·5493.

Comparison of the physical constants obtained for homocatechol, creosol, *isocreosol*, and homoveratrole shows that, on the whole, they are in accordance with the general rules. As found generally by Brühl (Trans., 1907, 91, 115), there is a small exaltation of the observed over the calculated refractive indices and dispersive powers. The exaltations of the dispersive powers for the hydroxy- and methoxy-groups are approximately the same as those found in other phenols. E. H.

Tannin Methyl Ether. JOSEF HERZIG and V. RENNER (*Monatsh.*, 1909, 30, 543—554. Compare Herzig and Tscherne, Abstr., 1905, i, 354).—Since tannin methyl ether is an amorphous substance, its degree of purity is determined better by a methoxyl estimation than by ultimate analysis. Tannin methyl ether is practically unaffected by further treatment with diazomethane, and also by a mixture of boiling glacial acetic acid, zinc, sodium acetate, and acetic anhydride. Its decomposition by 10% potassium hydroxide is slow, and the undissolved portion, after five to six hours' treatment, possesses the same properties as the original substance. It appears very probable, therefore, that tannin methyl ether either is an individual substance or consists of substances which have not only nearly the same composition, but also contain the same number of substituted hydroxyl groups. The authors retain this opinion despite the fact that the rotation of tannin methyl ether varies greatly according to the treatment it receives.

The decomposition of tannin methyl ether by potassium hydroxide with the production of gallic acid di- and tri- methyl ethers has been examined by Herzig and Tscherne (*loc. cit.*). The authors have repeated the experiments, using 10% potassium hydroxide, and confirm the previous results. They show also that the ethers are stable to the potassium hydroxide, and that no other decomposition product can be detected.

From the two constitutions proposed by Nierenstein for the two constituents which he claims to be present in commercial tannin, it appears probable that tannin methyl ether is a pentamethoxy-derivative of either or of both constituents.

C. S.

Cholesterol. IV. J. MAUTHNER (*Monatsh.*, 1909, 30, 635—647. Compare Abstr., 1907, i, 921).—Windaus's claim that the constitution of ψ -cholestene differs from that of cholestene only in a shifting of the olefinic linking from the ultimate to the penultimate pair of carbon atoms in the side-chain is untenable, since the two unsaturated hydrocarbons yield, by the addition of hydrogen, isomeric and not identical saturated hydrocarbons, cholestane and ψ -cholestane. The existence of these two isomeric saturated hydrocarbons, one of which is obtained directly, and the other indirectly, from cholestene, does not harmonise with the theory of a terminal methylene group in cholestene, and gives rise to the question, which still awaits an answer, whether cholestene really has a constitution similar to that of cholesterol.

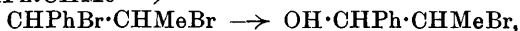
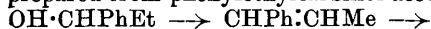
Cholestane, $C_{27}H_{46}$, m. p. 80° , obtained by passing hydrogen for fifty to seventy hours through an ethereal solution of cholestene in the presence of platinum-black, crystallises in leaflets and has $[\alpha]_D + 24.42^\circ$ in chloroform. ψ -*Cholestane*, $C_{27}H_{46}$, m. p. $69-70^\circ$, obtained in a similar manner from ψ -cholestene, crystallises in needles, and has $[\alpha]_D + 25.45^\circ$ in chloroform. A mixture of equal weights of the two hydrocarbons has m. p. $50-51^\circ$. *Chlorocholestane*, $C_{27}H_{45}Cl$, m. p. $115-116^\circ$, obtained in a similar way from cholesteryl chloride, has $[\alpha]_D + 29.49^\circ$ in chloroform and 24.22° in benzene. The halogen is firmly retained, and is practically unattacked by fourteen hours' boiling with zinc dust and zinc acetate in glacial acetic acid or by boiling solutions of sodium methoxide and sodium amyl oxide. Chlorocholestane is reduced, however, to cholestane by sodium and boiling amyl alcohol.

neoCholestene, $C_{27}H_{44}$, m. p. 69° , $[\alpha]_D + 64.07$, is an unsaturated hydrocarbon obtained by boiling chlorocholestane with quinoline for one to two hours. It forms a *dibromide*, $C_{27}H_{44}Br_2$, m. p. 125° , $[\alpha]_D^{25} + 75.27^\circ$, and is reduced in ethereal solution by hydrogen and platinum-black to cholestane, thus proving that *neocholestene* and cholestene differ only in the position of the double linking. C. S.

Saturated α -Hydroxy- β -alkyloxy-derivatives of Aromatic Olefins with Propenyl Chains. EFISIO MAMELI (*Gazzetta*, 1909, 39, ii, 154—165).—The author has studied the action of alkali alkylloxides on β -bromo- α -hydroxydihydro-derivatives of the following aromatic compounds containing the propenyl group, in order to ascertain whether the corresponding α -hydroxy- β -alkyloxy-derivatives are obtained: propenylbenzene, anethole, *isosafrole*, asarone, and *isoapiole*. The results show the possibility of the formation of certain α -hydroxy- β -alkyloxy-derivatives of the type $OH \cdot CHR \cdot CHMe \cdot OMe$, substitution of the bromine in the β -position by the alkyloxy-group failing only when the latter is met by steric hindrance within the molecule; this is the case with the β -bromo- α -hydroxy-derivatives of bromo*isosafrole* and bromo*isoapiole*.

[With EDOARDO BROCCA].— β -*Bromo- α -hydroxy- α -phenylpropane*,
 $OH \cdot CHPh \cdot CHMeBr$,

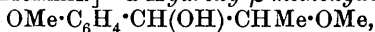
prepared from phenylethylcarbinol according to the scheme:



is a greenish-yellow, oily liquid, b. p. 126—129°/45 mm., with an extremely irritating odour.

α-Hydroxy-β-methoxy-α-phenylpropane, $\text{OH} \cdot \text{CHPh} \cdot \text{CHMe} \cdot \text{OMe}$, prepared by the action of sodium methoxide on *β*-bromo-*α*-hydroxy-*α*-phenylpropane, is a colourless oil, b. p. 145—147°/70—80 mm.

[With CESARE BIGNAMI.]—*α-Hydroxy-β-methoxydihydroanethole*,



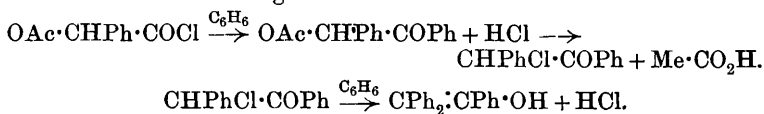
prepared by the action of sodium methoxide on the hydroxy-bromide, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CHMeBr}$ (compare Höring, Abstr., 1906, i, 951), is an oily liquid, b. p. 171—175°/65—70 mm.

[With RAIMONDO BONU.]—*β*-Bromo-*α*-hydroxydihydroisosafole, in ethereal solution at 0°, absorbs hydrogen chloride, forming a mixture of chloro- and bromo-derivatives from which no definite product could be separated. In ethereal solution, it also combines slowly with sodium, but yields no definite compound. It reacts vigorously with concentrated nitric acid, giving a resinous mixture of nitro-derivatives. When treated with sodium methoxide, it yields *α-hydroxy-β-methoxy-dihydroisosafole*, $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CHMe} \cdot \text{OMe}$, as a colourless oil, b. p. 182—185°/10—20 mm., $D^{17} 1.19$; the corresponding *acetyl* derivative, $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}(\text{OAc}) \cdot \text{CHMe} \cdot \text{OMe}$, is a colourless oil, b. p. 200—205°/10—20 mm.

T. H. P.

Action of Benzene and Aluminium Chloride on the Chlorides of Acetylated Hydroxy-acids. RICHARD ANSCHÜTZ and PAUL FÖRSTER (*Annalen*, 1909, 368, 89—94. Compare Anschütz, Abstr., 1906, i, 516).—It was thought possible that benzoylcarbonyl acetate would be obtained by acting on a solution of acetylglycolyl chloride (acetoxycetyl chloride) in benzene with aluminium chloride, but although this compound is probably formed, it must be decomposed at once by the hydrogen chloride, yielding benzoylcarbinol and acetyl chloride, which latter substance reacts with benzene under the influence of the aluminium chloride, forming acetophenone.

Acetylmandelyl chloride, when similarly treated, does not yield benzoin acetate, but triphenylvinyl alcohol, which probably owes its formation to the following series of reactions:



This explanation receives support from the fact that triphenylvinyl alcohol is readily obtained by the action of aluminium chloride on a solution of desyl chloride in benzene.

W. H. G.

Benzoyl Iodide and its Relation towards Simple Ethers. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 651—659).—The interaction of benzoyl chloride and the compound of magnesium iodide with ether yields 45% of the quantity of benzoyl iodide calculated from the equation: $\text{MgI}_2 + 2\text{Ph} \cdot \text{COCl} = \text{MgCl}_2 + 2\text{Ph} \cdot \text{COI}$. The amount of ethyl benzoate formed at the same time is 26.6% of the quantity calculated on the assumption that the reaction proceeds according to Blaise's scheme (Abstr., 1905, i, 111). Benzoyl iodide (compare Liebig and Wöhler, *Annalen*, 1832, 266) forms acicular

crystals, m. p. $+3^{\circ}$. At the ordinary temperature it is slowly but completely decomposed by water, or by an alkali carbonate or hydroxide. Concentrated ammonia solution acts on it very readily, yielding ammonium benzoate and benzamide. In absence of a magnesium salt it reacts readily with ethers according to the equation: $\text{Ph}\cdot\text{COI} + \text{R}\cdot\text{O}\cdot\text{R} = \text{RI} + \text{Ph}\cdot\text{CO}_2\text{R}$. With mixed ethers, both iodides are formed, but mainly the one with the smaller radicle. Thus, of the two possible reactions with ethyl *iso*amyl ether, $\text{Ph}\cdot\text{COI} + \text{Et}\cdot\text{O}\cdot\text{C}_5\text{H}_{11} = \text{Ph}\cdot\text{CO}_2\text{Et} + \text{C}_5\text{H}_{11}\text{I}$ and $\text{Ph}\cdot\text{COI} + \text{Et}\cdot\text{O}\cdot\text{C}_5\text{H}_{11} = \text{Ph}\cdot\text{CO}_2\cdot\text{C}_5\text{H}_{11} + \text{EtI}$, the second predominates. The same two reactions occur when ethyl *iso*amyl ether is treated with benzoyl chloride and potassium iodide, the predominating one being that in which ethyl iodide and *iso*amyl benzoate are formed.

T. H. P.

Preparation of Acids and Amides by the Action of Ammonium Sulphide on Aliphatic Aromatic Ketones. CONRAD WILLGERODT (*J. pr. Chem.*, 1909, [ii], 80, 183—191).—The paper gives an account of the amides and acids obtained since 1887 by the author's method of heating aliphatic aromatic ketones and yellow ammonium sulphide at a high temperature.

Ketone.	Temp.	Product.	M.p.
α -Naphthyl methyl ketone..	210—230°	α -Naphthylacetamide	—
„ ethyl „	—	α -Naphthylpropionamide ...	140°
„ propyl „	—	α -Naphthylbutyramide	160
<i>as-m</i> -Xylol methyl „	—	<i>as-m</i> -Xylolacetamide	183
Cymyl methyl „	270—300	Cymylacetamide	123
ψ -Cumyl methyl „	260—280	ψ -Cumylacetamide	174
Mesityl methyl „	260—280	Mesitylacetamide.....	208
—	—	<i>as-m</i> -Xylolbutyramide	123—124
—	—	<i>as-m</i> -Xylolpropionamide ..	107
<i>as-m</i> -Xylol <i>isopropyl</i> „	235—240	<i>as-m</i> -Xylol <i>isobutyramide</i> ...	120
—	—	<i>p</i> -Xylolbutyramide.....	125
<i>as-o</i> -Cymyl methyl „	250	<i>as-o</i> -Cymylacetamide	112
β -Naphthyl methyl „	220—225	β -Naphthylacetamide.....	200
„ ethyl „	250—260	β -Naphthylpropionamide ...	168
<i>p</i> -Tolyl methyl „	250	<i>p</i> -Tolylacetamide.....	185
2-Bromo-5-tolyl methyl ketone	250—270	2-Bromo-5-tolylacetamide...	168
4-Bromo-3-tolyl methyl ketone	250—270	4-Bromo-3-tolylacetamide ...	152
2-Chloro-5-tolyl methyl ketone	250—270	2-Chloro-5-tolylacetamide ...	162
4-Chloro-3-tolyl methyl ketone	250—270	4-Chloro-3-tolylacetamide ...	141

C. S.

Preparation of Acids and Amides from Phenyl Alkyl Ketones by means of Yellow Ammonium Sulphide. CONRAD WILLGERODT and FRANZ HUBERT MERK (*J. pr. Chem.*, 1909, [ii], 80, 192—200).—The authors find that the best conditions for the preparation of amides from ketones (preceding abstract) are to heat the ketone and yellow ammonium sulphide solution, in the proportion 1 : 5, for five to six hours at 200—220° in sealed glass tubes; the yellow ammonium sulphide solution is prepared by saturating con-

centrated ammonium hydroxide with hydrogen sulphide and dissolving 1 gram of sulphur per each 10 grams of the resulting liquid. When ammonium sulphide prepared from hydrogen sulphide and alcoholic ammonia is used, the reaction takes a somewhat different course, and hydrocarbons and arylthiophens are produced in addition to amides and acids. With regard to the limits within which the Willgerodt reaction is applicable, experiments on the ketones $\text{Ph}\cdot\text{CO}\cdot\text{R}$, where R is Me, Et, Pr^a , Pr^s , C_4H_9 (*iso*), C_6H_{13} , and $\text{C}_{15}\text{H}_{31}$, show that the yield of amide and acid decreases as the molecular weight of R increases. Thus phenyl methyl ketone gives 49·6% of phenylacetamide and 13·5% of phenylacetic acid, phenyl hexyl ketone gives 25% of heptamide and no acid, whilst phenyl pentadecyl ketone yields neither amide nor acid of the same carbon content as the original ketone.

C. S.

Preparation of *o*-Nitro-derivatives of Nitriles. KALLE & Co. (D.R.-P. 210563).—When *o*-nitrophenylpyruvic acid (10·5 parts) is dissolved in 100 parts of water and treated successively with a 10% solution of nitric acid (36·5 parts) and a concentrated solution containing 3·6 parts of sodium nitrite, *o*-nitrobenzonitrile slowly crystallises out.

F. M. G. M.

Action of Silver Cyanide on Acetoxycarboxylic Chlorides. RICHARD ANSCHÜTZ (*Annalen*, 1909, 368, 76—88).—An investigation on the transformation of acetoxycarboxylic chlorides into nitriles of α -ketocarboxylic acids.

[With RUDOLF BÖCKER.]—*Acetoxyphenylpyruvonitrile*,
 $\text{OAc}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{CN}$,

is formed by heating acetylmandelyl chloride with silver cyanide at 120° for 2—3 hours; it crystallises in tufts of long, colourless needles, m. p. $52\cdot5^\circ$, b. p. $150\text{—}151^\circ/10$ mm., and is converted by fuming hydrochloric acid into mandelic acid.

[With REINHOLD CLAUS.]—*o*-Acetoxyphenylglyoxylonitrile,
 $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CN}$,


similarly prepared from acetylsalicylyl chloride, crystallises in long, stout plates, m. p. $111\text{—}112^\circ$, b. p. $149\text{—}151^\circ/14$ mm.; measurements of the monoclinic crystals are given. It is converted by concentrated sulphuric acid or a solution of hydrochloric acid in glacial acetic acid into the corresponding *amide*, $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$, which crystallises in hard, small, white prisms, m. p. 170° (decomp.).

o-Acetoxyphenylglyoxylic acid, $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$, cannot be obtained by treating the amide just described with nitrous acid, but is prepared by acting on this substance for several days with 38% hydrochloric acid at a temperature not above 15° ; it crystallises with $1\text{H}_2\text{O}$ in fern-like aggregates of long, flat, colourless needles, m. p. $101\text{—}106^\circ$; the water is eliminated at 90° , yielding the anhydrous acid, m. p. $134\cdot5\text{—}135\cdot5^\circ$. It is probable that the hydrated acid has the formula $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})_2\cdot\text{CO}_2\text{H}$. The *silver*, $\text{C}_{10}\text{H}_7\text{O}_5\text{Ag}$, and *sodium*, $\text{C}_{10}\text{H}_7\text{O}_5\text{Na}$, salts are amorphous, white substances. The *methyl* ester, $\text{C}_{11}\text{H}_{10}\text{O}_5$, crystallises in white leaflets, m. p. $109\text{—}110^\circ$. Attempts to obtain the lactone by heating the acid were unsuccessful.

W. H. G.

Refractometric Researches. JOHAN F. EYKMAN (*Chem. Weekblad*, 1909, 6, 699—712. Compare Abstr., 1908, ii, 1).—The refractometric constants of the following substances for the hydrogen and helium spectrum have been determined: *cyclohexane*, *cyclohexene*, *bromocyclohexane*, 1:2-dibromocyclohexane, ethyl malonate, ethyl ethanetetracarboxylate, ethyl Δ^2 -cyclopentenemalonate, ethyl Δ^2 -cyclohexenemalonate, ethyl cyclohexylmalonate, cyclohexanecarboxylic acid, cyclopentylacetic acid, heptioic acid, cyclohexylacetic acid, cyclopenteneacetic acid, and cyclohexeneacetic acid.

Ethyl Δ^2 -cyclohexenemalonate, $C_{13}H_{20}O_4$, prepared by condensing ethyl disodiummalonate with dibromocyclohexene, has b. p. $128^\circ/2$ mm.

Δ^2 -cycloHexenemalononic acid, m. p. about 165° , loses carbon dioxide at this temperature, and yields Δ^2 -cyclohexeneacetic acid, $C_8H_{12}O_2$, m. p. $11-12^\circ$, b. p. $135-136^\circ/14$ mm., $120^\circ/5$ mm. Its lactone has b. p. about $250^\circ/760$ mm., $143^\circ/22$ mm. The amide has m. p. $147-148^\circ$. Both acids readily decolorise an acetic acid solution of bromine and an alkaline solution of permanganate. The refractometric results accord with the Δ^2 -structure:  $CH(CO_2R)_2$.

Bromocyclohexane and ethyl sodiomalonate yield *ethyl cyclohexylmalonate*, $C_{13}H_{22}O_4$, b. p. $131-133^\circ/16$ mm. *cycloHexylmalonic acid* has m. p. about 180° (decomp.) (compare Wallach, Abstr., 1907, i, 617).

Ethyl cyclopentenemalonate, prepared from chlorocyclopentene (compare Kraemer and Spilker, Abstr., 1896, i, 189) and ethyl sodiomalonate, has b. p. $141^\circ/16$ mm. *cycloPentenemalononic acid* has m. p. about 150° (decomp.), and, on distillation under diminished pressure, yields *cyclopenteneacetic acid*, $C_5H_7 \cdot CH_2 \cdot CO_2H$, b. p. $93-94^\circ$ /about 2.5 mm., m. p. -19° , which decolorises alkaline permanganate instantly, and combines with bromine in acetic acid solution to form a bromolactone, m. p. 76° . The amide of cyclopenteneacetic acid has m. p. $131-132^\circ$. The constitution of the acid is probably

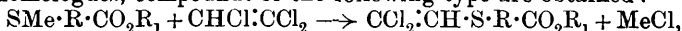
$CO_2H \cdot CH_2 \cdot CH < \begin{matrix} CH_2 \cdot CH_2 \\ CH : CH \end{matrix}$. *cycloPentylacetic acid*, $C_7H_{12}O_2$, prepared

by reducing *cyclopenteneacetic acid* with nickel and hydrogen at $170-175^\circ$, forms large leaflets, m. p. $13-14^\circ$, b. p. $133-134^\circ/23$ mm. (Verwey, Abstr., 1896, i, 671, gives b. p. $139-140^\circ/26$ mm.). It does not decolorise either bromine or alkaline permanganate.

Dibromocyclohexene reacts with two molecules of ethyl sodiomalonate to form *cyclohexene* and ethyl ethanetetracarboxylate, and not a cyclohexanedimalonic ester.

A. J. W.

Preparation of Derivatives of Thiolbenzoic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 210644).—By the action of ethylene-trihalides (trichloroethylene, &c.) on the salts of thiolbenzoic acid and its homologues, compounds of the following type are obtained:



R being a simple or substituted benzene or naphthalene residue, R_1 a metal, alkyl, or aryl group. The new substances are readily soluble in benzene or alcohol, but only sparingly so in petroleum or water.

ω -Dichlorovinylthiolbenzoic acid, $CO_2H \cdot C_6H_4 \cdot S \cdot CH : CCl_2$, forms

colourless crystals, m. p. 173° ; its *ethyl* ester is a brown, viscous oil. *ω*-Dichloro-*p*-bromovinylthiolbenzoic acid forms colourless crystals, m. p. 188° . *ω*-Dichloro-*m*-ethoxyvinylthiolbenzoic acid has m. p. 155° . 1-*ω*-Dichlorovinylthiol-2-naphthoic acid is a yellow, crystalline powder, m. p. 174 — 175° . *ω*-Dibromovinylthiolbenzoic acid is a colourless, crystalline powder, m. p. 181° . F. M. G. M.

Salts of Phenylthioglycollic [Thiolphenylacetic] Acid. NICOLA PARRAVANO and G. TOMMASI (*Gazzetta*, 1909, 39, ii, 60—64).—Thiolphenylacetic acid (compare Ulpiani and Ciancarelli, *Abstr.*, 1904, i, 162) may be prepared by heating together mandelonitrile and a solution of hydrogen chloride saturated at 0° , in a sealed tube at 120 — 130° .

In aqueous solution the sodium salt has a molecular weight equal to one-half the calculated value, so that it undergoes dissociation into $\text{SH}\cdot\text{CHPh}\cdot\text{CO}_2$ and Na. This aqueous solution dissolves the carbonates or hydroxides of cadmium, bismuth, copper, nickel, and cobalt; these metals cannot be detected in the liquids by the ordinary reagents. The *cobalt* compound, $\text{C}_{16}\text{H}_{12}\text{O}_4\text{S}_2\text{CoNa}_2\cdot 2\text{H}_2\text{O}$, was obtained crystalline, and was found to have a molecular weight one-third of the calculated value in aqueous solution. It behaves, therefore, as the normally-dissociated sodium salt of cobaltothiophenylacetic acid, $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{S}\cdot\text{Co}\cdot\text{S}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, a conclusion supported by conductivity measurements of the solution. T. H. P.

Disengagement of the Formyl Group from Certain Aromatic Aldehydes. CURIO M. MUNDICI (*Gazzetta*, 1909, 39, ii, 123—133).—When treated with hydrochloric acid, β -hydroxynaphthaldehyde readily loses the formyl group, but with chlorine or nitric acid it gives only substituted β -naphthols. When, however, its bispyrazolone derivative is boiled with dilute acid or alcohol, decomposition into β -naphthol and methylenebispyrazolone takes place (compare Betti and Mundici, *Abstr.*, 1907, i, 322). β -Methoxynaphthaldehyde exhibits similar behaviour, although to a less degree; with nitric acid it gives the methyl ether of a nitro- β -naphthol and a nitroaldehyde, and with phenylmethylpyrazolone the bispyrazolone compound, decomposition of the latter with formation of methylene derivative only occurring on heating with dilute acid or in a sealed tube with alcohol. With phenylmethylpyrazolone, 2:4:6-trihydroxybenzaldehyde behaves in the cold like β -hydroxynaphthaldehyde, whilst 2:4:6-trimethoxybenzaldehyde gives a bispyrazolone derivative, which is readily resolved into trimethylphloroglucinol and methylpyrazolone by dilute acids.

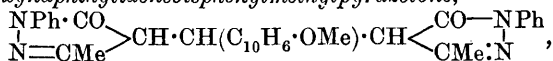
The instability of the aldehyde group in β -hydroxynaphthaldehyde is hence not peculiar to the naphtholic derivative, but is inherent to the nature and position of the substituents.

The action of chlorine on β -hydroxynaphthaldehyde yields the tetrachloro- β -ketohydronaphthol obtained by Zincke (*Abstr.*, 1889, 265) by the action of chlorine on β -naphthol in acetic acid solution. The action of nitric acid gives 1:6-dinitro- β -naphthol.

An improved method is given for the preparation of β -methoxy-

naphthaldehyde (compare Rousset, Abstr., 1898, i, 591). The action of nitric acid on this compound yields: (i) a nitro- β -methoxynaphthaldehyde, $C_{12}H_9O_4N$, which forms crystals, m. p. 174° : its constitution was not determined; (2) the methyl ether of 1-nitro- β -naphthol, $C_{11}H_9O_3N$, which crystallises from benzene in lemon-yellow plates, m. p. 126° .

β -Methoxynaphthylidenebisphenylmethylpyrazolone,



prepared from phenylmethylpyrazolone and β -methoxynaphthaldehyde, forms white needles, m. p. 195° , and is soluble in dilute alkali solution and in concentrated sulphuric acid, giving a yellow coloration. This compound is accompanied by *β -methoxynaphthylidenephenylmethylpyrazolone,*

β -methoxynaphthylidenephenylmethylpyrazolone,

$$\begin{array}{c} \text{NPh} \cdot \text{CO} \\ | \\ \text{N} = \text{CMe} \end{array} > \text{C} \cdot \text{CH} \cdot \text{C}_{10}\text{H}_6(\text{OMe}),$$

which crystallises in

aggregates of small needles, m. p. $219\text{--}2^\circ$, and gives an intense red coloration with concentrated sulphuric acid. When boiled in alcoholic solution, this compound is converted into an isomeride, which crystallises in slender, yellowish-red prisms, m. p. 135° , and in alcoholic solution in presence of a few crystals of the original compound, m. p. $219\text{--}2^\circ$, is converted into the latter.

The *bispyrazolone* derivative of 2:4:6-trimethoxybenzaldehyde, $C_{30}H_{30}O_5N_4$, crystallises in mammillary aggregates of white needles, m. p. 204° . T. H. P.

Condensation of Aminohydroxy-acids with Aromatic Aldehydes. III. and IV. ERNESTO PUXEDDU (*Gazzetta*, 1909, 39, ii, 21—32, 32—43).—The following results have been obtained in continuance of the author's previous work (Abstr., 1908, i, 286; this vol., i, 238).

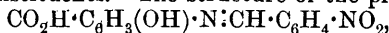
6-Amino-*m*-hydroxybenzoic acid condenses with the three nitrobenzaldehydes to give *compounds*, all of which have the formula $C_{14}H_{10}O_5N_2$; that from *o*-nitrobenzaldehyde crystallises in golden-yellow, prismatic needles, decomposing at 220° ; that from the meta compound crystallises in greenish-yellow, six-faced prisms, decomposing at above 240° , and that from the para forms greenish-yellow, prismatic needles, decomposing at above 240° . The same acid gives with salicylaldehyde the *compound*, $C_{14}H_{11}O_4N$, which separates in yellow needles, decomposing at 248° ; with *p*-hydroxybenzaldehyde, a mixture of two compounds, one golden-yellow and the other dark red; with anisaldehyde, the *compound*, $C_{15}H_{13}O_4N$, which crystallises in yellow, silky needles, m. p. $227\text{--}8^\circ$; with catechualdehyde, a brown, crystalline powder, which is almost insoluble in all the organic solvents and was not analysed, and with vanillaldehyde, the *compound*, $C_{15}H_{13}O_5N$, m. p. 267° (decomp.), which is apparently a mixture of red and yellow crystals and, when dissolved in alcohol, exhibits feeble blue fluorescence.

5-Aminosalicylic acid gives with *o*-nitrobenzaldehyde the *compound*, $C_{14}H_{10}O_5N$, which crystallises from alcohol in yellow, prismatic needles, m. p. 223° (decomp.); with *p*-hydroxybenzaldehyde, the *compound*,

$C_{14}H_{11}O_4N$, which forms orange-yellow, prismatic needles, decomposing at $240-260^\circ$, and when dried in an oven assumes a dark red colour and exhibits a blue reflection; on pouring into water, it again becomes orange-coloured and shows green reflection.

The same acid gives with anisaldehyde a small quantity of a reddish-yellow, crystalline substance, which was not analysed, and with catechualdehyde, the compound, $C_{14}H_{11}O_5N$, a brownish-green powder.

Hydrolysis of the condensation product of 6-amino-*m*-hydroxybenzoic acid and *o*-nitrobenzaldehyde by means of dilute hydrochloric acid yields the two constituents. The structure of the product is hence



the H_2 of the amino-group and the O of the aldehydic group being eliminated in the condensation. The *hydrochloride* of the condensation product, $C_{14}H_{10}O_5N_2 \cdot HCl$, prepared by the action of fuming hydrochloric acid, forms transparent crystals.

Amino-m-cresotic acid hydrochloride, $C_8H_9O_3N \cdot HCl$, separates in colourless, prismatic needles, m. p. 263° (decomp.). The condensation product obtained from amino-*m*-cresotic acid and *o*-nitrobenzaldehyde behaves towards concentrated or dilute hydrochloric acid in the same manner as the product given by 6-amino-*m*-hydroxybenzoic acid and *o*-nitrobenzaldehyde.

In addition to hydrochlorides, these condensation products form sodium salts, which can be obtained crystalline.

Many of the condensation products exhibit fluorescence, in some cases in alcoholic solution, and in others in acid or alkaline solution. It is probable that the fluorescence is connected with the presence of the group $\cdot CH : N \cdot$, which has a fluorogenic character intermediate between those of the groups $\cdot CH : CH \cdot$ and $\cdot N : N \cdot$.

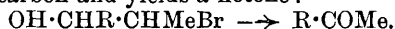
In some instances these condensation products appear to exist in two forms, which are probably the stereoisomerides rendered possible by the presence in the molecule of a carbon atom doubly linked to a nitrogen atom.

In general, the capacity of an aldehyde for reacting with amines increases with an increase in the negative character of the substituent groups in its molecule. The double linking of cinnamaldehyde also appears to stimulate the activity of the aldehyde in this respect.

A table is given showing the degrees of readiness with which the four amino-acids—5-aminosalicylic, 6-amino-*m*-hydroxybenzoic, and amino-*o*- and amino-*m*-cresotic—react with the twelve aldehydes examined.

T. H. P.

Formation of Acetophenones from Derivatives of Propylbenzene. EFISIO MAMELI [with RAIMONDO BONU and CESARE BIGNAMI] (*Gazzetta*, 1909, 39, ii, 165—172. Compare this vol., i, 714).—When a β -bromo- α -hydroxydihydro-derivative of an aromatic olefine containing the propenyl group is oxidised, either by chromic acid or by boiling with hydrochloric acid under a reflux condenser, it loses an atom of carbon and yields a ketone:



For the occurrence of this reaction, which furnishes a new method of preparation of acetophenones, it is necessary that the compound em-

ployed should not contain double linkings and that the hydroxyl group should be in the α -position and the bromine atom in the β -position. If one of these conditions is not observed, a ketone is obtained with all three carbon atoms in the side-chain (compare Hell, Abstr., 1896, i, 169; Hell and Gärtner, Abstr., 1895, i, 341; Hell and von Günther, Abstr., 1896, i, 20; Hoering, Abstr., 1904, i, 577; 1905, i, 902; Balbiano, Abstr., 1906, i, 186; 1907, i, 522; Tiffeneau and Daufresne, Abstr., 1907, i, 701; Mameli, Abstr., 1904, i, 1023).

β -Bromo- α -hydroxydihydroisosafole, under the above conditions, yields acetylpipecone (compare Feuerstein and Heimann, Abstr., 1901, i, 465), whilst β -bromo- α -hydroxydihydroanethole gives *p*-methoxyacetophenone, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{COMe}$, as a greenish-yellow oil, b. p. 185–190°/120 mm., difficult to purify from traces of bromo-derivative (Eykmann, Bergema, and Henrard, Abstr., 1905, i, 361, give m. p. 35°); the *semicarbazone* has m. p. 181–182°.

T. H. P.

Transformation of 4:4':4'':4'''-Tetrachlorobenzopinacone into β -4:4':4'':4'''-Tetrachlorobenzopinacolin and the Velocity of the Reaction. PIETER A. MEERBURG (*Rec. trav. chim.*, 1909, 28, 267–269).—It has been shown previously (*ibid.*, 1905, 24, 131) that, making certain assumptions, the transformation of 4:4':4'':4'''-tetrachlorobenzopinacone into the β -pinacolin by acetyl chloride at 70° is probably a unimolecular reaction, intermediate products not being formed. At 30°, however, it was observed that the quantity of β -pinacolin formed increased with the time to a maximum, then diminished to a minimum, and then rapidly increased again. The experiments at 30° have been repeated, certain improvements having been made in the method employed. The results do not give the characteristic curves obtained previously, but trustworthy conclusions cannot be drawn from them, since among the values calculated for the constant (K), assuming the reaction to be unimolecular, one or more occur widely different from the rest. The cause of these deviations was not discovered.

E. H.

Transformation of α -4:4':4'':4'''-Tetrachlorobenzopinacolin into β -4:4':4'':4'''-Tetrachlorobenzopinacolin and the Velocity of the Reaction. PIETER A. MEERBURG (*Rec. trav. chim.*, 1909, 28, 270–271. Compare Montagne, Abstr., 1907, i, 141).— β -4:4':4'':4'''-Tetrachlorobenzopinacolin when heated with alcoholic potassium hydroxide solution is decomposed into 4:4':4''-trichlorotriphenylmethane and potassium *p*-chlorobenzoate. Accordingly, the rate of change of the α - into the β -pinacolin was measured by heating the alcoholic solution of the reaction products (after increasing periods of time) with known amounts of potassium hydroxide dissolved in alcohol, and estimating the alkali used. From the experimental results the values of the constant K , calculated on the assumption that the change is a unimolecular one, indicate that this assumption is justified, and that accordingly the transformation of the α - into the β -pinacolin is an intramolecular reaction.

E. H.

Intramolecular Atomic Migrations. IX. Conversion of α -Glycols into Aldehydes. P. J. MONTAGNE (*Rec. trav. chim.*, 1909, 28, 272–275. Compare Abstr., 1905, i, 445).—Tiffeneau supports

the view that in the transformation of α -glycols into the corresponding aldehydes, intermediate compounds, probably diethylene oxides, are formed (Abstr., 1908, i, 165).

The determinations made by Meerburg (preceding abstracts) of the rate of change of tetrachlorobenzopinacone into β -tetrachlorobenzopinacolin agree with the formula for a unimolecular reaction. The transformation can therefore only proceed through the formation of an intermediate compound (α -4 : 4' : 4'' : 4'''-tetrachlorobenzopinacolin) if one or other of the two changes involved proceeds with relatively very great velocity. Meerburg has shown that the change of the α - into the β -pinacolin is not a rapid one, and an experiment made by the author showed that after thirty minutes' heating with acetyl chloride at 70° the greater proportion of the tetrachlorobenzopinacone remains unchanged, indicating that the first assumed change is not more rapid. The conclusion is drawn that the transformation of the pinacone into the β -pinacolin does not involve the formation of the intermediate α -pinacolin, and therefore is not in accordance with Tiffeneau's hypothesis. E. H.

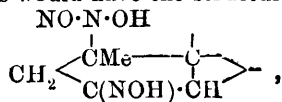
Action of Sulphuric Acid on Santonin. I. GUIDO BARGELLINI and A. MANNINO (*Gazzetta*, 1909, 39, ii, 101—105).—According to Andreocci and Bertolo (Abstr., 1899, i, 301), the action of hydrochloric acid on santonin yields desmotroposantonin, $[\alpha]_D + 112^\circ$, whilst that of sulphuric acid (D 1.44) gives *l*-desmotroposantonin, $[\alpha]_D - 140^\circ$.

The authors find, however, that these two acids do not exert specific actions on santonin. For, if sulphuric acid (D 1.44) acts on santonin at a low temperature, *l*-desmotroposantonin is formed, whilst at a high temperature the *d*-form, $[\alpha]_D + 112^\circ$, is obtained.

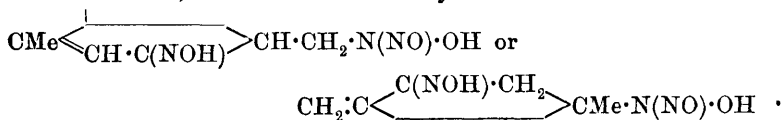
It is further shown that *l*-desmotroposantonin, and also *isodesmotroposantonin*, m. p. 188°, $[\alpha]_D + 129^\circ$, are converted by the action of sulphuric acid (D 1.44) into desmotroposantonin, $[\alpha]_D + 112^\circ$, which is therefore the stable form.

Under the conditions which result in the formation of *isodesmotroposantonin* from desmotroposantonin (heating with potassium hydroxide at 210°), *l*-desmotroposantonin remains unchanged. T. H. P.

Hydroxylamineoximes of Santonin. III. LUIGI FRANCESCONI and GUIDO CUSMANO (*Gazzetta*, 1909, 39, ii, 105—115).—The authors have examined further α - and β -hydroxylaminosantoninoximes and their derivatives (see Abstr., 1908, i, 272), in particular the action on them of nitrous acid (compare following abstract). The nitroso-compounds obtained are nitrosohydroxylamines and not pernitroso-compounds, the hydroxylamino-group being attacked by nitrous acid in preference to the oxime grouping. They give intense Liebermann's reactions, are soluble in alkali hydroxide solution, and are readily decomposed in the cold by mineral acids and in the hot by acetic acid, yielding alcohol-oximes by the replacement of the group N_2O_2H by OH. On the basis of Angeli and Marino's constitution for santonin, these nitroso-compounds would have the structure :



whilst according to the authors' formula for *santonin*, they would have one of the two following structures if the α - and β -compounds are stereoisomerides, or both of them if they are structural isomerides :



Attempts were made to eliminate the oxime grouping from these compounds in order to ascertain whether a saturated tertiary ketonic alcohol (Angeli and Marino's formula) is formed, or either a primary ketonic alcohol or an unsaturated tertiary ketonic alcohol (authors' formula). It is found, however, that these oxime-alcohols only partly lose hydroxylamine, giving resinous products; in preference to such change, dehydration and molecular rearrangement occur, the product being, for both the α - and β -compounds, a single compound, $\text{C}_{15}\text{H}_{19}\text{O}_3\text{N}$, which contains the group $\cdot\text{CO}\cdot\text{NH}\cdot$, but no oxime or nitrile group, and is possibly a lactam derived from the oxime by Beckmann's transformation. From this ready elimination of water, it is concluded that both the oxime-alcohols contain a tertiary alcoholic group, and that the α - and β -compounds are stereoisomerides.

α -Hydroxylaminosantoninoxime has $[\alpha]_D^{25} + 47.41^\circ$. Its *hydrochloride*, $\text{C}_{15}\text{H}_{22}\text{O}_4\text{N}_2\cdot\text{HCl}$, crystallises in massive prisms or minute needles, m. p. 212° (decomp.).

β -Hydroxylaminosantoninoxime has $[\alpha]_D^{25} - 3.00^\circ$. The *hydrochloride*, $\text{C}_{15}\text{H}_{22}\text{O}_4\text{N}_2\cdot\text{HCl}$, forms shining, flattened, pentagonal crystals, m. p. 163° (decomp.).

Hydroxylammoniohydroxylaminosantoninoxime has $[\alpha]_D^{25} + 8.97^\circ$.

T. H. P.

Nitrosohydroxylaminosantoninoximes and their Derivatives. IV. LUIGI FRANCESCONI and GUIDO CUSMANO (*Gazzetta*, 1909, 39, ii, 115—123. Compare preceding abstract).—Oxidation of β -hydroxylaminosantoninoxime by means of mercuric oxide or ferric chloride yields a reddish-yellow powder, $\text{C}_{15}\text{H}_{20}\text{O}_5\text{N}_2$, which reduces Fehling's solution, dissolves in acids or alkalis, begins to blacken at 200° , and decomposes completely at about 230° . If the oxidation is effected by means of permanganate, a substance is obtained having the same composition and properties as the above, with the exception that it decomposes completely at 200° .

Oxidation of α -hydroxylaminosantoninoxime yields a pale yellow powder, decomposing at about 240° .

Reduction of the two hydroxylaminosantoninoximes by various means led to no definite products.

Nitroso- β -hydroxylaminosantoninoxime, $\text{C}_{15}\text{H}_{21}\text{O}_5\text{N}_3$, crystallises in yellow prisms, decomposing at 160 — 172° , and is converted by the action of acetic acid into

β -Hydroxysantoninoxime, $\text{C}_{15}\text{H}_{21}\text{O}_4\text{N}$, which forms tufts of white, silky prisms, softening at 175° and evolving gas at 195° , and dissolves in the cold in acids or alkali hydroxide solutions, giving liquids which only reduce Fehling's solution after boiling; $[\alpha]_D^{25} + 126.8^\circ$.

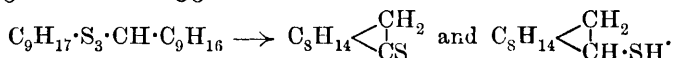
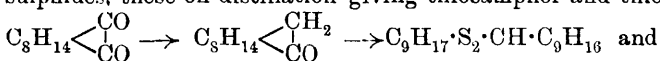
Nitroso- α -hydroxylaminosantoninoxime, $C_{15}H_{21}O_5N_3$, crystallises in tufts of white, feathery needles, which turn yellow at 100° and decompose at 164° ; $[\alpha]_D^{12} - 112.8^\circ$.

α -Hydroxysantoninoxime, $C_{15}H_{21}O_4N$, crystallises in large, pyramidal prisms, m. p. $199-200^\circ$, $[\alpha]_D^{12} + 219.6^\circ$.

The lactam compound, $C_{15}H_{19}O_3N$, obtained by the action of dilute hydrochloric acid or sodium hydroxide solution on either α - or β -hydroxysantoninoxime, crystallises in shining, rectangular plates, which turn yellow at 200° and decompose rapidly at 250° . When boiled with 10% sodium hydroxide solution, this lactam yields a small quantity of a nitrogenous compound, containing 62.61% C and 7.65% H, and crystallising in long, hard prisms, which soften at 190° and decompose rapidly at 230° ; this compound gives an aqueous solution which has an acid reaction towards litmus, and when heated at 180° for some time yields the original lactam, $C_{15}H_{19}O_3N$. T. H. P.

New Researches in the Camphor Group. III. ENRICO RIMINI (*Gazzetta*, 1909, 39, ii, 196—212. Compare this vol., i, 728).—The action of concentrated sulphuric acid on tanacetone or pernitrosotanacetone yields isotanacetone, which is more readily prepared by this reaction than by Wallach and Scharfenberg's method (*Abstr.*, 1895, i, 620). Tanacetone, when heated, is converted into carvotanacetone, whilst by the action of hot 50% sulphuric acid, or cold concentrated sulphuric acid, it yields isotanacetone; carone, on the other hand, gives one and the same product, namely, carvenone, when heated or when treated in the cold with concentrated sulphuric acid.

Camphorquinone, when gradually heated to 150° in a sealed tube with solid ammonium hydrosulphide and alcohol, is first reduced to camphor, part of which reacts with the excess of ammonium hydrosulphide, yielding a mixture consisting principally of bornyl di- and trisulphides, these on distillation giving thiocamphor and thioborneol:



The behaviour of fenchone towards ammonium hydrosulphide is quite similar to that of camphor, the product of the reaction being *thiofenchone*, $C_{10}H_{16}S$, which is obtained as a red oil, b. p. $207-208^\circ/734$ mm., m. p. 24° . When reduced with aluminium amalgam, thiofenchone yields *thiofenchyl alcohol*, b. p. $206^\circ/732$ mm., m. p. 24° , which, with mercuric acetate, gives the *mercury mercaptide*, $C_{20}H_{34}S_2Hg$, crystallising in white, silky needles, m. p. 149° . With semicarbazide, phenylhydrazine, or hydroxylamine, thiofenchone yields the semicarbazone, hydrazone, or oxime of fenchone.

The thioterpenones of the camphor series may be readily prepared by heating the pernitrosoterpenones with ammonium hydrosulphide on the water-bath, the reaction: $>CN_2O_2 + H_2S = >CS + N_2O + H_2O$, being analogous to that effected by dilute acid or alkali: $>CN_2O_2 + H_2O = >CO + N_2O + H_2O$.

Thiocamphor, prepared in this way from pernitrosocamphor, has

m. p. 136°, and the mercury mercaptide corresponding with thioborneol, 175° (compare Wuyts, Abstr., 1903, i, 428). Accompanying the thio-camphor is a substance, $C_{40}H_{68}S_5$, m. p. 178—179°, probably identical with the pentasulphide, m. p. 183—185°, obtained by Wuyts (*loc. cit.*). The mercaptide of thioborneol, obtained from camphorquinone, has m. p. 153°, the higher m. p. of the product prepared from pernitroso-camphor being unexplained.

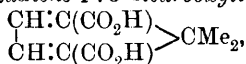
The action of ammonium hydrosulphide on pernitrosofenchone yields thiofenchone as principal product, and small proportions of fenchone and of a sulphur-containing oil, presumably composed of a mixture of polysulphides. Further, pernitrosomenthone gives a mixture of menthone and thiomenthone, and tanacetone yields thioisotananacetone.

T. H. P.

Syntheses in the Camphor and Terpene Series. I. Complete Synthesis of *apo*Camphoric Acid and its Derivatives. GUSTAV KOMPPA (*Annalen*, 1909, 368, 126—155).—Many unsuccessful attempts to synthesise *apocamphoric* acid are briefly mentioned, whilst the method which led finally to the complete synthesis of this compound is described in detail. A short account of this work has already appeared (compare Abstr., 1901, i, 668). The following are the compounds which have not been described in detail hitherto.

Methyl diketo*apocamphorate* (1 mol.), when treated with hydroxylamine hydrochloride (2 mols.) and potassium carbonate (1 mol.) in aqueous methyl alcohol, yields the *oxime*, $C_{11}H_{15}O_6N$, which crystallises in small, flat, white needles, m. p. 149—150°.

2 : 2-Dimethylcyclopentadiene-1 : 3-dicarboxylic acid,



may be prepared from 4 : 5-dihydroxy*apocamphoric* acid (1) by distillation under 25 mm. pressure; (2) by boiling with 45% sulphuric acid or 10% hydrochloric acid; (3) by heating with anhydrous oxalic acid at 120—130°. It crystallises in rosettes of flat needles, m. p. 242—243°.

2 : 2-Dimethyl- Δ^4 -cyclopentene-1 : 3-dicarboxylic acid (*isodehydroapocamphoric acid*), $\begin{array}{c} \text{CH}\cdot\text{CH(CO}_2\text{H)} \\ | \\ \text{CH}\cdot\text{CH(CO}_2\text{H)} \end{array} > \text{CMe}_2$, is prepared by reducing

4 : 5-dihydroxy*apocamphoric* acid with sodium amalgam or hydriodic acid and red phosphorus. It crystallises in triclinic plates or flat, pointed needles, m. p. 208—209·5°. The *anhydride*, $C_9H_{10}O_3$, prepared by the action of acetyl chloride or acetic anhydride on the acid, forms crystalline nodules, m. p. 193—195°.

2 : 2-Dimethyl- Δ^5 -cyclopentene-1 : 3-dicarboxylic acid (*dehydroapocamphoric acid*), $\begin{array}{c} \text{CH}=\text{C(CO}_2\text{H)} \\ | \\ \text{CH}_2\cdot\text{CH(CO}_2\text{H)} \end{array} > \text{CMe}_2$, results from the action of aqueous sodium hydroxide on β -bromo*apocamphoric* acid; it crystallises in long needles, m. p. 223—224°.

W. H. G.

Terpenes and Ethereal Oils. C. OTTO WALLACH (*Annalen*, 1909, 368, 1—22. Compare this vol., i, 383).—I. *Synthesis of*

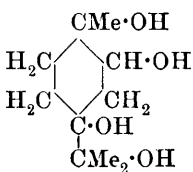
Active α -Pinene from Nopinone.—When nopinolacetic acid is submitted to slow, dry distillation in a current of hydrogen it yields a mixture of *l*- α -pinene, *l*- β -pinene, and fenchene (compare Abstr., 1908, i, 997); the fraction which passes over below 165° is composed almost entirely of the isomeric pinenes, and contains about 10% of the α -compound. The presence of *l*- α -pinene was established by carefully oxidising the mixture of isomerides by means of 1% potassium permanganate solution, whereby it was possible to detect *l*-pinonic acid (compare Barbier and Grignard, Abstr., 1908, i, 852) among the oxidation products.

When nopinolacetic acid is distilled with acetic anhydride it yields β -pinene and an acid, $C_{13}H_{22}O_5$, which crystallises in needles, m. p. $58-59^\circ$, sublimes when heated rapidly, and behaves as a saturated compound towards permanganate. It loses 1 mol. of acetic acid when boiled with aqueous sodium hydroxide, yielding the acid, m. p. $85-86^\circ$, obtained previously (Abstr., 1908, i, 998) by heating nopinolacetic acid with potassium hydrogen sulphate.

β -Pinene, when treated with 3% sulphuric acid or a mixture of equal parts of alcohol and nitric acid (D 1.255), is converted into terpene hydrate.

The formula assigned to the glycol, m. p. $75-77^\circ$, obtained from β -pinene (Abstr., 1908, i, 999) is shown to be correct, since this substance when oxidised by a 1% aqueous solution of potassium permanganate at 0° is converted into nitric acid.

II. *The Erythritol of Terpinolene.*—Terpinolene is most readily obtained by the action of anhydrous formic acid on γ -terpineol.



When oxidised by potassium permanganate it yields *terpinolene erythritol*, m. p. $149-150^\circ$, having the annexed formula; the substance also crystallises with $1H_2O$ in hard, well-defined crystals, which sinter at 90° , m. p. $100-130^\circ$ (decomp.). It is thus definitely established that the erythritol obtained from ordinary terpinene is not derived from terpinolene (compare Abstr., 1908, i, 813).

The product obtained by the dry distillation of anhydrous dihydrocarvylamine hydrochloride contains but a very small quantity of "terpinene," whilst that derived from the phosphate by similar treatment is composed almost entirely of α -terpinene.

Chlorocarvenene, likewise the hydrocarbon derived from it by reduction (compare Semmler, this vol., i, 110), are shown to belong to the terpinene series, since they both yield $\alpha\alpha'$ -dihydroxy- α -methyl- α' -isopropyladipic acid when oxidised. It is made evident, however, that a relatively pure chloroterpinene (chlorocarvenene) can only be obtained with the greatest difficulty by the action of phosphorus pentachloride on carvenone. The density of the chloro-compound cannot be greatly removed from 1 (compare Semmler, *loc. cit.*; Klages and Kraith, Abstr., 1900, i, 42).

[With ERICH GROSSE.]—III. *The Sesquiterpene Present in Siberian Pine-oil.*—A *sesquiterpene*, $C_{15}H_{24}$, has been isolated from Siberian pine-oil, having b. p. $260-268^\circ/760$ mm. (slight decomp.), D_{20}^{20} 0.8725, n_D^{20} 1.4903. The trihydrochloride, $C_{15}H_{24}\cdot 3HCl$, crystallises in colour-

less needles, m. p. 79—80°; the trihydrobromide, $C_{15}H_{21}Br_3$, has m. p. 84°. It is probable, therefore, that three ethylene linkings are present in the sesquiterpene, although only four atoms of bromine combine immediately with the hydrocarbon.

The hydrochloride is undoubtedly identical with limene trihydrochloride (compare Burgess and Page, *Trans.*, 1904, 85, 414); it has not been established whether the hydrocarbon itself is identical with limene or the sesquiterpene obtained from opoponax-oil (Schimmel & Co., *Abstr.*, 1904, i, 603).

W. H. G.

Biological Oxidation of Carone and Fenchone. II. ENRICO RIMINI (*Gazzetta*, 1909, 39, ii, 186—196. Compare *Abstr.*, 1901, i, 393; ii, 522).—When carone is administered by ingestion to a dog and the urine is boiled with dilute sulphuric acid, carvacrol is obtained. Hence in the animal organism the carone undergoes oxidation to hydroxycarone (compare von Baeyer and Baumgärtel, *Abstr.*, 1899, i, 223), which is eliminated in the urine as caroneglycuronic acid; by boiling with dilute sulphuric acid, the latter yields successively hydroxycarone, ketoterpine, and carvacrol. Consequently carone is not hydrolysed, but oxidised, in the animal organism.

Cryoscopic comparison of oxyfenchone (*loc. cit.*) with hydroxycamphor indicates that the former is a keto-alcohol, and its resistance to permanganate in the cold, and the fact that it is not oxidised by Beckmann's chromic mixture to give a diketone, point to its being a saturated tertiary alcohol. According to Glover's formula for fenchone (*Trans.*, 1908, 93, 1285), hydroxyfenchone would have the annexed structure, which appears to the author to be the most probable one.

Fenchonephenylhydrazone, b. p. 202—203°/18 mm., may be prepared by the action of phenylhydrazine acetate on pernitrosofenchone.

T. H. P.

Chemistry of Hops. RUD. SILLER (*Zeitsch. Nahr. Genussm.*, 1909, 18, 241—271).—By extracting the lupulin of hops with ether, evaporating the solvent, dissolving the residue in methyl alcohol, and precipitating by means of methyl-alcoholic lead acetate, the author obtains a lead salt of the α -bitter acid, which, when crystallised from acetic acid, corresponds with the formula $(C_{20}H_{31}O_5Pb)_2O$. He is, however, inclined towards the formula $C_{20}H_{30}O_5Pb$ (compare Barth, *Abstr.*, 1900, ii, 746; 1901, i, 40), the discrepancy in the analytical numbers being ascribed to the ready formation of basic salts and to the presence of traces of resin. The factor for converting the lead salt into free α -acid is 0.6319. In precipitating the lead salt, excess of the precipitant is to be avoided, as it dissolves the precipitate, apparently with formation of basic salts. Traces of the α -acid hence give only a yellow coloration with methyl-alcoholic lead acetate. A method of procedure for the complete precipitation of the α -acid is described.

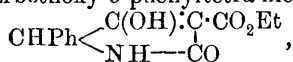
In order to obtain the pure crystallised α -acid, the lead salt is recrystallised once from glacial acetic acid and then decomposed with dilute sulphuric acid and ether. The pure α -acid is extremely resistant

to chemical reagents, but it is rapidly transformed into a resin by heating at a high temperature, absorption of oxygen taking place. Impure α -acid undergoes slow autoxidation. The α -acid contains at least two double linkings, since the molecule unites with four atoms of bromine, giving the compound $C_{20}H_{33}O_5Br_4$. When extracted with light petroleum, disintegrated hops yield far greater amounts of bitter substances than the whole hops.

The γ -resin, generally supposed to be an individual substance, is found to be a mixture of at least two different resins, differing in carbon-content and in solubility in ether.

T. H. P.

The Tetric Acid Group. II. Action of Acetylmandelyl Chloride on Ethyl Sodiomalonate and Ethyl Sodiocyanacetate. RICHARD ANSCHÜTZ and RUDOLF BÖCKER (*Annalen*, 1909, 368, 53—75. Compare Anschütz and Bertram, *Abstr.*, 1903, i, 271).—Acetylmandelyl chloride, similarly to acetylsalicyl chloride (compare this vol., i, 660), condenses with ethyl sodiomalonate, yielding 3-carbethoxy-5-phenyltetric acid, from which 5-phenyltetric acid is obtained on treatment with aqueous potassium hydroxide. Condensation with ethyl sodiocyanacetate leads to the formation of ethyl acetylphenylglycolyl- α -cyanoacetate, $OAc \cdot CHPh \cdot CO \cdot CH(CN) \cdot CO_2Et$, but, unlike the analogous ethyl *o*-acetoxybenzoyl- α -cyanoacetate (*loc. cit.*), this compound, when boiled with ethyl or methyl alcohol, or when treated with cold concentrated hydrochloric acid, yields a substance which is possibly 3-carbethoxy-5-phenyltetric acid,



or, since it does not possess acidic properties, more probably α -carbethoxy- β -keto- γ -phenylbutyrolactam, $CHPh \begin{array}{l} \diagup CO-CH \cdot CO_2Et \\ \diagdown NH \cdot CO \end{array}$.

Attempts to prepare the acid corresponding with this ester by hydrolysing with alkali led to the isolation of two isomeric acids. The relationship existing between these acids and the parent substance is not yet clear.

Acetylmandelic acid, $OAc \cdot CHPh \cdot CO_2H$, prepared by the action of acetyl chloride on mandelic acid, crystallises with $1H_2O$ in slender needles, which effloresce when kept in the air; the anhydrous acid has m. p. 80° ; the *ammonium* salt, $C_{10}H_{13}O_4N$, crystallises in glistening, white scales; the *chloride*, $C_{10}H_9O_3Cl$, is a colourless, oily liquid, b. p. $129^\circ/10$ mm., $132^\circ/12$ mm., $142^\circ/18$ mm.; the *amide*, $C_{10}H_{11}O_3N$, forms tufts of slender, white needles, m. p. 112 — 113° ; the *anilide*, $C_{16}H_{15}O_3N$, crystallises in slender, white needles, m. p. 117.5° ; the *p-phenetidine*, $C_{18}H_{19}O_4N$, forms small, slender, white needles, m. p. 157° ; the *piperidine*, $C_{15}H_{19}O_3N$, crystallises in glistening, white needles, m. p. 98° .

3-Carbethoxy-5-phenyltetric acid, $CHPh \begin{array}{l} \diagup C(OH):C \cdot CO_2Et \\ \diagdown O-----CO \end{array}$, crystallises in small, white needles, m. p. 140° ; the *ammonium* salt, a white powder; *sodium* salt, $C_{13}H_{11}O_5Na$; *ferric* salt, $(C_{13}H_{11}O_5)_3Fe$, a bright red powder, and *cobalt* salt, $(C_{13}H_{11}O_5)_2Co$, small, dark red

crystals, were analysed; the crystalline *nickel*, *lead*, *magnesium*, and *copper* salts were also prepared.

5-Phenyltetronic acid, $\text{CHPh} \begin{array}{c} \text{C(OH):CH} \\ \text{O} \text{---} \text{CO} \end{array}$, crystallises in feathery aggregates of felted, white needles, m. p. 127.5—128.5°; the *ammonium* salt, $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$, forms white, stellate scales, m. p. 148—149° (decomp.); the *sodium* salt, $\text{C}_{10}\text{H}_7\text{O}_3\text{Na}$, has m. p. 105—110°. The acid is converted by sodium nitrite and dilute hydrochloric acid into *α-oximino-β-keto-γ-phenylbutyrolactone*, $\text{CHPh} \begin{array}{c} \text{CO:C:N.OH} \\ \text{O} \text{---} \text{CO} \end{array}$, which crystallises in pale yellow leaflets, m. p. 92—93° (decomp.).

Ethyl phenylacetylglucyl-α-cyanoacetate (*ethyl phenylacetoxycetyl-α-cyanoacetate*) is a brownish-yellow oil; the *silver* salt, $\text{OAc} \cdot \text{CHPh} \cdot \text{C(OAg):C(CN) \cdot CO}_2\text{Et}$, is a white powder. *α-Carbethoxy-β-keto-γ-phenylbutyrolactam*,

$\text{C}_{13}\text{H}_{13}\text{O}_4\text{N}$, crystallises in small, white, thick leaflets, m. p. 220—223° (decomp.); when treated with dilute aqueous sodium hydroxide, it yields two isomeric *acids*, $\text{C}_{11}\text{H}_9\text{O}_4\text{N}$; the one crystallises in silvery-white spangles, m. p. 183° (decomp.), and the other is obtained as a fine, soft, white powder, m. p. 178—179°, at which temperature carbon dioxide is eliminated.

W. H. G.

The Benzotetronic Acid [4-Hydroxycoumarin] Group. I. RICHARD ANSCHÜTZ (*Annalen*, 1909, 368, 23—52. Compare this vol., i, 660).—The present communication treats of the condensation reactions of ethyl sodiomalonate, ethyl sodiocyanoacetate, and ethyl sodioacetoacetate with 3:5-dichlorosalicylyl chloride, 3:5-dibromosalicylyl chloride, 3:5-di-iodosalicylyl chloride, 3:5-dinitrosalicylyl chloride, and 1-hydroxy-2-naphthoyl chloride.

[With JEFF HENRY SHORES].—I. *Condensation of 3:5-Dichlorosalicylyl Chloride with Ethyl Sodiomalonate*.—The product of this reaction is 6:8-dichloro-3-carbethoxybenzotetronic acid (*ethyl 6:8-dichloro-4-hydroxycoumarin-3-carboxylate*),

$\begin{array}{c} \text{CH:CCl} \cdot \text{C} \text{---} \text{O} \text{---} \text{CO} \\ \text{CCl:CH} \cdot \text{C} \cdot \text{C(OH):C} \cdot \text{CO}_2\text{Et} \end{array}$ crystallising in long, slender, white needles, m. p. 135°; the *sodium* salt, $\text{C}_{12}\text{H}_7\text{O}_5\text{Cl}_2\text{Na}$, forms small, colourless crystals; the *ammonium* salt forms stellate aggregates of white needles; the *silver* salt is a white powder, which, when heated with ethyl iodide under pressure at 110°, yields the corresponding *ethyl ether*, $\text{C}_{14}\text{H}_{12}\text{O}_5\text{Cl}_2$, long, slender, white needles, m. p. 148°.

6:8-Dichlorobenzotetronic acid (6:8-dichloro-4-hydroxycoumarin), $\text{C}_9\text{H}_4\text{O}_3\text{Cl}_2$, is formed by boiling the parent ester with a solution of potassium hydroxide in 50% alcohol; it crystallises in short, white needles, m. p. 284—285° (decomp.); the *silver* salt, $\text{C}_9\text{H}_3\text{O}_3\text{Cl}_2\text{Ag}$, a white powder, when treated with ethyl iodide, yields the *ethyl ether*, $\text{C}_{11}\text{H}_8\text{O}_3\text{Cl}_2$, long, slender, white needles, m. p. 159°.

[With EMANUEL LÖWENBERG].—II. *Condensations with 3:5-Dibromosalicylyl Chloride*.—6:8-Dibromo-3-carbethoxybenzotetronic acid (*ethyl 6:8-dibromo-4-hydroxycoumarin-3-carboxylate*), $\text{C}_{12}\text{H}_8\text{O}_5\text{Br}_2$, crystallises in long, slender, white needles, m. p. 153—154°; the *sodium*,

ammonium, and *silver* salts were analysed; the *ethyl ether*, $C_{14}H_{12}O_5Br_2$, crystallises in silky, white needles, m. p. 155° . 6 : 8-Dibromo-4-hydroxycoumarin, $C_9H_4O_3Br_2$, crystallises in yellow, woolly needles, m. p. $268-269^\circ$; the *silver* salt was analysed; the *ethyl ether*, $C_{11}H_8O_3Br_2$, forms small, silky, pale yellow needles, m. p. 202° .

6 : 8-Dibromo-3-cyanobenzotetronic acid (6 : 8-dibromo-3-cyano-4-hydroxycoumarin), $C_{10}H_3O_3NBr_2$, prepared by the action of 3 : 5-dibromosalicyl chloride on ethyl sodiocyanoacetate, crystallises in silvery spangles, also in small, slender needles, m. p. 270° (decomp.).

6 : 8-Dibromo-3-acetylbenzotetronic acid (6 : 8-dibromo-4-hydroxy-3-acetylcoumarin), $C_{11}H_6O_4Br_2$, prepared by condensing ethyl sodioacetate with 3 : 5-dibromosalicyl chloride, crystallises in microscopic, pale yellow, silky needles, m. p. $209-210^\circ$; the *ammonium* salt was analysed.

[With FRITZ SCHMITZ.]—III. Condensations with 3 : 5-Diiodosalicyl Chloride.—Ethyl 6 : 8-di-iodo-4-hydroxycoumarin-3-carboxylate, $C_{12}H_8O_5I_2$, forms white, silky needles, m. p. $235-240^\circ$; the *sodium*, *ammonium*, and *silver* salts were analysed; the *ethyl ether*, $C_{14}H_{12}O_5I_2$, crystallises in small, colourless needles, m. p. 159° ; the *phenylhydrazide*, $C_6H_2I_2 \begin{smallmatrix} \text{O} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CH} \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPh} \end{smallmatrix}$, forms small, yellow needles, m. p. 238° .

6 : 8-Di-iodo-3-cyano-4-hydroxycoumarin, $C_{10}H_3O_3NI_2$, melts above 285° ; the *sodium*, *ammonium*, *copper*, and *silver* salts were analysed; the *ethyl ether*, $C_{12}H_7O_3NI_2$, crystallises in small, colourless needles, m. p. 226° . The parent substance, when boiled with dilute hydrochloric acid, yields the corresponding *amide*, $C_{10}H_5O_4NI_2$, crystallising in tufts of small, glistening needles, m. p. 256° .

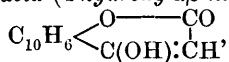
6 : 8-Di-iodo-4-hydroxy-3-acetylcoumarin, $C_{11}H_6O_4I_2$, forms pale yellow crystals, m. p. $240-245^\circ$ (decomp.); the *sodium*, *ammonium*, and *silver* salts were analysed; the *ethyl ether*, $C_{13}H_{10}O_4I_2$, has m. p. 125° .

The three condensation products derived from 3 : 5-di-iodosalicyl chloride do not yield 6 : 8-di-iodo-4-hydroxycoumarin when treated with aqueous potassium hydroxide, but are decomposed, yielding 3 : 5-di-iodosalicylic acid.

[With JULIUS SIEBEN.]—IV. Action of Ethyl Sodiomalonate on 3 : 5-Dinitrosalicyl Chloride.—These two substances do not interact to yield derivatives of benzotetronic acid. The product of the reaction is mainly 3 : 5-dinitrosalicylide (compare Abstr., 1906, i, 505).

[With KARL RUNKEL.]—V. Condensations with 1-Hydroxy-2-naphthoyl Chloride.—3-Carbethoxy-(1 : 2)-naphthatetronic acid (ethyl 4-hydroxy- α -naphthapyrone-3-carboxylate), $C_{10}H_6 \begin{smallmatrix} \text{O} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) : \text{C} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$, forms yellow needles, m. p. 179° ; the *ammonium*, *potassium*, and *silver* salts were analysed; the *ethyl ether*, $C_{18}H_{16}O_5$, crystallises in pale yellow needles, m. p. 147° .

(1 : 2)-Naphthatetronic acid (4-hydroxy- α -naphthapyrone),



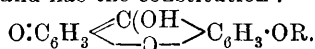
forms greyish-white crystals, m. p. $256-258^\circ$.

3-Cyano-(1:2)-naphthatetronic acid (3-cyano-4-hydroxy- $\alpha\beta$ -naphthapyrone), $C_{14}H_7O_5N$, crystallises in yellow needles, m. p. 235° ; the potassium and silver salts were analysed; the ethyl ether, $C_{16}H_{11}O_5N$, crystallises in leaflets, m. p. 52° . 4-Hydroxy- $\alpha\beta$ -naphthapyrone-3-carboxylamide, $C_{14}H_9O_4N$, has m. p. 182° .

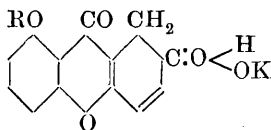
4-Hydroxy-3-acetyl- $\alpha\beta$ -naphthapyrone, $C_{15}H_{10}O_4$, crystallises in yellow needles, m. p. 180° ; the potassium, copper, and silver salts were analysed; the ethyl ether, $C_{17}H_{14}O_4$, forms yellow needles, m. p. 183° .

W. H. G.

Constitution and Colour of Xanthenes and Allied Substances. JOSEF HERZIG and K. KLIMOSCH (*Monatsh.*, 1909, 30, 527—541. Compare this vol., i, 46).—Some hydroxy-derivatives of the xanthenes, flavones, and flavonols present interesting problems with regard to the relation between colour and constitution. The substances in question are coloured. Hydroxyl groups ortho to the carbonyl are etherified with difficulty, and the resulting ethers are also coloured. Completely etherified derivatives, however, are colourless. The paper deals mainly with exceptions to these generalisations. Euxanthone forms two types of ethers. One is coloured and insoluble in alkalis, and has the constitution:



The other is colourless and soluble in alkalis, and has hitherto received the constitution: $OR \cdot C_6H_3 \begin{array}{c} \diagup CO \diagdown \\ \diagdown O \diagup \end{array} C_6H_3 \cdot OH$. It forms, however, a yellow potassium derivative (which is easily converted into the normal colourless di-alkyl ether), a yellow hydrochloride and stannichloride, and its hydroxyl group is stable to diazomethane, whereas the corresponding group in euxanthone itself is readily methylated by this reagent. The authors suggest, therefore, that the ether has the constitution: $OR \cdot C_6H_3 \begin{array}{c} \diagup CO \cdot C \cdot CH_2 \cdot CO \diagdown \\ \diagdown O - C - CH \cdot CH \diagup \end{array}$, and that the potassium salt is an oxonium derivative (annexed constitution) which yields the colourless dialkyl ether owing to transformation into the enol form by loss of water.



Ethers of the first-mentioned type are coloured, and can receive a quinonoid formula. The ethers of morin and of alizarin - yellow (2:3:4-trihydroxybenzophenone) are exceptions, being almost colourless. The first case is explained by the fact that morin itself is almost colourless, and the second by the theory that the colour intensity is repressed by the methoxy-groups.

In 2:5-dihydroxybenzophenone, 2:3:4-trihydroxybenzophenone, euxanthone, morin, and alizarin, the hydroxyl group in the ortho (or peri) position to the carbonyl group is not attacked by diazomethane. Only in the case of morin is evidence of such action obtained by the formation of a pentamethoxy-derivative. All other hydroxyl groups are methylated, and the resulting ethers are coloured, with the two

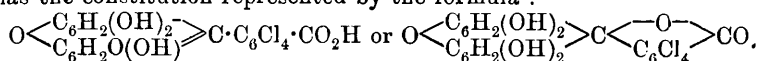
exceptions mentioned above. Fisetin, which does not contain a hydroxyl group thus situated, yields a colourless tetramethyl ether, m. p. 149—150°, with diazomethane.

Some conflicting statements in the literature of 2:3:4-trihydroxybenzophenone receive attention. Graebe and Eichengrün describe a colourless dimethyl ether, and state that further alkylation is impossible. Bartolotti mentions a citron-yellow dimethyl ether, and also a liquid trimethyl ether. The authors find that, in addition to the almost colourless dimethyl ether, m. p. 131°, obtained by the action of diazomethane, 2:3:4-trihydroxybenzophenone yields with methyl sulphate and potassium hydroxide a *trimethyl ether*, m. p. 55°, which crystallises in colourless prisms, and is also obtained by distilling Bartolotti's liquid ether.

C. S.

Tetrachlorogallein and some of its Derivatives. WILLIAM R. ORNDORFF and T. G. DELBRIDGE (*Amer. Chem. J.*, 1909, 42, 183—271). —Orndorff and Brewer (Abstr., 1900, i, 447) have shown that gallein is the true anhydride of the phthalein of pyrogallol, and reacts tautomerically with formation of two classes of derivatives, namely, coloured compounds of quinonoid structure and colourless compounds of lactoid structure. In the present paper, a résumé is given of recent work on the constitution of the phthaleins, and an account is given of a study of tetrachlorogallein.

The method of preparing tetrachlorogallein described by Graebe (Abstr., 1887, 833) can be improved by the addition of zinc chloride to the mixture of tetrachlorophthalic anhydride and pyrogallol, and in this way a yield amounting to 82% of the theoretical has been obtained. It is shown that tetrachlorogallein is strictly analogous to gallein, and has the constitution represented by the formula :

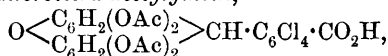


The presence of the carboxyl group is shown by the fact that tetrachlorogallein is capable of forming metallic salts and esters. All these compounds are coloured, and therefore have a quinonoid structure. Anhydrous tetrachlorogallein has only a faint colour, and probably exists in the lactoid form. The presence of the three phenolic hydroxyl groups in the quinonoid modification is demonstrated by the formation of a coloured tetramethyl derivative, which, on hydrolysis, yields a colourless trimethyl ether. Several other colourless derivatives, such as the tetra-acetyl derivative, the tetraphenylcarbamate, and the tetramethyl ether, have also been prepared, and to all of these the lactoid formula is assigned. The existence of these compounds indicates the presence of four phenolic hydroxyl groups in the lactoid modification. It has been found that the trimethyl ether, like tetrachlorogallein itself, is tautomeric; it yields a colourless acetyl derivative and methyl ether, and coloured salts and esters. It is pointed out that this fact does not seem to be in harmony with Baeyer's oscillation theory of the cause of colour in the aniline and aurin dyes (Abstr., 1907, i, 759). Tetrachlorogallein is less basic than gallein, but yields a hydrochloride, as do also its esters.

Tetrachlorogallein has a faint red colour, decomposes at about

320° with evolution of hydrogen chloride, and forms intensely blue solutions with sodium or potassium hydroxide, a bluish-purple solution with ammonia, and reddish-purple solutions with alkali carbonates. On adding acid to a freshly prepared solution in alkali hydroxide, the *hydrate*, $C_{20}H_8O_7Cl_4 \cdot H_2O$, is obtained as a red precipitate. The *hydrochloride*, and *sodium*, *potassium*, *lead*, and *barium* salts are described. The *tetra-acetyl* derivative melts at 261° (corr.), and the *tetraphenyl-carbamate* at 182° (uncorr.). *Tetrachlorogallein methyl ester*, m. p. 285—290° (decomp.), forms a dark red, crystalline powder with a slight green lustre, and behaves towards solutions of alkalis in the same manner as tetrachlorogallein itself; its *hydrochloride* is described. The *ethyl ester* melts at 275—280° (decomp.). *Tetrachlorogallein trimethyl ether*, m. p. 253—254° (uncorr.), forms colourless crystals, has fairly strong acid properties, and yields red *sodium* and *ammonium* salts; it is also somewhat basic, and gives a red *hydrochloride*, which decomposes quantitatively at 157° into hydrogen chloride and the colourless trimethyl ether. The *acetyl* derivative of the trimethyl ether, m. p. 252—254°, forms colourless crystals. The *tetramethyl ether* (or, rather, the methyl ester of the trimethyl ether), m. p. 217° (uncorr.), crystallises in prisms, which appear red in transmitted and dark green in reflected light; it yields a red *hydrochloride*. When heated with sodium hydroxide solution, the tetramethyl derivative undergoes hydrolysis, with formation of the colourless trimethyl ether. Evidence has also been obtained of the existence of a colourless tetramethyl ether. *Tetrachlorodiacetylgallein dimethyl ether*, m. p. 225° (uncorr.), forms colourless crystals.

By the reduction of the tetra-acetyl derivative of tetrachlorogallein, a colourless *tetrachlorotetra-acetylgallin*,



m. p. 221—222°, is obtained, which has acid properties; its *silver* salt is white and decomposes at 230—240°. Tetrachlorogallin therefore contains four phenolic hydroxyl groups and one carboxyl group, Orndorff and Brewer's formula for gallin (*loc. cit.*) being thus confirmed.

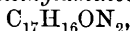
Although tetrachlorogallein and its trimethyl ether contain substituents in both of the ortho-positions to the carboxyl group, they nevertheless yield esters by the ordinary catalytic method of esterification, and are therefore exceptions to Victor Meyer's rule. E. G.

The Basic Power of Dinaphthapyranol is only Manifested in Acid Solution. IX. ROBERT FOSSE (*Bull. Soc. chim.*, 1909, [iv], 5, 827—828).—It has been shown previously (this vol., i, 667) that dinaphthapyranol in acetic acid solution displaces potassium from potassium picrate. It cannot, however, be concluded that the pyranol is a strong base, since its neutral salts (chloride, bromide, etc.), which do not dissolve in cold water, are decomposed by boiling water with liberation of the acid and formation of the pyryl oxide. This hydrolysis explains the absence of basic power of the pyranol in neutral aqueous solution. Dinaphthapyranol differs in this respect, not only from the metallic hydroxides, but also from the carbinols of

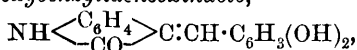
the triphenylmethane series (compare Prud'homme, *Bull. Soc. chim.*, 1895, [iii], 13, 218). E. H.

Action of Iodine and its Compounds on Adrenaline. GIUSEPPE COMESSATTI (*Arch. Farmacol. sper. Sci. affini.*, 1909, 8).—In aqueous solutions, iodine compounds exert *in vitro* a distinct anti-adrenaline action, the adrenaline undergoing oxidation to oxy-adrenaline. The action is most active with free iodine, and is more active with potassium iodide than with sodium iodide. When mixed with organic liquids, such as blood-serum, iodine and its compounds no longer exhibit this action. T. H. P.

isoIndogenides. ANDRÉ WAHL and P. BAGARD (*Compt. rend.*, 1909, 149, 132–134. Compare this vol., i, 330; Czaplicki, Kostanecki, and Lampe, this vol., i, 236).—A description of new *iso*-indogenides prepared by the method already described. *Benzylidene-oxindole*, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{C}:\text{CHPh}$, obtained from benzaldehyde and oxindole, forms sulphur-yellow needles, m. p. 175–176°. *p*-Methoxybenzylideneoxindole, $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}$, crystallises in yellow needles, m. p. 157°. *m*-Nitrobenzylideneoxindole, $\text{C}_{15}\text{H}_{10}\text{O}_3\text{N}_2$, occurs in orange leaflets, m. p. 255–257°. *p*-Dimethylaminobenzylideneoxindole,



forms orange-yellow needles, m. p. 194–195°, turning red on exposure to air; it is a basic dye. *o*-Hydroxybenzylideneoxindole, $\text{C}_{15}\text{H}_{11}\text{O}_3\text{N}$, forms needles, m. p. 195°; the *meta*-derivative has m. p. about 280°, whilst the *para*-derivative forms small, yellow crystals, m. p. above 300°. 2:4-Dihydroxybenzylideneoxindole,



occurs in small, yellow crystals, m. p. above 300°. 3:4-Dihydroxybenzylideneoxindole has m. p. 246°. The hydroxy-derivatives dissolve in aqueous alkalis, giving yellow or orange solutions. W. O. W.

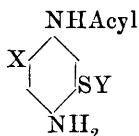
Preparation of a Sulphur Derivative of Isatin. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 210343).—By the action of sodium tetrasulphide (30 parts) on indoxyl (30 parts) in alcoholic solution at 80–90°, and subsequent distillation of the solvent, a crystalline paste is obtained, which, when decomposed with dilute hydrochloric acid, gives rise to the compound, $\text{C}_8\text{H}_5\text{ONS}$, a brown powder decomposing above 300°. F. M. G. M.

[Preparation of Carbazole Derivatives.] HANS T. BUCHERER and FRANZ SEYDE (D.R.-P. 208960. Compare Japp and Maitland, *Trans.*, 1903, 83, 267).—The condensation of amino- and hydroxy-compounds with phenylhydrazine and sodium hydrogen sulphite is shown to take place in aqueous solution, and therefore at a lower temperature than that indicated by previous workers. With α - and β -naphthols the chief product is sodium pheno- α - or - β -naphthacarbazole-N-sulphonate, $\begin{smallmatrix} \text{R} \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} \text{N}\cdot\text{SO}_3\text{Na}$, which, on heating with mineral acids,

becomes converted into phenonaphthacarbazole. With α -naphthol two other compounds are also formed.

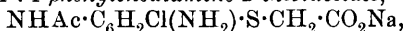
F. M. G. M.

Preparation of Aromatic Acyl-*p*-diamines. KALLE & Co. (D.R.-P. 210886).—The *p*-diamines having the annexed general

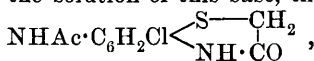


formula (where X may be chlorine, an alkyl or alkyloxy-group; SY thioalkyl, thioacyl, or chlorine) are prepared as follows: 3:6-Dichloro-4-nitroacetanilide is boiled for four or five hours in 95% alcoholic solution with sodium disulphide prepared by fusing sodium sulphide with the requisite amount of sulphur. On cooling, the mixture sets to a crystalline mass of a

nitrodisulphide compound, which, after washing with alcohol and water, is sufficiently pure for use in subsequent operations. The nitrodisulphide may be heated in aqueous solution with iron filings and dilute acetic acid, and the reduction mixture treated with sodium hydroxide and chloroacetic acid, when a theoretical yield of *sodium 5-chloro-4-acetyl-1:4-phenylenediamine-2-thiolacetate*,



is obtained in a sufficiently pure condition for use in the preparation of dyes. On acidifying the solution of this base, the *anhydride*,



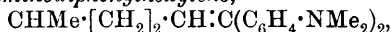
is precipitated in colourless crystals, and, on heating this with dilute sodium hydroxide at 120°, the acetyl group is removed and *sodium 5-chloro-1:4-phenylenediamine-2-thiolacetate* results.

If the reduced nitrodisulphide is treated in alkaline solution with methyl sulphate, the *methyl ether* separates in colourless needles; this compound is almost insoluble in water, but dissolves readily in benzene, alcohol, or acetone.

F. M. G. M.

Some Ethylenic Compounds Containing Nitrogen. G.

BUSIGNIES (*Compt. rend.*, 1909, 149, 348—350. Compare Klages, *Abstr.*, 1902, i, 666).—The action of magnesium methyl iodide on Michler's ketone has been studied by Freund (*Abstr.*, 1906, i, 384); the present communication contains an account of the action of organo-magnesium compounds on other aromatic ketones containing alkylamino-groups. The following new compounds are mentioned: *p*-Dimethylaminodiphenylethylene, $\text{CH}_3 \cdot \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, m. p. 47°. *p*-Dimethylaminodiphenylpropylene, $\text{CHMe} \cdot \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, m. p. 91°. *pp*-Tetramethyldiaminodiphenylhexylene,



m. p. 61°. *pp*-Tetraethyldiaminodiphenylethylene, $\text{C}_{22}\text{H}_{30}\text{N}_2$, m. p. 102°. *pp*-Tetraethyldiaminodiphenylpropylene, $\text{C}_{23}\text{H}_{32}\text{N}_2$, m. p. 56°. When dimethylaminobenzophenone was treated with magnesium benzyl chloride, an intermediate compound was isolated, *dimethylaminodiphenylbenzylcarbinol*, $\text{CH}_2\text{Ph} \cdot \text{CPh}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2) \cdot \text{OH}$, m. p. 131—132°.

The following substances have been obtained by reduction of the corresponding unsaturated compounds: *pp*-Tetramethyldiaminodiphenylethane, $\text{CHMe}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, m. p. 67°. *pp*-Tetramethyldiamino-

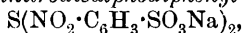
diphenyl-phenylethane, $\text{CMePh}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, m. p. 127° . *Tetraethyl-diaminodiphenylethane*, $\text{C}_{22}\text{H}_{32}\text{N}_2$, m. p. 45° .

The foregoing bases are soluble in organic solvents and in dilute acids.

W. O. W.

Preparation of Sulphonic Derivatives of Thioanilines.

AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 210564).—When sodium *p*-nitrothiolphenyl-*o*-sulphonate (25 parts) is treated in aqueous solution with sodium 2-chloro-5-nitrobenzenesulphonate (26 parts) and boiled during three to four hours, condensation takes place, and the sodium salt of *dinitrodisulphodiphenyl sulphide*,



separates on cooling as a yellow, crystalline powder.

This on reduction with zinc dust in alkaline solution, and subsequent acidification, yields *diaminodisulphodiphenyl sulphide*, a crystalline, grey powder. With sodium *p*-nitrothiophenoxide and sodium 2-chloro-5-nitrobenzenesulphonate, the orange-yellow, crystalline sodium salt of *dinitrosulphodiphenyl sulphide* is obtained.

F. M. G. M.

Basic Properties of the Hydrazones. ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 100—104).—The basic character of hydrazones is appreciable only in those of aliphatic or hydroaromatic ketones, being very feeble with aromatic hydrazones. This difference is exhibited by the difference in behaviour shown by the two classes of hydrazones with aromatic polynitro-derivatives (compare Abstr., 1906, i, 891, 962; 1907, i, 553).

The author has prepared a number of such additive compounds of hydrazones and aromatic polynitro-derivatives, in order to ascertain if any relation exists between the colours of the compounds and the compositions of the hydrazones from which they are formed. Of the polynitro-derivatives employed, picramide and picryl chloride give the most stable and most intensely coloured compounds, and of the hydrazones, piperonaldehyde phenylhydrazone and phenylmethylhydrazone, which contain an oxymethylene group, give the most stable and intensely coloured compounds.

Another property which is common to the aromatic hydrazones, indoles, carbazoles, and diphenylamine, and should be related to their constitutions, is that of giving with an ethereal solution of tetrachloro-*p*-benzoquinone intense colorations which are sometimes different for substances of similar constitution. The following are the colorations obtained in this way: the phenylhydrazones of benzaldehyde, piperonaldehyde, *m*-nitrobenzaldehyde, and cinnamaldehyde, green; that of anisaldehyde, blue; piperonaldehydephenylmethylhydrazone, green; benzaldehydephenylmethylhydrazone, blue; diphenylamine, dark green; indole, brownish-red; 2-methylindole, violet; 3-methylindole, dirty red; 1-methylindole, blue; pyrrole, wine-red; carbazole, red; tetrahydrocarbazole, violet.

The hydrazones of aliphatic aldehydes and ketones give stable, colourless salts with mineral acids, but the salts formed by the hydrazones of aromatic aldehydes have a more or less intense yellow or brownish-yellow colour. These hydrochlorides, which may be readily

prepared by passing dry hydrogen chloride into the dry ethereal solutions of the hydrazones, remain unchanged when dried out of contact with air, give up their acid more or less easily in a vacuum, and are immediately hydrolysed by water. The hydrazones also give coloured salts with hydrobromic, hydriodic, and sulphuric acids, and with ferric chloride they yield dark green salts. Between the colours of the hydrochlorides and the structures of the corresponding aldehydes there seems to be no close connexion, and when it is considered that colourless benzaldehydephenylhydrazone gives an orange-coloured hydrochloride which forms reddish-brown additive products with trinitrobenzene derivatives, it appears that the intense colour of these additive products is a consequence, partly of the halochromism of the hydrazones, and partly of the nature of the nitro-derivatives themselves. The hydrochlorides of the hydrazones most probably have a quinonoid structure.
T. H. P.

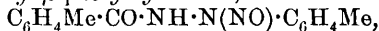
Action of Water on Nitrosohydrazines. R. GIOVETTI (*Atti. R. Accad. Sci. Torino*, 1909, 44, 949—956).—It was found by Ponzio (Abstr., 1908, i, 482) that β -nitroso- α -benzoyl- β -phenylhydrazine, when boiled with water, is converted into α -benzoyl- β -phenylhydrazine. The author finds that this replacement of the nitroso-group by hydrogen also takes place with the following hydrazine derivatives on boiling them with water: β -nitroso- α -formyl- β -phenylhydrazine; β -nitroso- α -formyl- β -*p*-tolylhydrazine; β -nitroso- α -*p*-toluoyl- β -*p*-tolylhydrazine; β -nitroso- α -anisoyl- β -*p*-tolylhydrazine; β -nitroso- α -formyl- β -*p*-bromophenylhydrazine; β -nitroso- α -*p*-toluoyl- β -*p*-bromophenylhydrazine, and β -nitroso- α -anisoyl- β -*p*-bromophenylhydrazine.

α -Formyl- β -*p*-tolylhydrazine, $\text{CHO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, prepared from formic acid (2 mols.) and *p*-tolylhydrazine (1 mol.), crystallises from alcohol in shining, white needles, m. p. 164° .

β -Nitroso- α -formyl- β -*p*-tolylhydrazine, $\text{CHO}\cdot\text{NH}\cdot\text{N}(\text{NO})\cdot\text{C}_6\text{H}_4\text{Me}$, separates in almost white leaflets, m. p. 85 — 86° (decomp.), gives Liebermann's reaction, and dissolves in concentrated sulphuric acid, giving a reddish-yellow coloration.

α -*p*-Toluoyl- β -*p*-tolylhydrazine, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, crystallises from alcohol in white needles, m. p. 177° .

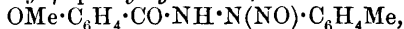
β -Nitroso- α -*p*-toluyl- β -*p*-tolylhydrazine,



is precipitated from sodium hydroxide solution by addition of acid in yellow plates, m. p. 110° (decomp.), gives Liebermann's reaction, and forms a green solution in concentrated sulphuric acid.

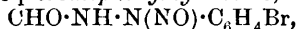
α -Anisoyl- β -*p*-tolylhydrazine, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, crystallises from alcohol in white needles, m. p. 158° .

β -Nitroso- α -anisoyl- β -*p*-tolylhydrazine,



separates in yellow laminae, m. p. 107 — 109° (decomp.), gives Liebermann's reaction, and dissolves in concentrated sulphuric acid, giving a blue solution.

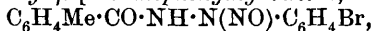
β -Nitroso- α -formyl- β -*p*-bromophenylhydrazine,



crystallises from a mixture of ether and light petroleum in yellow

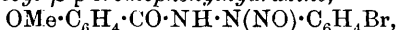
plates, m. p. 84—85° (decomp.), gives Liebermann's reaction, and forms a red solution in concentrated sulphuric acid.

β-Nitroso-α-p-toluoxy-β-p-bromophenylhydrazine,



separates in yellow laminæ, m. p. 99—102° (decomp.), gives Liebermann's reaction, and yields a violet coloration in concentrated sulphuric acid.

β-Nitroso-α-anisoxy-β-p-bromophenylhydrazine,



separates in pale yellow laminæ, m. p. 100—101° (decomp.), gives Liebermann's reaction, and dissolves in concentrated sulphuric acid, giving a yellowish-red solution.

T. H. P.

Decomposition of Certain Salts of Silver. ANGELO ANGELI, VINCENZO CASTELLANA, and R. FERRERO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 38—46. Compare Angeli and Marchetti, *Abstr.*, 1908, ii, 841).—The silver salt of nitrosophenylhydroxylamine, prepared by double decomposition from the sodium salt, darkens with separation of silver and formation of nitrosobenzene and nitric oxide: $\text{C}_6\text{H}_5\cdot\text{N}_2\text{O}_2\text{Ag} = \text{Ph}\cdot\text{NO} + \text{NO} + \text{Ag}$. At the same time, benzenediazonium nitrate is formed, thus: $\text{Ph}\cdot\text{NO} + 2\text{NO} = \text{Ph}\cdot\text{N}_2\cdot\text{NO}_3$ (compare Bamberger, *Abstr.*, 1897, i, 288), and then decomposes with evolution of nitrogen.

The silver salt of menthonebisnitrosylic acid (compare v. Baeyer, *Abstr.*, 1895, i, 549) decomposes, yielding bisnitrosomenthone, nitric oxide, and silver: $2\text{C}_{10}\text{H}_{17}\text{O}\cdot\text{N}_2\text{O}_2\text{Ag} = (\text{C}_{10}\text{H}_{17}\text{O}\cdot\text{NO})_2 + 2\text{NO} + 2\text{Ag}$.

The silver salt of benzenediazoic acid (phenylnitroamine) is, however, stable, and can be crystallised from boiling water, benzenediazoic acid being a stronger acid than nitrosophenylhydroxylamine (compare Hantzsch, *Abstr.*, 1902, i, 209).

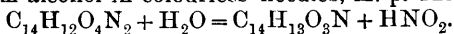
The compound, $(\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}_2)_2$, yielded by the decomposition of pernitrosocamphor is probably a derivative of dicamphor, and, like pernitrosocamphor, gives nitrous oxide when treated with concentrated sulphuric acid. It forms a *sodium* salt, $(\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2)_2\text{Na}_2$, and a *diethyl* derivative, $(\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2)_2\text{Et}_2$, which separates from light petroleum in colourless needles, m. p. 140° (decomp.). When treated with carbon dioxide or dilute sulphuric acid, the sodium salt yields a basic compound: $(\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}_2)_2 = \text{HNO}_2 + \text{C}_{20}\text{H}_{29}\text{O}_2\text{N}_3$, which separates from benzene in colourless crystals, m. p. 142° (decomp.), and yields a *picrate*, $\text{C}_{32}\text{H}_{35}\text{O}_{16}\text{N}_9$, m. p. 147°.

Pernitrosodicamphor also yields a silver salt, which decomposes spontaneously into silver, and a compound, $(\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_2)_2$, which separates from ether in crystals, m. p. 153°, and is formed according to the equations: $(\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2)_2\text{Ag}_2 = (\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_2)_2 + 2\text{Ag}$ and $(\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2)_2 = (\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_2)_2 + \text{H}_2$, the hydrogen being probably readily removed by the silver oxide which is formed.

Silver salts of *isopernitrosufenchone* and *isopernitrosobromocamphor* could not be obtained.

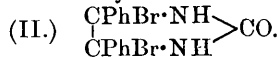
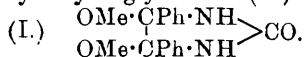
ω-isoNitrotoluene forms a white *silver* salt, which, in presence of ice and ether, decomposes, yielding *α*- and *β*-dinitrodiphenylethanes

(compare Schmidt, Abstr., 1902, i, 21): $2\text{CHPh}\cdot\text{NO}_2\text{Ag} = 2\text{Ag} + \text{NO}_2\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{NO}_2$, whilst stilbene and silver nitrite are formed at the same time: $2\text{CHPh}\cdot\text{NO}_2\text{Ag} = \text{CHPh}\cdot\text{CHPh} + 2\text{AgNO}_2$. The action of sodium ethoxide on β -dinitrodiphenylethane in alcoholic solution yields a small quantity of a product, $\text{C}_{14}\text{H}_{13}\text{O}_3\text{N}$, which crystallises from alcohol in colourless needles, m. p. 125° :

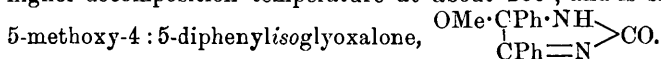


The silver salt, $\text{CN}\cdot\text{CPh}\cdot\text{NO}_2\text{Ag}$, is extremely stable. T. H. P.

Glycols and Glycol-ethers of Glyoxalones and their Isomerism. HEINRICH BILTZ (*Annalen*, 1909, 338, 156—242).—Whilst investigating the chemical properties of 4:5-diphenylglyoxalone (compare Biltz and Rimpel, Abstr., 1908, i, 573) it was found that the action of small quantities of bromine in methyl alcohol on this compound resulted in the formation of 4:5-dimethoxy-4:5-diphenyldihydroglyoxalone (I), which separated with 1 mol. $\text{Me}\cdot\text{OH}$. This compound is probably formed by the action of the alcohol on 4:5-dibromo-4:5-diphenyldihydroglyoxalone (II) formed intermediately.



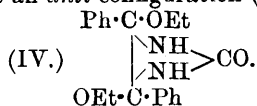
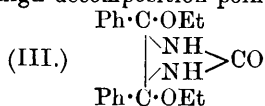
The dimethoxy-compound, with 1 $\text{Me}\cdot\text{OH}$, when recrystallised from methyl alcohol, yields an isomeride, which decomposes at a higher temperature and loses the alcohol of crystallisation at 100° . The isomeride with the lower temperature of decomposition, when heated at about 100° , loses 2 MeOH , but 1 MeOH may be removed by shaking the substance with cold ethyl alcohol. The compound formed by the elimination of 2 $\text{Me}\cdot\text{OH}$ from the isomeride with the lower temperature of decomposition is also formed by heating the isomeride with the higher decomposition temperature at about 200° , and is shown to be



Analogous compounds are obtained by replacing the methyl alcohol by ethyl alcohol. Similar compounds have also been prepared by the same method from 4:5-di-*p*-bromophenylglyoxalone, 4:5-diphenyl-1-methylglyoxalone, and 4:5-diphenyl-1-ethylglyoxalone.

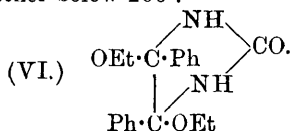
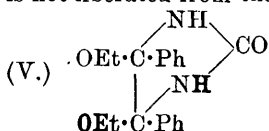
That the alkoxy-groups occupy positions 4 and 5 is proved (1) by the production of acetylenediureine from the compounds and carbamide; (2) by the formation of benzil and carbamide or their substitution products when the compounds are treated with acids.

The isomerism of these derivatives may be best explained on the assumption that the labile form with the lower temperature of decomposition has a *syn*-configuration (III), whilst the stable modification with the high decomposition point has an *anti*-configuration (IV).



The fact that only the *syn*-compounds give rise to isoglyoxalone derivatives at 100° shows that the imino-hydrogen atoms do not lie in the same plane as the glyoxalone ring; further, the imino-hydrogen

atoms lie on opposite sides of this plane, otherwise the *anti*-ethers would readily part with 1 mol. of alcohol, whilst the *syn*-ethers would give up 2 mois. of alcohol or none at all. The first result of the addition of the two ethoxy-groups to the diphenylglyoxalane is the formation of the *syn*-ether, in which one ethoxy-group must necessarily lie on the same side of the ring as one of the imino-hydrogen atoms: these are printed in heavy type (V). The ease with which 1 mol. of alcohol is eliminated is due to the close proximity of this hydrogen atom and ethoxy-group. The configuration of the *anti*-ether is represented by (VI), in which the imino-hydrogen atoms and the ethoxy-groups are situated on either side of the ring, and, in consequence, alcohol is not liberated from the *anti*-ether below 200°.



The *anti*-forms naturally pass into the *syn*-modifications at the temperatures at which alcohol is eliminated. *anti*-4:5-Diethoxydiphenyldihydroglyoxalane with ethyl alcohol of crystallisation, however, passes into the *syn*-modification when kept in an atmosphere containing a trace of acid.

The alkyloxy-compounds just described may also be prepared directly from the corresponding hydroxy-compounds by treating the alcoholic solutions with a mineral acid. The fact that 4:5-dihydroxy-4:5-di-*p*-bromophenyldihydroglyoxalane when treated with ethyl alcohol and a small quantity of hydrochloric acid below 0° yields the *syn*-ether, shows that the dihydroxy-compound is itself also a *syn*-compound.

The dihydroxy-compounds may be prepared by the following methods: (1) treatment of the glyoxalane with a solution of nitric acid in glacial acetic acid; this method is of general applicability; (2) boiling an alkaline alcoholic solution of benzil or substituted benzil with symmetrical disubstituted carbamides. Carbamide and mono-substituted carbamides yield hydantoin (compare Biltz and Rimpel, Abstr., 1908, i, 462); (3) oxidation of glyoxalones with alkyl groups in positions 1 and 3 by means of potassium permanganate in aqueous acetone; (4) treatment of 4:5-dibromodihydroglyoxalones with water.

The dihydroxy-derivatives are colourless, crystalline substances, which melt and decompose, yielding hydantoin. They are likewise converted by hot acetic anhydride into hydantoin. The same compounds are also formed by boiling with alcohol containing alkali, provided that at least one imino-hydrogen atom is present in the molecule.

The 5-alkyloxyisoglyoxalones are obtained by the following methods: (1) fusion of any ether of the necessary dihydroxydihydroglyoxalane, also by boiling solutions of the ethers in chloroform, benzene, etc.; (2) boiling dihydroxydihydroglyoxalones with alcohol and a small quantity of a mineral acid; (3) action of bromine and ethyl alcohol on the glyoxalane. The last two methods are applicable only when an alkyl group is attached to nitrogen. When treated with alcohol containing acid, they yield dialkyloxy-derivatives, provided the latter are capable of existence.

In conclusion, attention is drawn to many similarities in the chemical properties of uric acid, which contains a glyoxalone ring, and the glyoxalones. The fact that ethers of dihydroxytrimethyluric acid, unlike those of the dihydroxydihydroglyoxalones, do not undergo isomeric change when crystallised from alcohol, is due to the fact that the alkyloxy-groups cannot change places with the CO or NMe group of the pyrimidine ring. It is also evident from this fact that the *anti*-modifications of the dialkyloxydihydroglyoxalones are not produced from the *syn*-isomerides by the hydrogen and nitrogen atoms of one of the imino-groups changing positions.

[With CHAIM RIMPEL.]—4 : 5-Dihydroxy-4 : 5-diphenyldihydroglyoxalone, $\text{CO} < \begin{smallmatrix} \text{NH} \cdot \text{CPh} \cdot \text{OH} \\ \text{NH} \cdot \text{CPh} \cdot \text{OH} \end{smallmatrix}$, forms faintly yellow, compact, rhombic crystals, decomposing at 170°. A substance, $\text{C}_{17}\text{H}_{18}\text{O}_3\text{N}_2$, was isolated from the product of the oxidation of 4 : 5-diphenylglyoxalone with potassium permanganate; it crystallises in stout, rhombic plates, and decomposes at 215°, yielding diphenylacetylenediureine. *syn*-4 : 5-Diethoxy-4 : 5-diphenyldihydroglyoxalone, as prepared by the methods just described, is obtained with 1Et·OH in microscopic, long, flat, pointed needles; it sinters at about 93°, subsequently becomes solid, and then melts at 185—186°, being the m. p. of 5-ethoxy-4 : 5-diphenylisoglyoxalone. Attempts to remove the 1Et·OH by shaking with methyl alcohol led to displacement of both the ethyl groups by methyl, the compound formed being dimethoxydiphenyldihydroglyoxalone with 1Me·OH. *anti*-4 : 5-Diethoxy-4 : 5-diphenyldihydroglyoxalone,

$\text{C}_{19}\text{H}_{22}\text{O}_3\text{N}_2$, obtained by crystallising the *syn*-modification from ethyl alcohol, separates with 1Et·OH in four-sided prisms, and decomposes at about 225—230°; the alcohol of crystallisation is eliminated by heating in a vacuum at 100°. The *anti*-compound, free from alcohol of crystallisation, may also be obtained by treating the *syn*-isomeride just described with ether; it decomposes at 224—225°, and crystallises with $\frac{1}{2}\text{CHCl}_3$ in long prisms. 4 : 5-Dichloro-4 : 5-diphenyldihydroglyoxalone, $\text{C}_{15}\text{H}_{12}\text{ON}_2\text{Cl}_2$, prepared by the action of chlorine on a solution of 4 : 5-diphenylglyoxalone in chloroform, crystallises in tufts of thin, pale yellow prisms; it yields the *anti*-ethyl compound just described when crystallised from ethyl alcohol. 5-Ethoxy-4 : 5-diphenylisoglyoxalone, $\text{CO} < \begin{smallmatrix} \text{NH} \cdot \text{CPh} \cdot \text{OEt} \\ \text{N} = \text{CPh} \end{smallmatrix}$, forms compact crystals, m. p. 185°

(190° with short thermometer). When boiled with acetic anhydride it yields the *acetate*, $\text{C}_{19}\text{H}_{18}\text{O}_3\text{N}_2$, m. p. 172—173°, and when treated with methyl alcohol and one drop of dilute nitric acid it yields dimethoxydiphenyldihydroglyoxalone with 1Me·OH; that is, the ethoxy-group is displaced by a methoxy-group. It is oxidised by chromic acid to dibenzoylcarbamide, and is reduced by zinc dust and acetic acid or by sodium amalgam to diphenylglyoxalone. When its solution in chloroform is treated with hydrogen chloride, it yields 4 : 5-dichloro-4 : 5-diphenyldihydroglyoxalone, and with chlorine, it yields 3 : 4-dichloro-5-ethoxy-4 : 5-diphenylisoglyoxalone, $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2\text{Cl}_2$, obtained in small, white crystals.

The following compounds, unless otherwise stated, are obtained by methods similar to those employed in the preparation of the analogous compounds just described.

syn-4 : 5 - *Dimethoxy* - 4 : 5 - *diphenyldihydroglyoxalone*, $C_{17}H_{18}O_3N_2$, crystallises in small, flat prisms, decomposing at about 115° ; the compound with $1Me \cdot OH$ forms rounded, mussel-shaped crystals, decomposing at about 118° . The *anti-isomeride* forms long needles, m. p. 217° (decomp.); the compound with $1Me \cdot OH$ crystallises in well-defined octahedra and decomposes at about $214-215^\circ$. 5-*Methoxy*-4 : 5-*diphenylisoglyoxalone*, $C_{16}H_{14}O_2N_2$, forms small, compact crystals with rhombic facets, m. p. $179-180^\circ$; the *acetate*, $C_{18}H_{16}O_3N_2$, crystallises in large prisms, m. p. 180° .

4 : 5-*Dihydroxy*-4 : 5-*diphenyl-1-methyldihydroglyoxalone*, $C_{16}H_{16}O_3N_2$, crystallises in nodular aggregates of prisms, m. p. 150° (decomp.); when heated alone, or with an alcoholic solution of alkali, it yields 5 : 5-diphenyl-3-methylhydantoin; the *syn-dimethyl ether*, $C_{18}H_{20}O_3N_2$, forms colourless crystals and decomposes at 110° ; the *anti-isomeride* crystallises in aggregates of glistening, long prisms and decomposes at 188° . 5-*Methoxy*-4 : 5-*diphenyl-1-methylisoglyoxalone*, $C_{17}H_{16}O_2N_2$, forms white crystals, m. p. 152° . Attempts to prepare the diethoxy-derivative of the glyoxalone were unsuccessful; in each case 5-*ethoxy*-4 : 5-*diphenyl-1-methylisoglyoxalone*, $C_{18}H_{18}O_3N_2$, was formed; it crystallises in rosettes of small crystals, m. p. 155° .

4 : 5-Diphenyl-1 : 3-dimethylglyoxalone is best prepared by the action of methyl sulphate on 4 : 5-diphenyl-1-methylglyoxalone; the dihydroxy-derivative has already been described (compare Abstr., 1908, i, 218). It does not yield ethers when treated by the methods described above. 4 : 5-*Dibromo*-4 : 5-*diphenyl-1 : 3-dimethyldihydroglyoxalone*, $C_{17}H_{18}ON_2Br_2$, crystallises in red, rhombic plates, sinters at 120° , m. p. about 140° (decomp.).

syn-4 : 5-*Diethoxy*-4 : 5-*di-p-bromophenyldihydroglyoxalone*, $C_{19}H_{20}O_3N_2Br_2$, forms white crystals and decomposes at $125-130^\circ$; the compound with $1Et \cdot OH$ crystallises in four-cornered plates and decomposes at $121-122^\circ$; the *anti-isomeride* crystallises in prisms, m. p. $266-268^\circ$ (decomp.). 5-*Ethoxy*-4 : 5-*di-p-bromophenylisoglyoxalone* was obtained as a vitreous mass which could not be crystallised.

[With P. KREBS.] — 4 : 5-*Dihydroxy*-4 : 5-*di-p-methoxyphenyl-1 : 3-dimethyldihydroglyoxalone*, $C_{19}H_{22}O_4N_2$, crystallises in prisms with rhombic facets, m. p. 193° (decomp.). 5 : 5-*Di-p-methoxyphenyl-1 : 3-dimethylhydantoin*, $C_{19}H_{20}O_4N_2$, forms small, slender, colourless needles, m. p. 114° .

[With TH. KOSEGARTEN.] — *Tetraphenylglyoxalone*, $C_{27}H_{20}ON_2$, prepared by boiling a solution of benzoin and diphenylhydantoin in glacial acetic acid, crystallises in colourless, small leaflets, m. p. 207° . When treated with chromic acid, it yields *s-dibenzoyldiphenylcarbamide*, $CO(NPhBz)_2$, crystallising in tufts of colourless, hexagonal leaflets, m. p. 200° (decomp.). The *dihydroxy*-derivative, $C_{27}H_{22}O_3N_2$, forms large crystals with rhombic and hexagonal facets, sinters at about 160° , and decomposes at about 178° . All attempts to prepare ethers of it were unsuccessful. 1 : 3 : 5 : 5-*Tetraphenylhydantoin*, $C_{27}H_{20}O_2N_2$, crys-

tallises in long, rhombic leaflets, m. p. 186°. Tetraphenylglyoxalzone does not condense with diphenylcarbamide when heated with glacial acetic acid and bromine; the only compound formed is *s*-di-*p*-bromophenylcarbamide, which commences to darken at 300°, sinters at 320°, and decomposes at about 330°. The m. p. recorded by Portner (Abstr., 1899, i, 136) is incorrect.

4:5-Diphenyl-1-ethylglyoxalzone, $C_{17}H_{16}ON_2$, prepared from benzoin and ethylcarbamide, or from diphenylglyoxalzone and ethyl sulphate, forms colourless crystals, m. p. 260°; the acetate, $C_{19}H_{18}O_2N_2$, crystallises in needles, m. p. 122—123°. The dihydroxy-derivative, $C_{17}H_{18}O_3N_2$, forms glistening, transparent crystals, m. p. 191—192° (decomp.); at this temperature it passes into 5:5-diphenyl-3-ethylhydantoin (compare Abstr., 1908, i, 462); the syn-dimethoxy-derivative, $C_{19}H_{22}O_3N_2$, forms small crystals, m. p. about 81° (slight decomp.); the anti-isomeride (?) has m. p. 185° (slight decomp.). Attempts to prepare the corresponding diethoxy-derivatives resulted in the formation of 5-ethoxy-4:5-diphenyl-1-ethylisoglyoxalzone, $C_{19}H_{20}O_2N_2$, colourless prisms, m. p. 104°. The latter substance when treated with methyl alcohol and a trace of hydrochloric acid yields 4:5-dihydroxy-4:5-diphenyl-1-ethyl-dihydroglyoxalzone. This, when treated with an alcoholic solution of carbamide in the presence of hydrochloric acid, yields 4:5-diphenyl-1-methyl-acetylenediureine, $CO < \begin{smallmatrix} NEt \cdot CPh \cdot NH \\ NH \cdot CPh \cdot NH \end{smallmatrix} > CO$, which crystallises in colourless, felted needles, m. p. 284—285° (decomp.); the diacetate, $C_{22}H_{22}O_4N_4$, forms long, slender prisms, m. p. 220° (decomp.).

4:5-Diphenyl-1:3-diethylglyoxalzone, $C_{19}H_{20}ON_2$, forms small, colourless crystals, m. p. 138°. When oxidised with chromic acid, it yields dibenzoyldiethylcarbamide, $CO(NEtBz)_2$, hexagonal leaflets, m. p. 151—152°. The dihydroxy-derivative, $C_{19}H_{22}O_3N_2$, forms colourless, glistening crystals, m. p. 157.5° (decomp.), and when fused yields 5:5-diphenyl-1:3-diethylhydantoin, $C_{19}H_{20}O_2N_2$, long, slender prisms, m. p. 110°. The glyoxalzone does not yield dialkyloxy-derivatives when treated with alcohol and bromine.

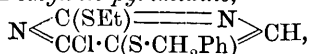
W. H. G.

Pyrimidines. XLV. Sulphur Derivatives of 5-Hydroxy-uracil: Preparation of 5-Benzylthioluracil and 5-Benzylthiol-cytosine. TREAT B. JOHNSON and HERBERT H. GUEST (*Amer. Chem. J.*, 1909, 42, 271—287).—It has been shown by several authors that the hydrogen atoms of the methylene group of cyclic compounds containing the $\cdot S \cdot CH_2 \cdot CO \cdot$ complex, such as rhodanic acids and ψ -thiohydantoins, react with aldehydes in presence of alkali with formation of unsaturated condensation products. It has also been found that the methylene group of aryl- ψ -thiohydantoins is capable of condensing with ethyl oxalate in presence of sodium ethoxide, but it does not appear that an attempt has ever been made to condense ethyl oxalate or ethyl formate with an acyclic compound containing the complex $\cdot S \cdot CH_2 \cdot CO \cdot$. Experiments have therefore been made in order to ascertain if ethyl formate would condense with a thio-ether of ethyl thioglycollate, $SH \cdot CH_2 \cdot CO_2Et$, with production of an α -thiol derivative of β -hydroxyacrylic acid.

When the sodium derivative of ethyl benzylthioglycollate (Gabriel,

Abstr., 1880, 34) is treated with ethyl formate in presence of sodium, *ethyl β-hydroxy-α-benzylthiolacrylate*, $\text{OH} \cdot \text{CH} : \text{C}(\text{S} \cdot \text{CH}_2\text{Ph}) \cdot \text{CO}_2\text{Et}$, m. p. 57—58°, is obtained, which gives a bright red colour with ferric chloride. The sodium derivative of this compound condenses smoothly with ethyl-ψ-thiocarbamide, yielding *5-benzylthiol-2-ethylthiol-6-pyrimidone*, $\text{NH} \langle \text{C}(\text{SEt}) = \text{N} \rangle \text{CH}$, m. p. 155—156°, which forms

tabular crystals, and is converted by strong hydrochloric acid into *5-benzylthioluracil*, $\text{NH} \langle \text{CO} = \text{NH} \rangle \text{CH}$, m. p. 290°, which crystallises in rhombic plates or tablets. *5-Benzylthiol-2-ethylthiol-6-pyrimidone* reacts with phosphoryl chloride with formation of *6-chloro-5-benzylthiol-2-ethylthiolpyrimidine*,



m. p. 47—48°, which crystallises in prisms and is converted by alcoholic ammonia into *6-amino-5-benzylthiol-2-ethylthiolpyrimidine*, m. p. 68—69°, which forms groups of needles. When this amino-derivative is boiled with concentrated hydrochloric acid, ethyl mercaptan is evolved and

5-benzylthiolcytosine, $\text{N} \langle \text{CO} = \text{NH} \rangle \text{CH}$, m. p. 240—241°, is produced, which crystallises in plates. When *5-benzylthiol-2-ethylthiol-6-pyrimidone* is heated in a current of dry hydrogen chloride at 160—170°, ethyl chloride is produced, together with *2-thio-5-benzylthiol-6-pyrimidone*, $\text{NH} \langle \text{CS} = \text{NH} \rangle \text{CH}$, m. p. 195—196°.

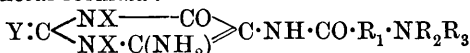
6-Chloro-5-ethoxy-2-methylthiolpyrimidine, $\text{N} \langle \text{C}(\text{SMe}) = \text{N} \rangle \text{CH}$, m. p. 75°, obtained by the action of phosphoryl chloride on *5-ethoxy-2-methylthiol-6-pyrimidone* (Johnson and McCollum, Abstr., 1906, i, 705), crystallises in slender prisms, and, when heated with alcoholic potassium hydrosulphide, is converted into *6-thio-5-ethoxy-2-methylthiolpyrimidine*, $\text{NH} \langle \text{C}(\text{SEt}) = \text{N} \rangle \text{CH}$, m. p. 190°, which forms light yellow prisms.

2:6-Dichloro-5-ethoxypyrimidine, $\text{N} \langle \text{CCl} = \text{N} \rangle \text{CH}$, m. p. 41—42°, obtained by the action of phosphoryl chloride on *5-ethoxyuracil* (Johnson and McCollum, *loc. cit.*), forms prisms or needles, and is converted by potassium hydrosulphide into *2:6-dithio-5-ethoxypyrimidine* (*dithio-5-ethoxyuracil*), $\text{NH} \langle \text{CS} = \text{NH} \rangle \text{CH}$, which crystallises in needles and decomposes above 255°.

The sodium derivative of ethyl β-hydroxy-α-phenoxyacrylate condenses with thiocarbimide with formation of *2-thio-5-phenoxy-6-pyrimidone*, $\text{NH} \langle \text{CS} = \text{NH} \rangle \text{CH}$, m. p. 253—254°, which forms clusters of prisms, and is converted by concentrated hydrochloric or hydrobromic acid into *5-phenoxyuracil*, $\text{NH} \langle \text{CO} = \text{NH} \rangle \text{CH}$, m. p. 290° (decomp.), which crystallises in needles.

E. G.

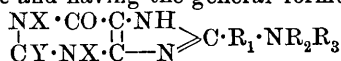
Preparation of Pyrimidine Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 209729).—Pyrimidine derivatives having the general formula :



(where X is hydrogen or an alkyl group ; Y acidic, sulphur, imino-, or cyanimino-residues ; R₁ an alkyl group, and R₂ and R₃ hydrogen, alkyl, or aryl residues) are intermediate products for the preparation of therapeutically active purine derivatives (following abstract). 4-Amino-2 : 6-diketo-5-chloroacetyl-amino-1 : 3-dimethylpyrimidine (200 parts) is heated in an autoclave with 30% ammonium hydroxide (1000 parts) to 50° during ten hours. The excess of water and ammonia are evaporated, and the residue treated with 90% alcohol (500 parts), when 4-amino-5-aminoacetyl-amino-2 : 6-diketo-1 : 3-dimethylpyrimidine, white powder, m. p. 220°, remains undissolved, being only sparingly soluble in this medium, ether, or benzene, but readily so in water.

If piperidine replaces the ammonium hydroxide in this reaction, the *piperidyl* derivative, prismatic crystals, m. p. 98°, is obtained ; it is readily soluble in hot water, alcohol, and alkali hydroxides, but only slightly soluble in cold water. 4-Amino-5(β)-chloro-α-hydroxypropionyl-amino-2 : 6-diketo-1 : 3-dimethylpyrimidine, when condensed with dimethylamine, yields the 5(β)-dimethylaminolactyl-amino-pyrimidine derivative, m. p. 228°, easily soluble in water and alkali hydroxides, but insoluble in alcohol or ether. 4-Amino-5-phenylaminoacetyl-amino-2 : 6-diketo-3-methylpyrimidine, m. p. 275°, soluble in the ordinary organic media, but insoluble in hot water, is obtained from 4-amino-5-chloroacetyl-amino-2 : 6-diketo-3-methylpyrimidine (m. p. 225°) on warming with aniline. F. M. G. M.

Preparation of Basic Purine Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 209728).—Basic purine derivatives of therapeutic value and having the general formula :

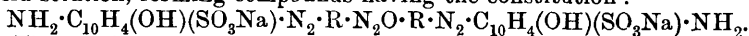


(where X is hydrogen or an alkyl group ; Y acyl, sulphur, imino-, or cyanimino-groups ; R₁ an alkyl group ; R₂ and R₃ hydrogen, alkyl, or aryl residues) are produced when aminoaminoacylpyrimidine derivatives (compare preceding abstract) are treated with alkaline condensing agents, and the preparation of the following is described in the patent. 8-Aminomethyl-1 : 3-dimethylxanthine, m. p. 252° (decomp.), from 4-amino-5-aminoacetyl-amino-2 : 6-diketo-1 : 3-dimethylpyrimidine and sodium hydroxide (30%), is soluble in alkalis, but only sparingly soluble in alcohol, ether, or chloroform ; with acids it forms soluble, stable, neutral salts. 1 : 3-Dimethyl-8-piperidylmethylxanthine, colourless needles, m. p. 203°, is obtained from 4-amino-2 : 6-diketo-1 : 3-dimethyl-5-piperidylacetylaminopyrimidine and sodium ethoxide.

Other reagents, such as barium hydroxide and magnesia, can be used for these condensations. F. M. G. M.

[Reduction of Nitrodiazo-compounds to Azoxy-derivatives.] LEOPOLD CASSELLA & Co. (D.R.-P. 211029).—p-Nitrodiazo-compounds

are reduced in alkaline solution, yielding the azoxydiamines; these are diazotised and coupled with 6-amino- α -naphthol-3-sulphonic acid in acid solution, forming compounds having the constitution:

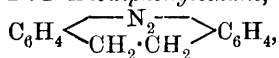


These substances dye cotton in yellow to violet-red shades, which are fast to light.

F. M. G. M.

Attempts at Benzidine Formation in the Diphenyl, Diphenylmethane, and Diphenylethane Series. HENRI DUVAL (*Compt. rend.*, 1909, 149, 401—402. Compare Abstr., 1905, i, 651; 1906, i, 314).—The author summarises his previous work on this subject. Reduction of 2:2'-dinitro-4:4'-tetramethyldiaminodiphenylmethane by zinc dust in presence of pyridine and hydrochloric acid, followed by oxidation in a current of air, the operation being repeated using zinc dust and sodium hydroxide as the reducing agent, leads to the formation of 4:4'-tetramethyldiamino-2:2'-azodiphenylmethane,

$\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{smallmatrix} \text{N}_2 \\ \text{CH}_2 \end{smallmatrix} \right\rangle \text{C}_6\text{H}_3 \cdot \text{NMe}_2$, red spangles, m. p. 213°. *Azoxydiphenylmethane-4:4'-dicarboxylic acid*, obtained by the reduction of ethyl dinitrodiphenylmethane-4:4'-dicarboxylate with zinc dust and ammonium chloride, followed by oxidation, forms an *ethyl ester*, which on reduction by zinc dust and acetic acid, and subsequent treatment with mercuric oxide, furnishes *ethyl azodiphenylmethane-4:4'-dicarboxylate*, $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_3 \left\langle \begin{smallmatrix} \text{N}_2 \\ \text{CH}_2 \end{smallmatrix} \right\rangle \text{C}_6\text{H}_3 \cdot \text{CO}_2\text{Et}$, crystallising in yellow spangles, m. p. 233°. 2:2'-Azodiphenylethane,



yellow needles, m. p. 112.5°, is obtained by boiling 2:2'-dinitrodiphenylethane with barium hydroxide and zinc dust in dilute alcoholic solution and then oxidising the product with mercuric oxide.

W. O. W.

Relations between α -Benzaldehydephenylhydrazine and other Nitrogen Compounds. ROBERTO CIUSA and UGO PESTALOZZA (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 90—93).—The authors have carried out experiments to ascertain whether there exists any analogy in chemical behaviour between α -benzaldehydephenylhydrazine and diazoaminobenzene (m. p. 96°), which may be regarded as the phenylhydrazine of nitrosobenzene.

The action of picric acid or picryl chloride on α -benzaldehydephenylhydrazine in benzene solution gives, in each case, the corresponding intensely brown additive compound. With diazoaminobenzene (1 mol.), picric acid (1 mol.) in 96% alcoholic solution yields benzene-diazonium picrate, which may conveniently be prepared in this way; picric acid evidently acts on diazoaminobenzene in the same manner as does hydrochloric acid: $\text{N}_2\text{Ph} \cdot \text{NHPh} + 2\text{HCl} = \text{Ph} \cdot \text{N}_2\text{Cl} + \text{Ph} \cdot \text{NH}_2 \cdot \text{HCl}$.

The action of amyl nitrate on diazoaminobenzene, studied with the view of obtaining oxidation products containing a chain of six nitrogen atoms, is very complex, the only identifiable product obtained being benzenediazonium nitrate.

The action of mercuric oxide on diazoaminobenzene in chloroform solution yields only a mercury salt of diazoaminobenzene,



m. p. 232°.

The differences in the behaviour of diazoaminobenzene and benzaldehydephenylhydrazone towards amyl nitrate and mercuric oxide (compare Minunni and Rap, *Abstr.*, 1897, i, 40; von Pechmann, *Abstr.*, 1893, i, 461) are explained by the acid character of the former compound and the feebly basic nature of the latter. T. H. P.

Nomenclature of Lipoids. OTTO ROSENHEIM (*Bio-Chem. J.*, 1909, 4, 331—336).—The author proposes to omit all names given to substances insufficiently characterised, or which are mixtures, and to adopt in the case of different names for the same substances, those proposed by the original discoverer. The following names should therefore be discarded: *cérébrote*, *cerebric acid*, *protagon*, *cerebrin*, *pseudocerebrin*, *cerebron*, *homo-cerebrin*, and *myelin*. The names retained would be: *cholesterin* and *phytosterin* in the group free from nitrogen and phosphorus; *phrenosin* and *kerasin* in the group of cerebro-galactosides; and *lecithin*, *kephalin*, *vesalthin*, *sphingomyelin*, *neottin*, and *cuorin* in the phosphatide group. According to Thudichum's original classification, the phosphatides are arranged according to their N:P ratio. The name *cholesterin* is preferred to *cholesterol*, as it has the advantage of long and international usage; the new termination represents only one characteristic of the substance, namely, its alcoholic nature.

W. D. H.

Action of Methyl Iodide on Casein. ZDENKO H. SKRAUP and E. KRAUSE (*Monatsh.*, 1909, 30, 447—465).—The reaction was studied with the object of ascertaining whether or not the protein molecule contains free amino-groups. The authors were able to obtain a 40% yield of methyl derivative containing iodine, which latter element they consider to be present, to some extent, in the quaternary form; on hydrolysis this substance yielded no tyrosine or lysine, and only traces of histidine and arginine, but considerable quantities of glutamic acid and leucine, and also phenylalanine; the substance does not give Millon's reaction, but gives the biuret and Molisch reactions just like ordinary casein; the Liebermann reaction, however, is rather less marked, while the glyoxylic acid reaction is more intense. From these facts the conclusion is drawn that, on methylation, the glutamic acid, leucine, and possibly phenylalanine residues remain intact, whereas the tyrosine complex and the hexone bases are destroyed.

Purified casein was found to contain a small, yet constant, quantity of methyl, both in the form of $\cdot\text{OMe}$ and $\cdot\text{NMe}$, and from the figures obtained the minimum molecular weight of casein was calculated to be 3500.

Methyliodocasein, when finely powdered, is a faintly yellow-coloured substance, which has a slightly acid reaction to litmus; when freshly prepared it is only partly soluble in water, but, after keeping for some time in closed vessels, it is completely soluble; concentrated aqueous solutions are practically clear, and are not rendered turbid by the

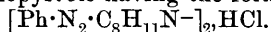
addition of ammonia, but sulphuric acid produces a marked precipitate. A heavy precipitate is also produced on half saturation with ammonium sulphate.

P. H.

Hæmatin. WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1909, 61, 164—176).—Mostly polemical against Piloty (this vol., i, 539). While recognising the importance of Piloty's discovery of hæmopyrrole-carboxylic acid, the author does not agree with the suggestion that each hæmatin molecule gives only one molecule of this acid, but thinks that the complex yielding it occurs twice. If, as Piloty believes, hæmopyrrole is formed by the reduction of an independent complex, $\text{CR}=\text{C} \begin{smallmatrix} \diagup \\ \text{NH} \end{smallmatrix}$, the imide of a $\beta\beta'$ -disubstituted maleic acid should be formed on oxidation, but no such compound can be detected. The oxidation of hæmatoporphyrin by chromic acid in sulphuric acid solution (instead of in glacial acetic acid) results in the formation of two molecules of hæmatic acid, one of acetic acid, and four of carbon dioxide.

G. B.

Blood-pigment. X. LEON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1909, 61, 276—278).—The product obtained by the action of benzenediazonium chloride on hæmopyrrole, which forms ruby-red, rhombic crystals, m. p. 268° (compare Abstr., 1908, i, 843), is shown to be the hydrochloride of a substance resulting from the coupling of two molecules of benzeneazohæmopyrrole having the formula



An analogous product, $[\text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_7\text{N}-]_2 \cdot \text{HCl}$, has been prepared by the action of benzenediazonium chloride on 2 : 4-dimethylpyrrole.

Comparison of the absorption spectra of the bisazo-derivatives of pyrrole with that of the azo-derivative obtained from hæmopyrrole, the hydrochloride of which has m. p. 233° (*loc. cit.*), points to the probability that hæmopyrrole is a dimethylethylpyrrole.

W. H. G.

Hippomelanin. II. OTTO RIESSER and PETER RONA (*Zeitsch. physiol. Chem.*, 1909, 61, 12—15).—The base described previously (compare Abstr., 1908, i, 1028), resulting from the action of a 3% solution of hydrogen peroxide containing a small quantity of hydrochloric acid on hippomelanin, is shown to be guanidine.

A second base, which is precipitated by phosphotungstic acid, was also isolated. The *picrate* is deposited as an oil sparingly soluble in alcohol; the *hydrochloride* crystallises in long, indistinct needles; a *platinichloride* insoluble in alcohol could not be obtained.

W. H. G.

Constitution of Gelatin. ZDENKO H. SKRAUP and A. VON BIEHLER (*Monatsh.*, 1909, 30, 467—479).—The fact that the combined weight of the products of hydrolysis of most proteins falls considerably short of the weight of the substance hydrolysed induced the authors to repeat the hydrolysis of gelatin with the object of ascertaining whether this discrepancy was due to the imperfection of Fischer's ester method or whether any products were formed which had escaped

detection. By repeated and exhaustive esterification of the products of hydrolysis of gelatin, the authors have been able to account for 86% of the substance, but have not been able to discover any new products.

P. H.

Formation of Oxalic Acid from Gelatinous Substances. W. S. SADIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 641—651; *Biochem. Zeitsch.*, 1909, 21, 35—45).—Oxidation of thioglutan (Abstr., 1907, i, 740) with concentrated nitric acid results in the formation of oxalic acid, the amount of which varies with the conditions employed. Glutin also gives oxalic acid when oxidised by concentrated nitric acid, but only when calcium salts are present; with collagen, the presence of calcium salts is unnecessary.

When heated with potassium hydroxide solution at 240° (under which conditions little or no decomposition of oxalic acid occurs), glutin gives oxalic acid, the greatest yield obtained being 146.9%, corresponding with 39.17% of the carbon of the glutin; traces of carbon are lost in the form of volatile products, such as pyrrole, indole, etc. The yield of oxalic acid under these conditions is not increased by energetic hydration of the glutin by means of concentrated hydrochloric acid. Similar formation of oxalic acid from thioglutan and collagen is observed, the rate of formation being in both cases less than with glutin.

T. H. P.

Mono-amino-acids in the Muscular Substance of Egyptian Mummies. I. EMIL ABDERHALDEN and CARL BRAHM (*Zeitsch. physiol. Chem.*, 1909, 61, 419—420).—The following amino-acids were identified, 50 grams of the neck muscle serving as the material worked with: glycine, alanine, leucine, phenylalanine, and glutamic acid.

W. D. H.

Comparative Investigation of the Composition and Structure of Various Kinds of Silks. III. The Mono-amino-acids of Shantung Tussore Silk. EMIL ABDERHALDEN and CARL BRAHM. IV. Mono-amino-acids from Bengal Silk. EMIL ABDERHALDEN and JAMES SINGTON (*Zeitsch. physiol. Chem.*, 1909, 61, 256—258, 259—260. Compare this vol., i, 343).—The following table gives the main results obtained; the figures are percentages.

	Shantung Tussore silk.	Bengal silk.
Glycine.....	14.5	30.5
Alanine.....	22.0	20.0
Serine	1.8	1.75
Leucine.....	1.0	1.2
Aspartic acid	1.0	0.8
Glutamic acid	1.75	traces
Phenylalanine.....	1.0	1.4
Tyrosine	9.7	10.0
Proline.....	2.5	1.0

W. D. H.

Comparative Hydrolysis of Silk by Boiling, Fuming Hydrochloric Acid, 25 per cent. Sulphuric Acid, 20 per cent. Aqueous Sodium Hydroxide, and Hot Saturated Baryta Solution. EMIL ABDERHALDEN, F. MEDIGRECEANU, and LUDWIG PINCUSOHN (*Zeitsch. physiol. Chem.*, 1909, 61, 205—209).—Within narrow limits the same quantities of amino-acids were obtained from silk whether the hydrolysis is accomplished by acids or by alkalis.

W. D. H.

Deaminoproteins. S. J. LEVITES (*Biochem. Zeitsch.*, 1909, 20, 224—230).—Skraup's observation (compare Abstr., 1906, i, 913) is confirmed that in deaminoproteins the amount of diamino-nitrogen is diminished, chiefly owing to the disappearance of lysine, which is apparently converted into a monoamino- or aminohydroxy-acid.

G. B.

Action of Ferments on Stachyose. J. VINTILESCO (*J. Pharm. Chin.*, 1909, [vi], 30, 167—173).—Tanret has shown that the hydrolysis of stachyose (manneotetrose) can be effected in two stages by the use of acetic acid followed by sulphuric acid (Abstr., 1902, i, 661; 1902, i, 606); the present communication shows that the same result may be brought about by the successive action of invertin and the emulsin of almonds. The latter contains a specific enzyme which brings about fission of the manninotriose formed in the first stage. This ferment, for which the name "*manninotriase*" is suggested, has been isolated from top fermentation yeast cultivated in a solution containing stachyose (extract of *Stachys tuberosa*). The hydrolytic action on stachyose is slow, and depends on the amount of enzyme present; acetic acid has an accelerating influence. It is without action on salicin and lactose, but partly hydrolyses amygdalin with formation of a reducing sugar, but not of hydrogen cyanide.

W. O. W.

The Enzymes of Gum-acacia and certain other Gums. FRIEDRICH REINITZER (*Zeitsch. physiol. Chem.*, 1909, 61, 352—394).—The author has repeated and confirmed his earlier observations (Abstr., 1890, 998), and combats many of the statements of Wiesner (*Sitz. Wiener Akad.*, 1885, 92, 40) and Grafe (*Wiesner-Festschrift, Wien*, 1908, 253). It is definitely established, in opposition to the statements of these authors, that gum-acacia, cherry gum, and gum-tragacanth contain an enzyme (gum-amylase), present in widely varying quantities, capable of converting starch into dextrin and maltose. Experiments are cited which tend to show that these gums also contain another enzyme, capable of bringing about the dissolution of starch, but unable to convert it into maltose. These enzymes may be separated more or less completely by filtering the solution of the gum through a porcelain filter.

All the gums investigated were also found to contain varying amounts of oxydases, probably identical with laccase (compare Bertrand, Abstr., 1895, i, 368) and peroxydases.

The enzymes present in gum-acacia are incapable of converting

insoluble gums into soluble gums or into sugar; it is to be inferred, therefore, that, contrary to the statements of Wiesner and Grafe, they would not have any action on celluloses or hemicelluloses.

W. H. G.

Invertin (Invertase) of Yeast. II. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1909, 61, 124—138).—Invertase does not contain carbohydrates; the yeast gum generally accompanying it is an impurity, and by extraction with cold chloroform water under certain conditions dilute invertase solutions may be obtained which are carbohydrate free. In contradistinction to what is generally supposed, press yeast gives off appreciable quantities of invertase to pure water. Invertase appears to be particularly resistant to putrefaction.

G. B.

Purification of Peroxydase. N. T. DELEANO (*Biochem. Zeitsch.*, 1909, 19, 266—269).—Peroxydase is abundant during the germination of the seeds of *Ricinus communis*. In the extracts it is mixed with other substances, especially protein. It can be separated from the protein by precipitating the latter with Kahlbaum's colloidal iron solution (lig. ferri oxyd. dialys. colloidal). When so obtained its activity is destroyed at 55° in three hours. When the protein impurity is present, this temperature does not destroy its activity.

W. D. H.

Formation of Organic Phosphorus Compounds and their Function in Zymase Fermentation. LEONID IWANOFF (*Centr. Bakt. Par.*, 1909, ii, 24, 1—12. Compare Abstr., 1907, ii, 191).—The organic phosphorus compound formed during the fermentation of sugar by zymase is apparently a compound of phosphoric acid with a triose which forms a phenylosazone, m. p. 127—128°. The formation of this compound is brought about by means of an easily soluble enzyme, contained in the zymase preparations, here termed synthease. The synthetical enzyme is destroyed in presence of hydrogen cyanide, or when the zymase filtrate is heated. This triose-phosphoric acid is fermented by zymase, forming carbon dioxide, alcohol and inorganic phosphoric acid; it is also fermented by the insoluble portion of zymase, which is quite without action towards dextrose. The stimulation of zymase fermentation by phosphates finds an explanation therefore in the formation of triose-phosphoric acid. The fermentation of dextrose may be considered to take place in three phases: (1) depolymerisation to a triose; (2) coupling of this with phosphoric acid by means of the soluble enzyme synthease; (3) destruction of the triosephosphoric acid by means of the sparingly soluble enzyme of zymase—termed alcoholase—to form carbon dioxide and alcohol.

E. F. A.

Organic Chemistry.

Some Gas Reactions. M. MAYER, F. HENSELING, V. ALTMAYER, and J. JACOBY (*J. Gasbeleuchtung*, 1909, 52, 166—171, 194—201, 238—245, 282—286, 305—313, 326—328).—An elaboration and continuation of the work of Sabatier and Senderens. The authors describe the preparation of the oxides of carbon and hydrogen, also of pure nickel, cobalt, and iron, for employment as catalysts in the experiments which culminated in the synthesis of methane from its elements. The processes are embodied in the following formulæ:

$\text{CO} + \text{H}_2\text{O (steam)} = \text{CO}_2 + \text{H}_2$; $\text{C} + 2\text{H}_2\text{O (steam)} = \text{CO}_2 + 2\text{H}_2$;
and finally, $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$; $\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$;
 $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$.

With carbon monoxide and hydrogen the employment of iron as catalyst yielded only small quantities of methane, this result being attributed to the oxidation of the metal. Experiments with steam instead of hydrogen, and with finely-divided carbon instead of the oxides, were also carried out, and in the latter case very little methane was formed.

A study of the velocity and equilibrium of the reactions under varying conditions showed them to be balanced, and to depend greatly on the physical constants of the reacting substances. Illustrations of the apparatus used, an explanation of the methods employed for calculating the analytical results, and a critical bibliography are also appended.

F. M. G. M.

Apparatus for the Preparation of Acetylene. WILHELM STEINKOPF (*Chem. Zeit.*, 1909, 33, 969).—The calcium carbide is contained in a gauze cylinder suspended in a vessel open at the bottom, and closed above by a cork through which the delivery tube passes. This vessel is suspended in an outer vessel containing water. The lime formed falls to the bottom of the outer vessel. C. H. D.

Electric Transport and Electrolytic Decomposition of Chloroform. FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 133—135).—When an emulsion of chloroform in water is placed in the middle vessel of an electric transport apparatus, and subjected to the action of a current, the chloroform migrates towards the anode, where it undergoes decomposition with formation of hydrochloric acid.

T. H. P.

Chlorination of Ethyl Chloride. WILHELM STAEDEL (*J. pr. Chem.*, 1909, [ii], 80, 303—304).—Forty years ago the author found that chlorine and the vapour of ethyl chloride react instantly in direct sunlight, and the product contains ethylidene chloride, but not ethylene

chloride. Twenty years later, V. Meyer found that the interaction of liquid ethyl chloride and antimony pentachloride gave a product containing ethylene chloride, and not ethylidene chloride.

The author now states that his original results are correct (following abstract); by using a mercury vapour lamp and quartz vessels, and liquid chlorine and ethyl chloride, the time of the experiment is very largely shortened. C. S.

Chlorination of Ethyl Chloride. JOH. D'ANS and J. KAUTZSCH (*J. pr. Chem.*, 1909, [ii], 80, 305—314).—When approximately equal molecular quantities of chlorine and ethyl chloride are condensed in a quartz vessel cooled by a mixture of ether and solid carbon dioxide, and are exposed, at a distance of 40—50 cm., to the rays of a Heraeus mercury vapour lamp, the product yields by fractionation about 70% of ethylidene dichloride and 10% of ethylene dichloride. When 1.5 mols. of chlorine are used, the lamp must be placed at a distance of 60—70 cm. to prevent explosive reaction; the product contains 50% ethylidene dichloride, and not any ethylene dichloride.

Ethylidene dichloride is more difficultly chlorinated in light than ethylene dichloride; hence the behaviour of the two substances under these conditions is just the converse of their behaviour when chlorinated in the presence of a "carrier" (Meyer and Müller, *Abstr.*, 1892, 577, 1414).

When iodine is added in the preceding experiments, the reaction is retarded to an astonishing degree. Ethyl chloride and iodine trichloride scarcely react at 105°. C. S.

Preparation of Nitromethane. II. WILHELM STEINKOPF and GEORG KIRCHHOFF (*Ber.*, 1909, 42, 3438—3440. Compare this vol., i, 78).—More convenient than that described previously is the following method, which proceeds smoothly and yields scarcely any hydrogen cyanide. Chloroacetic acid (500 grams) is dissolved in one litre of water, and neutralised by 280—300 grams of ignited sodium carbonate. The solution is mixed with 300 grams of sodium nitrite in 500 grams of water. About one-fourth of the mixture is placed in a two-litre flask connected to a condenser and also to a water-pump, and is heated to boiling; the remainder of the solution is run in from a dropping funnel at such a rate that a steady evolution of nitromethane is maintained. At the end of the reaction about 250 c.c. of the water are distilled over, and the remainder of the solution in the flask (consisting of sodium carbonate), excepting 100 c.c., is drawn off by the pump, neutralised by chloroacetic acid, mixed with sodium nitrite, and utilised over again. The other end of the condenser is connected to a convenient apparatus for the separation of the nitromethane in the aqueous distillate. The yield of purified nitromethane is about 50%. C. S.

Action of Nitrogen Trioxide on Tetramethylethylene [β -Dimethyl- Δ^2 -butylene]. NICOLAUS J. DEMJANOFF and K. W. SIDORENKO (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 832—838).—The results of Schmidt (*Abstr.*, 1903, i, 597) are not in accord with those obtained by Demjanoff (*Abstr.*, 1899, i, 845).

On adding an ethereal solution of nitrogen trioxide (from arsenious anhydride and nitric acid) to an ethereal solution of $\beta\gamma$ -dimethyl- Δ^2 -butylene, the latter being in slight excess, the liquid becomes blue and the following compounds are formed: (1) $\beta\gamma$ -dinitro- $\beta\gamma$ -dimethylbutane (compare Zelinsky, *J. Russ. Phys. Chem. Soc.*, 1894, 26, 610; Konowaloff, *Abstr.*, 1895, i, 633; Bewad and Pirinsky, *Abstr.*, 1906, i, 393); (2) the compound $\text{NO}_2 \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{NO}_2$, m. p. 88—89° (compare Demjanoff, *Abstr.*, 1899, i, 845), apparently mixed with the dinitro-compound, $\text{NO}_2 \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{NO}_2$; on reduction, this mixture, m. p. 101—104°, yields the diamino-compound, $\text{NH}_2 \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{NH}_2$, and the hydroxy-amine, $\text{OH} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{NH}_2$ (compare Demjanoff, *Abstr.*, 1899, i, 845). T. H. P.

Ethylene Ozonide. CARL D. HARRIES and RUDOLF KOETSCHAU (*Ber.*, 1909, 42, 3305—3311. Compare Harries and Haefner, *Abstr.*, 1908, i, 846).—*Ethylene ozonide*, $\text{C}_2\text{H}_4\text{O}_3$, may be prepared by the action of ozonised air on a solution of ethylene in methyl chloride at -70° in the complete absence of water. It is a colourless liquid, b. p. $18^\circ/16$ mm., with an unpleasant, intensely pungent odour, and explodes with great violence when heated in a tube or rubbed with a glass rod. Mol.-wt. determinations and the values $n_D^{17.5} 1.4099$ and $D_{17.5}^{17.5} 1.2650$ show that the compound has the formula $\begin{array}{c} \text{CH}_2 \cdot \text{O} \\ | \quad \diagup \\ \text{CH}_2 \cdot \text{O} \end{array} \text{O}$. It is decomposed by water according to the two equations: $\text{C}_2\text{H}_4\text{O}_3 + \text{H}_2\text{O} = 2\text{H} \cdot \text{CHO} + \text{H}_2\text{O}_2$ and $\text{C}_2\text{H}_4\text{O}_3 = \text{H} \cdot \text{CHO} + \text{H} \cdot \text{CO}_2\text{H}$. W. H. G.

Nitro-derivatives of Glycerol Ether. EMANUALE PATERNO and T. BENELLI (*Gazzetta*, 1909, 39, ii, 312—314).—The authors propose to replace the dinitromonoformin, dinitromonoacetin, etc., added to dynamite in order to lower its freezing point, by the corresponding derivatives in which an alkyl radicle is substituted for the acid radicle. Attempts to find a practicable method of preparing and separating the monomethyl and monoethyl ethers of glycerol were unsuccessful, so that the authors have confined their attention to the dimethyl and diethyl ethers, the nitro-derivatives of which have been prepared.

Glyceryl dimethyl ether nitrate, $\text{NO}_2 \cdot \text{O} \cdot \text{CH}(\text{CH}_2 \cdot \text{OMe})_2$, prepared by nitrating glycerol dimethyl ether, is a colourless, neutral liquid with a pungent odour, b. p. 180° , m. p. -15° . It is readily inflammable, but non-explosive, and when added to nitroglycerol in the proportion of 2%, lowers the m. p. from -18° to -34° ; even when present to the extent of 10%, it produces no appreciable diminution in the explosive properties of nitroglycerol. Replacement of all or part of the nitroglycerol employed in the manufacture of ballistite by glyceryl dimethyl ether nitrate results in a diminution of the explosive force.

Glyceryl diethyl ether nitrate, $\text{NO}_2 \cdot \text{O} \cdot \text{CH}(\text{CH}_2 \cdot \text{OEt})_2$, b. p. 168 — 170° (decomp.), decomposes to such an extent on boiling that the boiling is maintained by the heat generated by the decomposition; it becomes very dense, but does not solidify, at -75° . T. H. P.

Physico-chemical Researches on Lecithin and Cholesterol.
II. and III. OTTO PORGES and ERNST NEUBAUER (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 193—197. Compare Abstr., 1908, ii, 90).—Researches dealing with the physico-chemical properties of alcoholic and ethereal lecithin and cholesterol solutions.

II. Alcoholic solutions of cadmium chloride have been shown by Strecker to precipitate alcoholic lecithin solutions. Although the precipitate has well crystallised form, its composition, determined by analysis, does not indicate that it is a definite molecular compound; this has been attributed to its instability by several workers. The present work bears on the subject in that the action of salts dissolved in alcohol on alcoholic lecithin solutions has been investigated, and the author considers that the precipitates obtained are not chemical compounds, but of the same nature as the precipitates from aqueous lecithin suspensions. That the solution contains lecithin as a negative colloid is indicated by the reaction with ferric chloride and the precipitation by acid. This conclusion is further supported by the following considerations: Biltz (compare Abstr., 1904, ii, 324) has shown that oppositely charged colloids react together in a typical manner in that they in a certain optimum concentration are precipitated, while excess of either component inhibits precipitation. Ferric chloride solution contains the positive colloid ferric hydroxide. It was found that a 0.1% alcoholic lecithin solution is precipitated by an 0.01*N* ferric chloride solution, less so by one of 0.05*N* strength, whilst 0.2*N*, 0.002*N*, and 0.0005*N* solutions have no effect.

There are certain characteristic differences between the conditions of the lecithin in aqueous and alcoholic suspensions. The latter present a striking similarity to aqueous albumin solutions. In alcoholic solution the state of the lecithin is very like that of a "hydrophyllous" colloid in aqueous solution, whilst an aqueous lecithin suspension shows the phenomena peculiar to a "suspension" colloid.

III. Experiments on the precipitation of ethereal lecithin solutions are even more restricted in number than those dealing with alcoholic solutions. Ethereal ferric chloride solution gives, when concentrated, a precipitate, whilst mercuric chloride brings about no change. The presence of lecithin in ether increases in many cases the solubility of other substances therein. Many instances of this are well known, and an explanation of this lies in the fact that a dry ethereal lecithin solution can take up considerable quantities of water in addition to that taken up by dry ether alone. The existence of many "lecithides," it is suggested, may depend on this solubility, and it may also have some bearing on the jecorin question. In conclusion, the author states that similar experiments to the above in alcoholic and ethereal solutions of cholesterol bring about no change, and the conclusion is drawn that cholesterol is in true solution.

G. S. W.

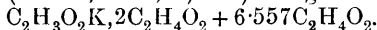
Cryo-acetates of Potassium, Sodium, and Lithium Acetates.
ALEXIS VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 753—757).—The author applies the term "cryo-acetates" to potassium, sodium, and lithium acetates united with acetic acid of crystallisation. Potassium or sodium acetate combines with $1\text{C}_2\text{H}_4\text{O}_2$ and $2\text{C}_2\text{H}_4\text{O}_2$, lithium

acetate only with $1\text{C}_2\text{H}_4\text{O}_2$, the compounds formed being all stable under ordinary conditions. The influence of the atomic weight of the metal on the stability of these compounds is shown by the fact that $\text{C}_2\text{H}_3\text{O}_2\text{K}, 2\text{C}_2\text{H}_4\text{O}_2$ melts (112°) without decomposing, whilst $\text{C}_2\text{H}_3\text{O}_2\text{Na}, 2\text{C}_2\text{H}_4\text{O}_2$ decomposes on melting, and lithium acetate yields only the compound $\text{C}_2\text{H}_3\text{O}_2\text{Li}, \text{C}_2\text{H}_4\text{O}_2$.

The method employed to obtain these compounds free from water, which they retain very persistently, consists in mixing the acetate with a small quantity of glacial acetic acid and repeatedly treating the mixture with acetic acid, the liquid formed being allowed to flow away before each new treatment with the acid.

The compound $\text{C}_2\text{H}_3\text{O}_2\text{K}, 2\text{C}_2\text{H}_4\text{O}_2$ reacts with acetic acid at the temperature $+7.9^\circ$, yielding the eutectic cryo-acetate,

$\text{C}_2\text{H}_3\text{O}_2\text{K}, 2\text{C}_2\text{H}_4\text{O}_2 + 6.599\text{C}_2\text{H}_4\text{O}_2$
(compare this vol., ii, 888), the composition calculated by means of Flawitzky's law (Abstr., 1906, ii, 152) being



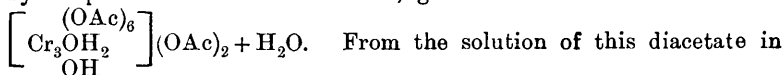
Similarly, the compound $\text{C}_2\text{H}_3\text{O}_2\text{Na}, 2\text{C}_2\text{H}_4\text{O}_2$ gives the cryo-acetate, $\text{C}_2\text{H}_3\text{O}_2\text{Na}, 2\text{C}_2\text{H}_4\text{O}_2 + 14.55\text{C}_2\text{H}_4\text{O}_2$, at 12.1° , and the compound

$\text{C}_2\text{H}_3\text{O}_2\text{Li}, \text{C}_2\text{H}_4\text{O}_2$
the cryo-acetate, $\text{C}_2\text{H}_3\text{O}_2\text{Li}, \text{C}_2\text{H}_4\text{O}_2 + 8.88\text{C}_2\text{H}_4\text{O}_2$ (calc. $8.441\text{C}_2\text{H}_4\text{O}_2$).
T. H. P.

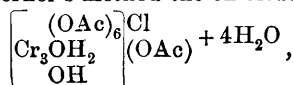
Salts of a Hexa-acetato(formato)-trichrome Base. II.

RUDOLF WEINLAND and P. DINKELACKER (*Ber.*, 1909, 42, 2997—3018). —In a former paper (Abstr., 1908, i, 847) Weinland has described the preparation of primary, secondary, and tertiary salts of a green triacid hexa-acetato-trichromo-base, $[\text{Cr}_3(\text{OAc})_6](\text{OH})_3$. Shortly after this, Werner (Abstr., 1908, i, 933) gave an account of some salts which he designated as hexa-acetato-diol-trichromo-salts, formulating the chloride, for example, as $[\text{Cr}_3(\text{OAc})_6(\text{OH})_2]\text{Cl} + 6\text{H}_2\text{O}$. Werner prepared only primary salts. The present paper gives an account of investigations proving that Werner's and the authors' compounds are identical; according to the former investigations only the platinichlorides were the same, although Werner found $6\text{H}_2\text{O}$ and the authors $5\text{H}_2\text{O}$.

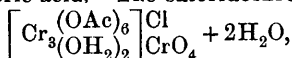
The chloride was first prepared as follows: From a solution of the dichromateacetate the chromic acid was precipitated by lead acetate. The excess of lead was precipitated as sulphide, and the filtrate, by evaporation on the water-bath, gave the diacetate of the base:



From the solution of this diacetate in dilute hydrochloric acid the chloride was obtained, and found to be identical with that prepared by Werner's method. Both preparations contained $8\text{H}_2\text{O}$, whereas Werner gives $6\text{H}_2\text{O}$. From the chloride made according to Werner's method the chlorideacetate,



was prepared by dissolving the former in 50% acetic acid and adding concentrated hydrochloric acid. The chloridechromate,



was also prepared by treating Werner's chloride with chromic acid and concentrated hydrochloric acid. Both these salts were identical with those previously obtained by the authors from the dichromateacetate.

The poly-acidity of the base was further proved by the preparation of the following salts, in addition to those previously described by Werner and the authors. Mono-, di-, and tri-acetates, bromide- and iodide-acetates, sulphate, stannichloride and antimonichloride, semichromateacetate, chromate, bromidechromate, perbromide, a double chloride of the chlorideacetate and ferric chloride, a compound of 3 molecules of the chloride with 1 molecule of the diacetate.

A new method of preparing the base is to heat the green or violet hydrate of chromic chloride, or the violet chromic nitrate, with glacial acetic acid.

A solution of the free base was prepared by the action of silver oxide on a concentrated solution of the chloride. The green filtrate from the silver chloride reacts alkaline, but in a few hours it becomes acid and has the odour of acetic acid. After a long time the solution becomes violet.

Assuming that the secondary and primary salts are hydroxo-salts, the salts are so formulated that the cation of the tertiary contains 2 molecules of water, that of the secondary 1 molecule of water and one hydroxyl group, and that of the primary two hydroxyl groups.

Werner also prepared some salts of a green hexaformato-diol-trichromo-base. The authors show that this base also gives secondary and tertiary salts. The triformate, chloridechromate, and chromate were prepared, the starting point being the monoformate in each case.

This latter compound, $\left[\text{Cr}_3(\text{H}\cdot\text{CO}_2)_6 \right] (\text{H}\cdot\text{CO}_2) + 5\text{H}_2\text{O}$, can not only be prepared by heating chromium hydroxide with formic acid of sp. gr. 1.15—1.20 (Häussermann, Abstr., 1895, i, 15), but also by warming chromic acid with aqueous formic acid, the latter reaction being similar to that used for the salts of the hexa-acetatotrichromo-base.

T. S. P.

Preparation of Esters of α -Halogenated Fatty Acids.

BERTHOLD RASSOW and R. BAUER (*J. pr. Chem.*, 1909, [ii], 261—270). —The various processes for the production of esters of α -halogenated fatty acids described in the literature have been examined. Auwers and Bernhardi's method of treating the free acid with bromine and amorphous phosphorus is the best. α -Ethylbutyric acid under these conditions yields α -ethylbutyryl bromide, which is changed by the addition of more bromine to bromo- α -ethylbutyryl bromide. This reacts with alcohol to form *ethyl α -bromo- α -ethylbutyrate*, $\text{C}\text{Et}_2\text{Br}\cdot\text{CO}_2\text{Et}$, b. p. 194—196°.

Ethyl α -hydroxy- α -ethylbutyrate reacts with phosphoric chloride or bromide, or with phosphorus bromide, to form, usually, ethyl α -ethyl- Δ^{α} -pentenoate. The elements of hydrogen bromide can be added to the

unsaturated ester by heating it in sealed tubes at 100° with a concentrated solution of hydrogen bromide in glacial acetic acid, but it is uncertain whether the halogen enters the α - or the β -position.

C. S.

Formation of Butyric Acid from Alcohol under the Influence of the Silent Discharge. WALTHER LÖB (*Biochem. Zeitsch.*, 1909, 20, 126—135).—Butyric acid is formed from alcohol vapour under the influence of the silent discharge, together with acetaldehyde, formaldehyde, alcohol, and other products. The theory of the formation of these products is discussed by the author, who describes in detail the apparatus employed and the method of isolation. S. B. S.

Preparation of Fatty Acids and their Anhydrides. H. FOURNIER (*Bull. Soc. chim.*, 1909, [iv], 5, 920—926. Compare Abstr., 1907, i, 271).—The acids are prepared, as described already (*loc. cit.*), by the oxidation of primary saturated alcohols with potassium permanganate in presence of potassium hydroxide, and the best conditions for securing good yields are given in detail. The anhydrides are prepared by the addition of acetyl chloride to the acid heated at 120—125°, the temperature being subsequently raised to 180°. The yield of anhydride varies from 55% to 75% of the theoretical.

In the following cases the substances are either new, or new constants are recorded for them. *n*-Valeric acid, b. p. 86—88°/15 mm., yields an anhydride, b. p. 110—111°/15 mm.; amide, m. p. 104—105°, and anilide, m. p. 63°. *iso*Valeric anhydride has b. p. 102—103°/15 mm.; the anilide has m. p. 113—114°. *iso*Hexoic anhydride has b. p. 130—131°/15 mm., and the anilide, m. p. 111°, crystallises in silky needles. *n*-Heptoic anhydride has b. p. 167—169°/20 mm. *iso*Heptoic acid has b. p. 212—214° under atmospheric pressure, and 107—108°/15 mm.; its anhydride has m. p. 154°/15 mm., and the amide, m. p. 103°, crystallises from water; the anilide has m. p. 75°.

T. A. H.

Hydrolysis of Fats and Oils. III. J. KELLNER (*Chem. Zeit.*, 1909, 33, 993. Compare this vol., i, 548).—Saponification of palm kernel oil with calcium oxide is like the saponification by alkali, a quadrimolecular reaction. The hydrolysis of palm oil by hydrochloric acid appears to proceed both as a uni- and a bi-molecular reaction, both mono- and di-glycerides being formed. L. DE K.

Linoleic Acid. ADOLF ROLLETT (*Zeitsch. physiol. Chem.*, 1909, 62, 410—421. Compare Hazura, Abstr., 1887, 359; Farnsteiner, *ibid.*, 1899, ii, 705).—Pure methyl linoleate, $C_{19}H_{34}O_2$, can be obtained by the action of zinc and methyl alcohol containing a small amount of hydrogen chloride on the tetrabromide (m. p. 114—115°). It can be extracted with light petroleum (b. p. 30—50°) and distilled under diminished pressure. It has b. p. 207—208°/11 mm., 211—212°/16 mm., and 221—224°/35 mm., D_4^{20} 0.8886, and iodine number 172 (Theory, 172.8). When hydrolysed with cold alcoholic potassium hydroxide the ester

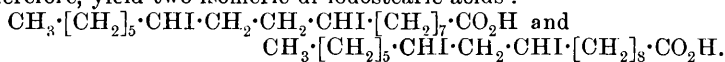
yields pure linoleic acid, which has b. p. $228^{\circ}/14$ mm. and D_4^{18} 0.9026. When brominated in different solvents, the pure acid does not give more than a 50% yield of the crystalline tetrabromide. A syrupy additive product is always formed, and this may be a stereoisomeric tetrabromide or merely impure crystalline tetrabromide. When reduced, this oil yields linoleic acid.

When oxidised with alkaline permanganate, linoleic acid yields sativic acid, m. p. $171-173^{\circ}$ (Hazura, Abstr., 1888, 817), together with a small amount of a substance insoluble in benzene. J. J. S.

Linolenic Acid and Linseed Oil. ADOLF ROLLETT (*Zeitsch. physiol. Chem.*, 1909, 62, 422—431. Compare Hazura and Friedreich, Abstr., 1887, 798; Hehner and Mitchell, *ibid.*, 1898, ii, 190; Erdmann and Bedford, this vol., i, 357).—Pure linolenic acid has been investigated in much the same manner as linoleic acid (preceding abstract). The methyl ester, prepared from linolenic acid hexabromide, is a clear, colourless liquid with b. p. $207^{\circ}/14$ mm. The acid has b. p. $230-232^{\circ}/17$ mm. and D_4^{18} 0.9141. When brominated in glacial acetic acid solution, the acid yields some 25% of the crystalline hexabromide, m. p. $181-182^{\circ}$. The oily by-product appears to be a tetrabromide, $C_{18}H_{30}O_2Br_4$, but when the bromine reacts for a longer time an oily hexabromide is formed.

These oils when reduced yield linolenic acid, which yields a mixture of solid and oily hexabromides (compare Erdmann and Bedford, *loc. cit.*). When oxidised with potassium permanganate, the acid yields *isolinusic* acid, m. p. $171-173^{\circ}$ (Hazura: $173-175^{\circ}$), and *linusic* acid, m. p. $201-203^{\circ}$. The conclusion is drawn that there is no evidence for the presence of an *isolinolenic* acid in linseed oil, or in the acid obtained by reducing the hexabromide. J. J. S.

Transformations of Ricinoleic Acid. BRONISLAW F. CHONOWSKY (*Ber.*, 1909, 42, 3339—3356).—The action of hydriodic acid on ricinoleic acid yields di-iodostearic acid, $C_{18}H_{34}O_2I_2$, and not iodo-stearidinic acid, as was stated by Claus (Abstr., 1877, ii, 314). Reduction of di-iodostearic acid by means of zinc dust and acetic acid yields only stearic acid; the halogen atoms of the di-iodo-acid are hence not situated at neighbouring carbon atoms, since, with such an arrangement, carbon atoms would be separated and an oleic acid formed. This reaction confirms the view that ricinoleic acid contains an alcoholic hydroxyl group combined with the twelfth carbon atom, and that the double linking is situated between the ninth and tenth carbon atoms. The action of hydriodic acid on ricinoleic acid should, therefore, yield two isomeric di-iodostearic acids:



The action of alcoholic potassium hydroxide on di-iodostearic acid yields an *acid*, $C_{18}H_{32}O_2$, which is isomeric with linoleic acid, and can also be obtained by the action of anhydrous zinc chloride on zinc ricinoleate; the *barium* and *silver* salts were analysed. When treated with bromine, this acid yields *tetrabromostearic acid*, $C_{18}H_{32}O_2Br_4$, and

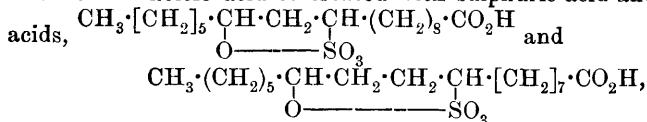
on oxidation with permanganate it gives a resin from which only azelaic acid could be separated.

The action of zinc oxide on di-iodostearic acid yields: (1) a mixture, m. p. 108—114°, of two isomeric oxyoleic or glycidic acids, the oxygen atom in one uniting the ninth and twelfth, and in the other the tenth and twelfth carbon atoms; the *sodium*, *silver*, and *barium* salts of these mixed acids were analysed; (2) an acid with two double linkings or one triple linking, mixed with a small proportion of other acids formed by the decomposition of di-iodostearic acid.

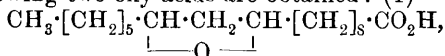
The action of moist silver oxide on di-iodostearic acid, like that of zinc oxide, results in the separation of hydrogen iodide, in addition to replacement of iodine by hydroxyl, a *dihydroxystearic acid*,

$\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot [\text{CH}_2]_8 \cdot \text{CO}_2\text{H}$,
m. p. 116—117°, solidifying point 113—114°, being formed; the *silver*, *barium*, and *sodium* salts of this acid were analysed, and the acetyl derivative prepared. Accompanying this acid are an acid resembling linoleic acid which does not solidify, and small proportions of acids formed by the decomposition of the di-iodostearic acid.

When ricinoleic acid is treated with sulphuric acid and the sulpho-



thus obtained boiled with water and hydrolysed with alkali hydroxide, the following two oxy-acids are obtained: (1)



m. p. 108—109°, which forms a crystalline *diacetyl* derivative, $\text{C}_{22}\text{H}_{40}\text{O}_6$; hydrolysis of the latter with alcoholic potassium hydroxide yields a dihydroxystearic acid, m. p. 115—116°, identical with that obtained by the action of moist silver oxide on di-iodostearic acid; (2) $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H}$, m. p. 73—74°, which

$$\text{O} \text{-----}$$

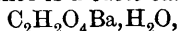
does not react so readily as the isomeric oxy-acid; when treated with acetic anhydride, and the resultant product hydrolysed with alcoholic potassium hydroxide and decomposed by means of hydrochloric acid, it gives a thick oil.

T. H. P.

Evolution of Hydrogen Occurring when Glyoxylic Acid is Warmed with Barium Hydroxide. WILHELM TRAUBE (*Ber.*, 1909, 42, 3295—3297).—Hydrogen is evolved when a solution of a glyoxylate is warmed with an excess of barium hydroxide (compare *Abstr.*, 1908, i, 75), probably owing to the occurrence of the reaction: $\text{CH}(\text{OH})_2 \cdot \text{CO}_2\text{H}$ or $\text{CHO} \cdot \text{CO}_2\text{H} + \text{H}_2\text{O} = \text{CO}_2\text{H} \cdot \text{CO}_2\text{H} + \text{H}_2$. Part of the glyoxylic acid is decomposed, however, with the formation of glycollic acid and oxalic acid, the volume of hydrogen evolved depending largely on the proportion of barium hydroxide present in the solution.

The addition of barium hydroxide solution to a solution of barium glyoxylate produces a flocculent precipitate, which is at first soluble in

acetic acid, but quickly passes into a crystalline powder insoluble in this reagent. The latter substance is a *basic barium glyoxylate*,



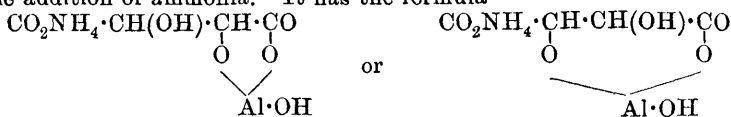
and liberates hydrogen when boiled with water.

W. H. G.

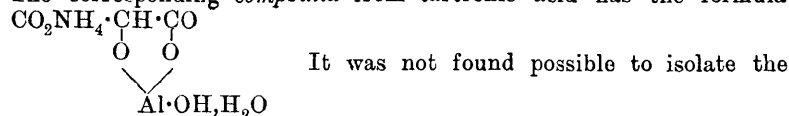
Complex Organic Aluminium Compounds. JOSEF HANUŠ and OT. QUADRAT (*Zeitsch. anorg. Chem.*, 1909, **63**, 306—317).—The formation of complex aluminium compounds, from which the metal is not precipitated by ammonia, depends on the number of carboxyl as well as of hydroxyl groups. Glyceric acid and glycerol only form complexes when the concentration is high, whilst malic and tartronic acids form complexes very readily. There is for each substance a limiting concentration at which precipitation by ammonia no longer takes place. Amino-, bromo-, and methoxy-succinic acids are without action, as are tartaric anhydride and malic hydrazide.

A $N/5$ solution of aluminium sulphate, acidified with sulphuric acid, is used, 20 c.c. being taken for each experiment, and varying quantities of the $N/5$ organic solution added. Water is added to 85 c.c., the solutions rapidly boiled, and 15 c.c. of ammonia added. The quantity of the organic solution which just prevents the production of an opalescence is noted.

The tartaric acid *compound* may be isolated by using aluminium nitrate instead of the sulphate, and precipitating with alcohol after the addition of ammonia. It has the formula



The corresponding *compound* from tartronic acid has the formula



corresponding compounds of malic and citric acids.

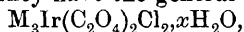
C. H. D.

Complex Iridium Compounds. Iridiodichloro-oxalates. MAURICE VÉZES and ALEXIS DUFFOUR (*Bull. Soc. chim.*, 1909, [iv], **5**, 869—872. Compare *Proc. verb. Soc. Sci. Bordeaux*, 1901).—*Potassium iridiodichloro-oxalate*, $\text{K}_3\text{Ir}(\text{C}_2\text{O}_4)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$, obtained by double decomposition between potassium iridosochloride or iridichloride and potassium oxalate, occurs in monoclinic crystals ($a : b : c = 1.1972 : 1 : 1.1996$; $\beta = 80.19^\circ 40''$), which affect polarised light and have a pomegranate-red colour, and is stable in air and in water, even on boiling. The salt is partly dehydrated at 100° , and decomposes at 245° , forming iridium, potassium iridate, carbonate, and chloride, and evolving carbon dioxide and monoxide.

A solution of the salt gives no reaction for chlorides or oxalates, but with silver nitrate yields a red precipitate of *silver iridiodichloro-oxalate*, $\text{Ag}_3\text{Ir}(\text{C}_2\text{O}_4)_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$, which separates from solution in warm water in ruby-red crystals. The silver salt is unaffected by light, and

is stable in cold water, but when heated in water slowly decomposes, giving a precipitate of silver chloride and oxalate. It is dehydrated at 130—140°, and decomposes at 270°, leaving a residue of iridium, silver chloride and oxide (?). The silver salt reacts readily with chlorides, and can thus be used for the preparation of other iridiochloro-oxalates (see succeeding abstract).
T. A. H.

Complex Iridium Compounds, Iridiodichloro-oxalic Acid and its Salts. ALEXIS DUFFOUR (*Bull. Soc. chim.*, 1909, [iv], 5, 872—876. Compare preceding abstract).—The preparation and properties of the acid and of a number of its salts are described. The salts crystallise well, often in isomorphous forms, and the crystals affect polarised light. They have the general formula



are all red in colour, mostly very soluble in water and all insoluble in alcohol or ether, and when heated are dehydrated with difficulty and usually decompose at 200—230°, yielding black residues containing metallic iridium and a mixture of chloride and carbonate of the second metal present.

Iridiodichloro-oxalic acid, $H_3Ir(C_2O_4)_2Cl_2 \cdot 4H_2O$, obtained by the action of hydrochloric acid on the silver salt suspended in warm water (see preceding abstract), crystallises in red, very deliquescent needles, is tribasic, acid to litmus or phenolphthalein, decomposes carbonates in solution, and changes slowly when kept or more rapidly when heated, either when dry or in aqueous solution, forming oxalic acid and leaving the iridium as a red soluble compound, not yet investigated.

The *rubidium*, *caesium*, and *ammonium* salts crystallise in hexagonal lamellæ with $1H_2O$. The *lithium* and *sodium* salts crystallise with $8H_2O$, and fuse in their water of crystallisation at 48° and 62° respectively; the former is very deliquescent, and both are readily soluble in water. The *thallium* salt forms prismatic needles, is anhydrous, and resembles the silver salt in being sparingly soluble in cold water; at 200° it blackens, and at a red heat the thallium in the residue volatilises in white fumes.
T. A. H.

Action of Alcohols, Acids, and Amines on Methyl Oxomalonate. RICHARD S. CURTISS and F. GRACE C. SPENCER (*J. Amer. Chem. Soc.*, 1909, 31, 1053—1057. Compare Anschütz and Parlato, *Abstr.*, 1893, i, 193).—*Methyl oxomalonate*, $CO(CO_2Me)_2$, b. p. 106°(uncorr.)/40 mm., obtained in a yield of 92% by leaving methyl dihydroxymalonate in contact with phosphoric oxide for two hours, is a yellowish-green oil, has $D_{27}^{20} 1.2464$, and is rapidly reconverted into the dihydroxymalonate on exposure to the air.

Ethyl alcohol unites with methyl oxomalonate to form the *ethyl ether* of methyl dihydroxymalonate, $OH \cdot C(CO_2Me)_2 \cdot OEt$, m. p. 58°, which forms colourless needles. Methyl and propyl alcohols also react with methyl oxomalonate, yielding thick oils resembling glycerol, which are converted by moist air into the respective alcohols and methyl dihydroxymalonate.

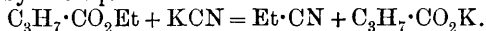
When methyl oxomalonate is treated with dry hydrogen chloride, *methyl chlorotartronate*, $OH \cdot CCl(CO_2Me)_2$, m. p. about 42°, is produced,

which forms colourless crystals and is very unstable, being rapidly converted into methyl dihydroxymalonate on exposure to moist air; ethyl alcohol reacts with this compound with formation of the ethyl ether of methyl dihydroxymalonate. Hydrogen bromide combines with methyl oxomalonate in a similar manner to produce *methyl bromotartronate*, m. p. 30° (decomp.), which dissociates at 40° into hydrogen bromide and the keto-ester. Hydrogen iodide also reacts with methyl oxomalonate, but the product is very unstable and has not been analysed.

When an ethereal solution of aniline is added gradually to methyl oxomalonate, *methyl anilinetartronate*, $\text{NPh}\cdot\text{C}(\text{CO}_2\text{Me})_2\cdot\text{OH}$, m. p. 102° , is obtained as a white, crystalline substance which is readily decomposed by hot water into aniline and methyl dihydroxymalonate. By the action of phosphoric oxide on this compound, *methyl phenyliminomalonate*, $\text{NPh}\cdot\text{C}(\text{CO}_2\text{Me})_2$, is produced, and is now being investigated.

Ammonia and urethane also form crystalline additive products with methyl oxomalonate. E. G.

Action of Potassium Cyanide on *iso*Butaldehyde. K. A. TAIPALE (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 815—832. Compare Claisen, *Abstr.*, 1893, i, 8; 1899, i, 667; Kohn, *Abstr.*, 1899, i, 328).—From a study of the products obtained by the action of potassium cyanide on *isobutaldehyde* (1) without solvent, (2) in ethereal and (3) in alcoholic solution, the author concludes that when potassium cyanide does not undergo hydrolysis, it acts on *isobutaldehyde* in the same way as on other aliphatic aldehydes, and in the same way as other alkaline condensing agents act. The formation of octylene glycol is a secondary reaction, and consists of a double exchange between the condensation products of the aldehyde and the alcoholic solvent under the influence of the potassium cyanide. One of the products of the action of potassium cyanide on *isobutaldehyde* in ethyl alcohol consists apparently of propionitrile, formed as a result of an accessory reaction represented by the equation:



The formation of *isobutaldol* cyanohydrin or the isomeric imino-ether, observed by Kohn and by Claisen (*loc. cit.*), is due to the hydrolysis of the potassium cyanide, these investigators studying the course of the reaction in presence of water; in all probability the cyanohydrin or imino-ether results from the action of hydrocyanic acid on the *isobutaldol* first formed. T. H. P.

Tautomerism of Aliphatic Ketones. ADRIANO OSTROGOVICH (*Ber.*, 1909, 42, 3186—3187).—Polemical. The author draws attention to discrepancies in the analytical data in Hâncu's paper on this subject (compare this vol., i, 364). The results of Hâncu's determinations of acetyl groups, stated by him to be in close agreement with the theory, actually work out to 149% and 195% of the esters analysed respectively. R. V. S.

Action of Sodium on Acetone. MAURICE DELACRE (*Bull. Soc. chim.*, 1909, [iv], 5, 884—889).—Since in the action of sodium on

acetone in presence of a solution of potassium hydroxide only 14% of pinacone and 10% of isopropyl alcohol are obtained, and these materials are generally regarded as the products of the principal reactions which take place, the author has investigated quantitatively, in large scale operations, the destination of that part of the acetone still unaccounted for. The results show that losses occur by (1) evaporation of acetone during the action; (2) the formation of water; (3) the production of phorone and other more complex condensation products; (4) the formation of mesityl oxide. Denigés' statement (Abstr., 1904, i, 706) that dimethylisopropylcarbinol is formed in this reaction could not be confirmed, but evidence of the formation of a ketonic substance boiling at 114° was obtained. Further, no propyl alcohol is produced.

T. A. H.

So-called ψ -Dichloroacetone, an Alleged Isomeride of Dichloroacetone. THEODOR POSNER and KARL ROHDE (*Ber.*, 1909, 42, 3233—3242).—The object of this work is to clear up the uncertainties and contradictions which exist in the literature regarding the chlorine substitution products of acetone.

The authors find that oxidation of α -dichlorohydrin, and also chlorination of acetone, lead to one and the same substance, *s*-dichloroacetone, which does not react with potassium phthalimide in the way formerly supposed, but yields only phthalimide. Hence Cloez's ψ -dichloroacetone and ψ -phthaliminoacetone do not exist. Further, the chlorination of acetone yields both *symmetrical* and *asymmetrical* dichloroacetone, but no polymeric dichloroacetones; the latter are therefore to be erased from the literature.

The product obtained by chlorinating acetone by the method of Fritsch (Abstr., 1894, i, 490) yielded on distillation a main fraction, which, on further purification, had b. p. $118-120^{\circ}$. A smaller portion of the oil distilled at $160-178^{\circ}$, and was fractionated until it had b. p. $167-175^{\circ}$. After a time it crystallised, and the separated crystals were white, had b. p. $172.6-173^{\circ}/748$ mm. (corr.), and m. p. 43° ; D_4^{46} 1.3843; n_D^{46} 1.47223; M_D 25.71 (ketonic form requires 25.99); molecular dispersion 0.708 (ketonic form requires 0.702, pseudo-form 0.625). The method of Hörmann (Abstr., 1881, 248) was found to give only 6% yield; it was therefore modified by shaking the distillate with ether, and extracting the dichloroacetone by shaking the ethereal solution with sodium hydrogen sulphite. The ether is then distilled off and the residual oil again subjected to oxidation, and so on until all the dichlorohydrin is oxidised. The distillate obtained on decomposing the hydrogen sulphite solutions yielded crystals of m. p. 43° and b. p. $173-173.4^{\circ}/759$ mm. (corr.); D_4^{46} 1.3809; n_D^{46} 1.47144; M_D 25.72; molecular dispersion 0.725.

s-Diphtaliminoacetone was prepared by Gabriel and Posner's method (*loc. cit.*), and had the correct m. p., 268° . Its ketonic nature follows from the formation of an *oxime*, which forms colourless crystals of m. p. 217° . Numerous repetitions of the reaction between potassium phthalimide and pure *s*-dichloroacetone yielded nothing but phthalimide. It was also not possible to obtain the compound previously

described by Posner, even when the raw distillate obtained in the oxidation of dichlorohydrin was used instead of pure dichloroacetone. An investigation of a sample of the ψ -diphthaliminoacetone formerly described by Posner indicated that it was a mixture of ordinary s -diphthaliminoacetone with phthalimide.

Optical Behaviour of α -Dichlorohydrin and of Epichlorohydrin.—Commercial α -dichlorohydrin was repeatedly fractionated; a small middle portion of a constant-boiling fraction then gave the following figures: D_D^{17} 1.3506; $n_D^{16.9}$ 1.480245; M_D 27.15; mol. dispersion 0.670. The ketonic formula requires M_D 27.33; mol. dispersion 0.703. R. V. S.

Preparation of Pure Ketones by means of Acetoacetic Ester. ARTHUR MICHAEL and KARL WOLGAST (*Ber.*, 1909, 42, 3176—3177).—The interaction of alkyl halides and sodioacetoacetic ester produces a mixture of mono- and di-alkylacetoacetic esters, from which the former can only be obtained pure by chemical means (Michael, *Abstr.*, 1905, i, 564). Ceresole showed (*Abstr.*, 1883, 41) that monoalkylacetoacetic esters are readily saponified by aqueous alkali hydroxides in the cold, whilst the dialkyl derivatives, with the exception of dimethylacetoacetic ester, are not attacked. This difference may be applied to the preparation of pure ketones, and obviates the necessity of starting with pure monoalkylacetoacetic esters. The mixture of esters is freed from acetoacetic ester by shaking with ammonia, fractionated once, then shaken for fifteen minutes with excess of 5% potassium hydroxide. The alkaline solution is separated from the insoluble oil and acidified with dilute hydrochloric acid. The ketone is isolated by distillation.

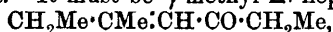
In the case of methyl propyl ketone (from ethylacetoacetic ester), the distillate contains alcohol which cannot be removed by fractionation. The ketone is therefore separated as the bisulphite compound.

R. V. S.

Electrolytic Reduction of Methyl *iso*-Amyl Ketone to *iso*-Heptane. JULIUS TAFEL (*Ber.*, 1909, 42, 3146—3148. Compare this vol., i, 545).—If lead cathodes are used in the reduction, as in the case of the acetoacetic esters, the yield is reduced to 25%, owing to the formation of organic lead compounds. The yield is now raised to 83.5% by employing an apparatus similar to that used for the reduction of acetoacetic esters, but containing as cathode a hollow cylinder of cadmium which can be cooled with water. The product after purification showed b. p. 89.1—89.6°/748 mm., in agreement with the value previously found for the pure hydrocarbon by Purdie (*Trans.*, 1881, 39, 464). The author proposes to employ the method extensively for the preparation of hydrocarbons.

R. V. S.

Action of Calcium Carbide on Some Ketones. II. F. BODROUX and FELIX TABOURY (*Bull. Soc. chim.*, 1909, [iv], 5, 950—952).—The unsaturated ketone described already (*Abstr.*, 1908, i, 854), obtained by the action of calcium carbide on butanone, has n_D^{15} 1.4497, and yields a *semicarbazone*, m. p. 114—115°, crystallising in colourless needles. It must be γ -methyl- Δ^7 -heptene- ϵ -one,



since on reduction by Sabatier and Senderens' method it yields γ -methylheptane- ϵ -one, $\text{CH}_2\text{Me}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\text{Me}$. The latter is a pleasant-smelling, colourless liquid, having D^{24}_D 0.820, n^{18}_D 1.4124, b. p. 153—155°/760 mm., and yielding a semicarbazone, m. p. 102°, crystallising in colourless prisms.

β -Methylpentan- δ -one reacts with calcium carbide to form $\beta\delta\delta$ -tri-methyl - Δ^5 - nonene - ζ - one, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHMe}_2$, D^{18}_D 0.838, n^{18}_D 1.4491, and b. p. 217—219°/760 mm., which yields a viscous oxime, b. p. 143—146°/17 mm., and, on reduction, furnishes the corresponding saturated ketone as a pleasant-smelling liquid, having D^{18}_D 0.820, n^{18}_D 1.4262, b. p. 210—212°/760 mm., which does not combine with sodium hydrogen sulphite, but yields a liquid oxime, b. p. 138—140°/15 mm.

Mesityl oxide reacts with calcium carbide, but does not give the expected ketone, $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CMe}_2$, but a mixture of products having D^{17}_D 0.937, n^{17}_D 1.5057, and b. p. 238—242°/741 mm., which furnishes two semicarbazones, the one gummy and the other, m. p. 165—166°, crystallising in colourless prisms. On reduction the mixture gives a colourless liquid of unpleasant odour and b. p. 200—230°, from which no definite product could be isolated.

T. A. H.

The Fission of Sugars. V. The Reversal of the Sugar Synthesis. WALTHER LÖB (*Biochem. Zeitsch.*, 1909, 20, 516—522. Compare Abstr., 1908, i, 715, 764; this vol., i, 352, 456).—The author discusses the conditions which cause the formation of a pentose and formaldehyde from a hexose, and the reverse reaction of the formation of a hexose from a pentose and formaldehyde. S. B. S.

Action of Fehling's Solution on Maltose. W. LEE LEWIS (*Amer. Chem. J.*, 1909, 42, 301—319).—An account is given of an investigation of the products of oxidation of maltose by Fehling's solution. The results show that the proportions of the acids produced, namely, carbonic, formic, hexonic, and probably glyceric and trihydroxybutyric, differ considerably from those obtained by Nef (Abstr., 1908, i, 5) with dextrose, lævulose, and mannose, and that a new hexonic acid, probably α -hydroxymethyl- d -ribonic acid, is formed in place of α -hydroxymethyl- d -arabonic acid. Further, whilst mannose, dextrose, and lævulose yield d -gluconic acid and traces of d -mannonic acid, maltose gives glucosido- d -mannonic acid only (compare Nef, *loc. cit.*). Another important point of difference between the oxidation of mannose, dextrose, and lævulose and that of maltose is that, whilst the former sugars yield large amounts of glyceric and trihydroxybutyric acids, it was not possible in the case of maltose to prove the presence of any monobasic acids containing three or four carbon atoms. It is evident that maltose is not appreciably hydrolysed into 2 mols. of dextrose, since the chief oxidation products are glucosido-monobasic acids, but it is possible that it may be converted to a small extent into 2 mols. of dextrose before oxidation takes place.

By the oxidation of 136.8 grams of anhydrous maltose, there were produced 10.6 grams of carbon dioxide, 4.74 grams of formic acid, and 132.8 grams of non-volatile substances, consisting chiefly of glucosido-

acids. The latter, on hydrolysis, gave 47.5 grams of dextrose and 82.35 grams of non-volatile acids, containing 0.35 gram of oxalic acid, 3.92 grams of glycollic acid, 30.25 grams of *d*-mannonolactone, 10.5 grams of α -hydroxymethyl-*d*-ribonic acid, and 37 grams of acids which were not identified.

*α -Hydroxymethyl-*d*-ribonic acid*, m. p. 183—186°, forms flat, transparent plates, and is soluble in 10 parts of boiling water, but only sparingly in cold water. The *phenylhydrazide*, m. p. 179—183°, has $[\alpha]_D + 8.38^\circ$. The *calcium* salt forms small cubes, and has $[\alpha]_D + 11.98^\circ$.

It appears probable that only two hexonic acids, namely, *d*-mannonic and *α -hydroxymethyl-*d*-ribonic acids*, are produced by the hydrolysis of the glucosido-acid formed by the oxidation of maltose with Fehling's solution. Both these acids must therefore be formed by an unsymmetrical benzilic acid rearrangement from 1:2-maltosone and 2:3-maltosone respectively (Nef, *loc. cit.*). 1:2-*d*-Glucosone, the intermediate product of the oxidation of dextrose, *d*-fructose, and *d*-mannose, however, gives mainly *d*-gluconic acid, together with small quantities of *d*-mannonic acid. In order to test these conclusions, a study has been made of the behaviour of alkali hydroxides towards *d*-glucosone and *d*-maltosone, but the results cannot be regarded as decisive.

E. G.

Cellulose Esters. R. G. WOODBRIDGE, jun. (*J. Amer. Chem. Soc.*, 1909, 31, 1067—1071).—*Cellulose tripropionate*, prepared by the action of propionic anhydride on cellulose in presence of sulphuric acid or zinc chloride, closely resembles the acetate, but can be distinguished from the latter by its solubility in ethyl acetate. A study has also been made of cellulose formate, and the results obtained accord with those of Berl and Smith (Abstr., 1907, i, 289), but do not confirm those of Bemberg (Abstr., 1908, i, 321).

E. G.

Pectins. A. WILHELMJ (*Zeitsch. Ver. deut. Zuckerind.*, 1909, 895—915).—Pectins, under the influence of moulds, are broken down into optically active arabinose. Freshly prepared pectin solutions likewise yield arabinose when hydrolysed with dilute acids. In years when the beets become mouldy, it is possible that sugar may in this way be formed from the pectins and so affect the accuracy of the sucrose estimations made in the ordinary manner. Hydrolysis of the pectins also takes place when the wet beets are heated, laevorotatory compounds being formed which are not precipitated by lead acetate. The amount formed depends on the temperature and time of heating. Lime produces a copious precipitate in the cold aqueous extract of beets which have been heated after the complete extraction of the sugar. The filtrate, which is laevorotatory, contains three calcium salts, probably those of a saccharate of arabinose, of a γ -hydroxy-acid or its lactone, and of the metapectic acid described by Scheibler. All these yield arabinose on hydrolysis. The calcium oxide precipitate is in part soluble in acetic acid; this fraction is laevorotatory, and is probably the *l*-parapectic acid described by Weisberg.

The residue is partly soluble in hydrochloric acid; this portion is

precipitated by alkalis, and is remarkable in being very resistant to hydrolysis and yielding no arabinose. It is evidently a pectin residue from which the arabinose-yielding group has already been eliminated. The residue insoluble in hydrochloric acid is an acid, probably the parapectic acid of Herzfeld. This is regarded as the mother substance of the products just described, and yields them when hydrolysed.

E. F. A.

Periodides of Organic Bases. A. LINARIX (*J. Pharm. Chim.*, 1909, [vi], 30, 241—247).—New *periodides* of the following bases are described. They crystallise well, and have the usual properties of the periodides.

Ethylenediamine, $B, 2HI, I_4$, m. p. 218° ; *piperazine*, $B, 2HI, I_4, 3H_2O$, m. p. 283° (the *anhydrous* form melts at 280°); *benzidine*, $B, 2HI, I_4$, m. p. 298° ; *piperidine*, B, HI, I_3 , m. p. 45° , and B, HI, I_4 , m. p. 35° ; *pilocarpine*, B, HI, I_2 , m. p. 148° , and B, HI, I_4 , m. p. 135° ; *ethylmorphine*, B, HI, I_2 , m. p. 150° , and *xanthine*, B, HI, I_3 (does not melt when heated).

In the case of the benzidine hydriodide periodide, the usual method of estimating the "external" iodine (*loc. cit.*) is inapplicable, as the substance is insoluble in alcohol, but good results were obtained by dissolving the periodide in a solution of potassium iodide in a mixture of water and alcohol and titrating with sodium thiosulphate.

T. A. H.

The Formation of Nitrogenous Compounds from Nitrogen and Alcohol under the Influence of the Silent Discharge. WALTHER LÖB (*Biochem. Zeitsch.*, 1909, 20, 136—142).—Under the conditions of experiment described, ammonium formate and hexamethylenetetramine were formed.

S. B. S.

Action of Calcium Oxide on Hydrazine Hydrate. ARTHUR STÄHLER (*Ber.*, 1909, 42, 3018—3019).—When hydrazine hydrate is mixed with about three times its weight of calcium oxide, partly in small lumps and partly in the form of powder, the mixture becomes heated to about 120° , and after a time the lumps disintegrate and the whole forms a dry powder. On raising the temperature, a distillate is obtained above 150° ; this at first consists of pure hydrazine, subsequently of hydrazine containing a little ammonia.

Probably a solid solution of hydrazine in calcium oxide is formed, or an additive compound, $Ca(ON_2H_5)_2$, which is subsequently dissociated into calcium hydroxide and hydrazine.

E. F. A.

Synthesis of Polypeptides: Derivatives of *iso*Leucine. I. EMIL ABDERHALDEN, PAUL HIRSCH, and JOSEF SCHULER (*Ber.*, 1909, 42, 3394—3411).—The authors have prepared a number of polypeptides derived from *dl*- and *d*-isoleucine (compare Brasch and Friedmann, *Abstr.*, 1908, i, 607; Ehrlich, *Abstr.*, 1908, i, 396).

Chloroacetyl-*dl*-isoleucine, $CH_2Cl \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CHMeEt$, forms crystals, m. p. 105 — 106° (corr.).

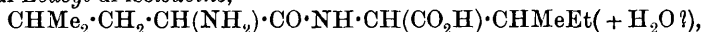
Glycyl-dl-isoleucine, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMeEt}$, prepared by the action of ammonia on the preceding compound, was not obtained crystalline; it turns brown at 215° and sinters at 219° , m. p. 242° (corr.).

dl- α -Bromoisohexoyl-dl-isoleucine,



prepared from α -bromoisohexoyl chloride and dl-isoleucine dissolved in sodium hydroxide solution, sinters at 135° , m. p. 146 — 149° (corr.).

dl-Leucyl-dl-isoleucine,

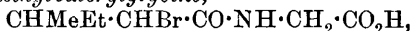


turns brown at 250° , m. p. 262 — 263° (corr.).

d- α -Bromo- β -methylvaleric acid, $\text{CHMeEt} \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$, prepared by the action of bromine on l-isoleucine hydrobromide in a current of nitric oxide, softens at 30° , m. p. 39° , $[\alpha]_D^{20}$ in benzene + 26.48° ($\pm 0.2^\circ$). On treatment with aqueous ammonia it is converted into l-isoleucine.

d- α -Bromo- β -methylvaleryl chloride, $\text{CHMeEt} \cdot \text{CHBr} \cdot \text{CO} \cdot \text{Cl}$, obtained by the action of thionyl chloride on the corresponding acid, has b. p. $67/3$ mm.

d- α -Bromo- β -methylvalerylglycine,



crystallises from water in flocculent aggregates of needles, sinters at 85° , m. p. 91 — 92° (corr.), $[\alpha]_D^{20}$ + 64.42° ($\pm 0.2^\circ$).

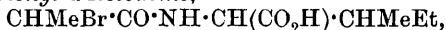
d-isoleucylglycine, $\text{CHMeEt} \cdot \text{CH}(\text{NH}_2) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, has m. p. 162° , $[\alpha]_D^{20}$ + 33.59° ($\pm 0.2^\circ$).

Chloroacetyl-d-isoleucine, $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMeEt}$, has m. p. 74 — 75° , $[\alpha]_D^{20}$ + 25.0° ($\pm 0.2^\circ$).

Glycyl-d-isoleucine, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMeEt}$, crystallises from aqueous alcohol in shining leaflets, m. p. 262° (corr.; decomp.), $[\alpha]_D$ - 14.7° ($\pm 0.4^\circ$).

Glycyl-d-isoleucine anhydride, [3 : 6-diketo-2-sec.-butylpiperazine], $\text{CH}_2 \cdot \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \cdot \text{CH} \cdot \text{CHMeEt}$, crystallises in spherical aggregates of needles, m. p. 262° (corr.; decomp.), $[\alpha]_D$ - 26.05° ($\pm 0.6^\circ$).

d- α -Bromopropionyl-d-isoleucine,

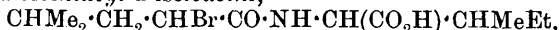


crystallises from water in branched needles, m. p. 151 — 152° (corr.), $[\alpha]_D^{20}$ + 24.5° ($\pm 0.4^\circ$).

d-Alanyl-d-isoleucine, $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMeEt}$, crystallises from aqueous alcohol in drusy masses composed of needles, sinters at about 220° , has m. p. 228 — 229° (corr.), and $[\alpha]_D^{20}$ + 6.1° ($\pm 0.6^\circ$) in *N*-hydrochloric acid and - 2.97° ($\pm 0.2^\circ$) in *N*-sodium hydroxide solution.

d-Alanyl-d-isoleucine anhydride, [3 : 6-diketo-2-methyl-5-sec.-butylpiperazine], $\text{CHMe} \cdot \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \cdot \text{CH} \cdot \text{CHMeEt}$, has m. p. 250 — 251° (corr.; decomp.), $[\alpha]_D^{20}$ - 16.6° ($\pm 0.1^\circ$).

d- α -Bromoisohexoyl-d-isoleucine,



separates from aqueous alcohol in rhombic crystals, sinters at 152° , m. p. 157 — 158° , $[\alpha]_D^{20}$ + 48.97° ($\pm 0.2^\circ$).

l-Leucyl-d-isoleucine,

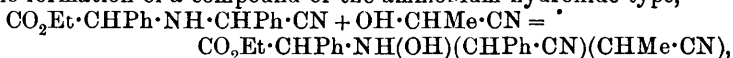
$\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMeEt}$,
crystallises from aqueous alcohol in cubes, m. p. 288° (corr.),
 $[\alpha]_D^{20} + 20.17^\circ (\pm 0.2^\circ)$ in *N*-hydrochloric acid; in *N*-sodium hydroxide
 solution it is feebly levorotatory. T. H. P.

The Degradation of Certain Di- and Hydroxy-amino-acids.

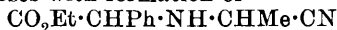
CARL NEUBERG (*Biochem. Zeitsch.*, 1909, 20, 531—536).—*iso*Serine yields on oxidation with hydrogen peroxide in presence of ferrous sulphate, aminoacetaldehyde, from which a *p*-nitrophenylesazone was prepared, and also pyrazine, which is formed from it by oxidation with sodium hydroxide and mercuric chloride. Serine on oxidation undergoes deamination and yields glycol aldehydes. $\alpha\beta$ -Diaminopropionic acid, on oxidation in similar circumstances, undergoes partial deamination only, the β -amino-group, as in *isoserine*, being stable, whereas the α -group, as in serine, undergoes change. Aminoacetaldehyde is, therefore, the chief oxidation product. *d*-Glucosamic acid yielded on oxidation a pentose. The course of oxidation of tyrosine under the same conditions is somewhat complicated. S. B. S.

Esbach's Protein Estimation and a New Creatinine Compound. ERNST MAYERHOFER (*Wien. Klin. Woch.*, 1909, 22, No. 3, Reprint).—When urine is boiled with 1% of picric acid and a strong mineral acid, there separates on cooling a crystalline *acid creatinine picrate*, $\text{C}_4\text{H}_7\text{ON}_3 \cdot (\text{C}_6\text{H}_3\text{O}_7\text{N})_2$, m. p. 161 — 166° , which is formed by decomposition of Jaffé's double picrate of creatinine and potassium, into which it can be converted by potassium hydroxide. G. B.

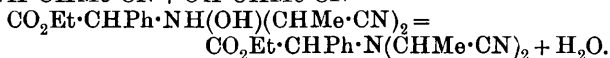
Interaction of Derivatives of Iminodicarboxylic Acids and α -Hydroxynitriles. GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 885—892. Compare Abstr., 1908, i, 251, 265; this vol., i, 106).—The interaction of the mixed nitrile and ethyl ester of *s*-di-*C*-phenyliminodiacetic acid with hydroxypropionitrile leads first to the formation of a compound of the ammonium hydroxide type,



which then decomposes with formation of

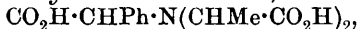


and $\text{OH} \cdot \text{CHPh} \cdot \text{CN}$. The nitrile ester of *s*-*C*-phenyl-*C*-methyliminodiacetic acid thus formed reacts with a fresh molecule of hydroxypropionitrile, giving another ammonium hydroxide compound, which loses water and yields a dinitrile ester of a substituted iminotriacetic acid:



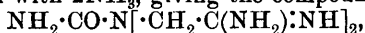
When heated with hydrochloric acid, this dinitrile ester yields the corresponding iminotriacetic acid.

s-*C*-Phenyl-di-*C*-methyliminotriacetic acid,



crystallises from water in silky needles, m. p. 206 — 208° .

The author explains the formation of 4-iminohydantoin-1-acetamide by the action of alcoholic ammonia on carbomethoxyiminodiacetonitrile (compare Jongkees, Abstr., 1908, i, 959) as due to the replacement of the methoxy-group by an amino-group and union of the compound thus formed with 2NH_3 , giving the compound

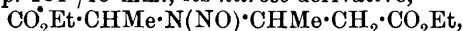


which, on boiling with water, loses ammonia, yielding 4-iminohydantoin-1-acetamide. An alternative explanation of the reaction is also given. T. H. P.

Iminodicarboxylic Acids. GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 893—900).—Having shown that imino-acid derivatives of high molecular weight may be converted into similar derivatives of lower molecular weight, and that these are resolved into amino- and hydroxy-acids on hydrolysis (compare this vol., i, 106 and preceding abstract), the author has prepared the following new iminodicarboxylic acids and derivatives.

The *hydrochloride* of the *nitrile* ester of C-isobutyliminodiacetic acid, $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{CN} \cdot \text{HCl}$, prepared from the ethyl ester of glycine and γ -methylpropaldehyde, has m. p. 142° (decomp.). The free *nitrile* ester, $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_2$, is a colourless, mobile liquid, b. p. $141\text{—}151^\circ/18$ mm., with a sweetish, stupefying odour. When boiled with dilute hydrochloric acid, the nitrile ester is converted into C-isobutyliminodiacetic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{CO}_2\text{H}$, which crystallises in thin needles, m. p. $210\text{—}215^\circ$. It forms a slightly soluble *lead* salt and an *ethyl* ester, $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{CO}_2\text{Et}$, b. p. $146^\circ/16$ mm., the *nitroso*-compound of which, $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{N}(\text{NO}) \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{CO}_2\text{Et}$, has b. p. $179^\circ/17$ mm. and gives Liebermann's reaction.

a-Propio- β -iminobutyric acid, $\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared by the interaction of ethyl β -aminobutyrate hydrochloride, acetaldehyde, and potassium cyanide, forms slender, silky needles, m. p. 216° (decomp.), and is monobasic towards sodium hydroxide. The *hydrochloride*, $\text{C}_7\text{H}_{14}\text{O}_4\text{NCl}$, decomp. $185\text{—}188^\circ$; *ethyl* ester, $\text{C}_{11}\text{H}_{21}\text{O}_4\text{N}$, b. p. $131^\circ/15$ mm., its *nitroso*-derivative,



b. p. $185^\circ/17$ mm., and the *picrate*, decomp. 216° , were prepared.

T. H. P.

Action of Ammonia on Unsaturated Acids. GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 900—908).—It was found by Eschweiler (Abstr., 1894, i, 267) that the result of the interaction of methylenecyanohydrin and ammonia depends on the active mass of the ammonia, and the author shows that, according to his explanation of the mechanism of the formation of derivatives of amino-, imino-, and nitrile acids (see preceding abstracts), the course of Eschweiler's reaction is in complete accord with Guldberg and Waage's law.

The author has studied the effect of the mass of the ammonia in the interaction of crotonic acid and ammonia by means of the following experiments: (1) 1 mol. crotonic acid and 4 mols. ammonia were heated in a sealed tube for twenty hours; of the crotonic acid which reacted

with the ammonia, 84.9% gave amino-acid and 15.1% imino-acid; (2) 1 mol. of crotonic acid and 2 mols. of ammonia were heated for ten hours; of the amount of crotonic acid reacting, 64% yielded amino-acid and 36% imino-acid. So that in the second case, despite the lessened duration of heating, the proportion of imino-acid obtained is considerably greater than in the first experiment.

Diethyl di-C-methyliminodipropionate, $\text{NH}(\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, prepared from the corresponding ammonium salt yielded by the action of ammonia on crotonic acid, is a colourless liquid, b. p. $150\text{--}150.5^\circ/15$ mm. The *copper* salt, $\text{C}_8\text{H}_{13}\text{O}_4\text{NCu}$, was analysed, but the following compounds could not be obtained crystalline: the free acid, which has an acid reaction with litmus, the amide, which is intensely alkaline towards litmus, and the hydrochloride.

When heated in a sealed tube, fumaric acid (1 mol.) and aqueous ammonia (3 mols.) (compare Körner and Menozzi, Abstr., 1890, 869) yield aspartic acid and iminodisuccinic acid, the *tetraethyl* ester of which, $\text{NH}[\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}]_2$, is an extremely viscous liquid, b. p. $215\text{--}217^\circ/15$ mm. T. H. P.

Action of Ammonia on the Homologues of Acetone. WILHELM TRAUBE (*Ber.*, 1909, 42, 3298—3304).—Contrary to the statements of Thomae (compare Abstr., 1905, i, 509; 1907, i, 113), methyl ethyl ketone and methyl propyl ketone behave like acetone towards ammonia.

It is found that the action of ammonia on methyl ethyl ketone leads, not only to the formation of 2:3:6-trimethyl-2:6-diethyl-4-piperidone (compare Abstr., 1908, i, 363), but also of *dimethyldiacetone-amine*, $\text{COEt}\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{NH}_2$ or $\text{COMe}\cdot\text{CHMe}\cdot\text{CMeEt}\cdot\text{NH}_2$, obtained as a basic oil which could not be purified, since it decomposes when distilled under greatly diminished pressure and does not form crystalline salts; it liberates ammonia when boiled, and yields *dimethylmesityl oxide*, $\text{COEt}\cdot\text{CH}\cdot\text{CMeEt}$ or $\text{COMe}\cdot\text{CMe}\cdot\text{CMeEt}$, probably identical with the compound obtained by Schramm by the action of sodium on methyl ethyl ketone (compare Abstr., 1883, 1079).

Diethyldiacetoneamine, $\text{COPra}\cdot\text{CH}_2\cdot\text{CMePra}\cdot\text{NH}_2$ or $\text{COMe}\cdot\text{CHEt}\cdot\text{CMePra}\cdot\text{NH}_2$,

appears to be the only base formed by the action of ammonia on methyl propyl ketone; it is an oil, b. p. $146^\circ/16$ mm. (slight decomp.), which when boiled under atmospheric pressure decomposes into ammonia and *diethylmesityl oxide*, $\text{C}_{10}\text{H}_{18}\text{O}$, a pale yellow liquid with an unpleasant odour, b. p. $198\text{--}199^\circ/760$ mm. Diethyldiacetone-amine when reduced with sodium amalgam and dilute acid yields the corresponding *alkamine*, which, however, could not be obtained in a pure state. W. H. G.

Rearrangements. GEORG SCHROETER (*Ber.*, 1909, 42, 3356—3362).—In preparing carbimides from azoimides (compare this vol., i, 617) it is not necessary, as a rule, to isolate the latter, but it is often sufficient to heat the acid chloride with commercial sodium azoimide in a suitable indifferent solvent until the evolution of

nitrogen is at an end. In this way the following carbimides have been prepared: (1) methylcarbimide; (2) *chloromethylcarbimide*, $\text{CH}_2\text{Cl}\cdot\text{N}\cdot\text{CO}$, b. p. $80-81^\circ$; with trichloroacetyl chloride and sodium azoimide, the evolution of nitrogen is incomplete, even after prolonged heating at a high temperature; (3) *n*-hexylcarbimide; (4) *n*-heptadecylcarbimide, $\text{C}_{17}\text{H}_{35}\cdot\text{N}\cdot\text{CO}$, b. p. $208-209^\circ/17\text{ mm.}$; (5) phenylcarbimide.

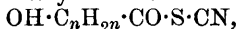
[With MOTSCHMANN.]—The constitution of 1:5-diphenyl-1:2:3:4-tetrazole (*loc. cit.*) is confirmed by the synthesis of this compound from benzenyliminophenyl chloride and sodium azoimide. In preparing 1:5-diphenyl-1:2:3:4-tetrazole from benzophenone chloride, it is not necessary to treat the chloride with silver azoimide, since sodium azoimide in amyl ether gives the same result.

The formation of diphenylketen from azibenzil (benzoylphenylazomethylene) (*loc. cit.*) is a result of the rearrangement of the grouping CPhBz: . The velocity of this rearrangement is studied by observing the transformation of azibenzil with alcohols (*loc. cit.*), in which about 70% of diphenylacetic ester and 30% of benzoin ether are formed. Hence at the temperature employed ($40-60^\circ$) the grouping CPhBz: is transformed into diphenylketen with measurable velocity, so that a part of the alcohol has time to occupy the free valencies of the phenylbenzoylmethylene.

T. H. P.

Ureides and Cyanamides of the Hydroxy-fatty Acids. II. ERIK CLEMMENSEN and ARNOLD H. C. HEITMAN (*Amer. Chem. J.*, 1909, 42, 319—340).—In an earlier paper (Abstr., 1908, i, 771) it has been shown that when the esters of the dialkylglycollic acids are treated with carbamide in presence of sodium ethoxide, ureides of the formula $\text{OH}\cdot\text{CR}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CR}_2\cdot\text{OH}$ are formed, whilst if thio-carbamide or guanidine is used instead of carbamide, dialkylglycollylcyanamides are produced.

The investigation has now been extended to glycollic, lactic, α -hydroxybutyric, and α -hydroxyisovaleric acids, and these have been found to behave in a similar manner. The ureides so obtained have low m. p.'s, and act as rather strong dibasic acids. The cyanamides are well-crystallised substances of high melting point, which, when boiled with dilute acids, are converted quantitatively into the corresponding ureides. The mother liquors from the cyanamides contain small quantities of acyl thiocyanates of the formula



these being the first acyl thiocyanates yet obtained (compare Dixon, *Trans.*, 1908, 93, 699); these compounds are stable, crystalline substances, and can be boiled with water or dilute acids without decomposition.

In preparing the esters of the α -hydroxy-fatty acids, it has been found that good yields can be obtained by heating the respective acids with excess of alcohol in presence of copper sulphate which has been dehydrated at a low temperature in order to obviate the formation of any sulphuric anhydride.

Diglycollylcarbamide, $\text{CO}(\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH})_2$, m. p. $88-89^\circ$, forms thin, colourless plates, and is not changed when boiled with solutions

of carbonates or dilute acids, but is decomposed by dilute alkali hydroxides with evolution of ammonia. The *silver* salt forms long, monoclinic prisms containing 2.5 mols. H_2O .

Dilactylcarbamide, $CO(NH \cdot CO \cdot CHMe \cdot OH)_2$, m. p. 49—50°, crystallises in small needles, and behaves towards alkalis in the same way as diglycollylcarbamide. On adding copper chloride to excess of concentrated solutions of calcium, barium, strontium, or magnesium salts of the carbamide, double salts of the formula $C_{14}H_{20}O_{10}N_4CuM$ are obtained as blue precipitates. The *silver* salt crystallises in small needles containing 1.5 mols. H_2O .

Di- α -hydroxybutyrylcarbamide, $CO[NH \cdot CO \cdot CH(OH) \cdot CH_2Me]_2$, m. p. 48—49°, forms short, prismatic crystals and yields blue double salts of the formula $C_{18}H_{28}O_{10}N_4CuM$ (where M is Ca, Ba, Sr, or Mg). The *silver* salt forms small, monoclinic needles containing 1.5 mols. H_2O .

Di- α -hydroxyisovalerylcarbamide, $CO[NH \cdot CO \cdot CH(OH) \cdot CHMe_2]_2$, b. p. 277—279°/760 mm., forms a colourless oil, has D^{15}_D 1.1922, and gives double salts of the formula $C_{22}H_{30}O_{10}N_4CuM$ (where M is Ca, Ba, Sr, or Mg). The *silver* salt forms slender, monoclinic needles containing 2.5 mols. H_2O .

Glycollylcyanamide, $OH \cdot CH_2 \cdot CO \cdot NH \cdot CN$, m. p. 217—237° (decomp.), forms large, lustrous, monoclinic prisms.

Glycollylthiocyanate, $OH \cdot CH_2 \cdot CO \cdot S \cdot CN$, m. p. 106°, crystallises in slender, yellow needles.

Lactylcyanamide (Merting, *J. pr. Chem.*, 1878, [ii], 7, 31) softens at 208° and melts at 212°.

Lactyl thiocyanate, $OH \cdot CHMe \cdot CO \cdot S \cdot CN$, m. p. 89—90°, forms small, colourless needles.

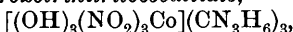
α -Hydroxybutyrylcyanamide, $CH_2Me \cdot CH(OH) \cdot CO \cdot NH \cdot CN$, m. p. 207—208°, forms thin, lustrous plates or silky needles.

α -Hydroxyisovalerylcyanamide, $CHMe_2 \cdot CH(OH) \cdot CO \cdot NH \cdot CN$, crystallises in needles, softens at 216°, and melts at 219°. E. G.

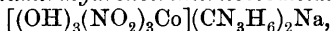
Carbonyldicarbamide as an Oxidation Product of Uric Acid. ALFRED SCHITTENHELM and KARL WIENER (*Zeitsch. physiol. Chem.*, 1909, 62, 100—106).—Scholz has already shown that by oxidising uric acid with hydrogen peroxide in alkaline solution, tetracarbonimide is obtained. A further oxidation product, carbonyldicarbamide, can be obtained by slightly varying the conditions employed by Scholz, in that the oxidation mixture is warmed from half to one hour on a water-bath. Oxalic acid was also obtained, and a substance which gives a derivative with α -naphthalenesulphonyl chloride.

S. B. S.

Action of Guanidine Carbonate on Sodium Cobaltinitrite: Trihydroxotrinitrocobaltiate. KARL A. HOFMANN and KARL BUCHNER (*Ber.*, 1909, 42, 3389—3392).—Guanidine carbonate acts on cobaltinitrites as though it were the carbonate of a mono-acid guanidinium base (compare Grossmann and Schück, *Abstr.*, 1907, i, 142), nitrito-groups being replaced by hydroxyl groups with formation of salts, $[(OH)_3(NO_2)_3Co](CN_3H_6)_3$ and $[(OH)_3(NO_2)_3Co](CN_3H_6)_2Na$, of one of the hydroxonitrito-acids, $[(OH)_n(NO_2)_{6-n}Co]H_3$, intermediate to the nitritocobalti-acids and cobaltihydroxide.

Guanidiniumtrihydroxotritocobaltiate,

crystallises in garnet-red, rhombic prisms, and is decomposed by water, rapidly on heating, into cobaltihydroxide and nitrite; the molecular weight in water, determined cryoscopically, is at first normal, but soon falls to the value, 151, indicated by this decomposition.

Sodium guanidiniumtrihydroxotritocobaltiate,

forms garnet-red crystals belonging to the rhombic system [STEINMETZ: $a:b:c=0.3775:1:0.32$], and is decomposed by water. The corresponding *silver* salt, $\text{C}_2\text{H}_{15}\text{O}_9\text{N}_9\text{AgCo}$, separates in reddish-brown, shining leaflets, is decomposed by water, and gives silver chloride or chromate when treated with potassium chloride or dichromate.

T. H. P.

Polymerisation of Fulminic Acid. F. CARLO PALAZZO (*Gazzetta*, 1909, 39, ii, 249—267. Compare Abstr., 1907, i, 298, 489).—The views of Wieland and Hess (this vol., i, 369) are criticised.

T. H. P.

Perthiocyanic Acid and Trithioallophanic Acid. ARTHUR ROSENHEIM, RICHARD LEVY, and HERBERT GRÜNBAUM (*Ber.*, 1909, 42, 2923—2929. Compare Hantzsch and Wolvekamp, Abstr., 1904, i,

718).—The formula $\begin{array}{c} \text{S} \text{---} \text{S} \\ | \quad | \\ \text{CS} \cdot \text{NH} \end{array} > \text{C} \cdot \text{NH}$ for xanthanic acid, proposed by Hantzsch and Wolvekamp, is supported by the following observations.

The ester of cyanamidodithiocarbonate undergoes rearrangement in aqueous solution containing hydrochloric acid into the ester of carbamidodithiocarbonate, $\text{C}(\text{SR})_2 \cdot \text{N} \cdot \text{CO} \cdot \text{NH}_2$. By the action of hydrogen sulphide on potassium cyanamidodithiocarbonate, reduction takes place as well as the addition of hydrogen sulphide, and *potassium trithioallophanate* is formed, $\text{S} \cdot \text{C}(\text{KS}) \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2$. This compound reacts with benzyl chloride, forming the benzyl trithioallophanate previously prepared by Fromm and Göncz (Abstr., 1907, i, 872).

Potassium trithioallophanate forms light yellow, lustrous crystals; the *copper* salt forms a characteristic amorphous, reddish-brown precipitate; the *silver* salt is bright red; the *lead* salt orange-red. The *methyl* ester forms yellowish-white crystals, m. p. 164° ; the *ethyl* ester has m. p. 174° .

Potassium trithioallophanate is also obtained by the direct action of hydrogen sulphide on molecular quantities of carbon disulphide and thiocarbamide in alkaline alcoholic solution. It is identical with the salt described by Klason as acid potassium perthiocyanate, but not obtained by him in the crystalline state.

Benzyltrithioallophanic acid forms bright yellow needles, m. p. 144° (Fromm, *loc. cit.*). *Benzyl perthiocyanate* forms colourless plates, m. p. 52° .

E. F. A.

Production of Hydrocyanic Acid from Ammonia and Wood. Charcoal, and also from Di- and Tri-methylamine G. A. VOERKELIUS (*Chem. Zeit.*, 1909, 33, 1025—1026, 1078—1081, 1090—1092).—In Dessau, Bueb's process (*Zeitsch. angew. Chem.*, 1906,

19, 609) for making cyanides from the organic compounds contained in beet molasses is worked. The molasses are first submitted to destructive distillation at 600° . The gases evolved contain water vapour, carbon monoxide and dioxide, hydrogen, methane, nitrogen, ammonia, and methylamine; they are heated to 800 — 1000° and then contain about 7% of hydrogen cyanide, the methylamine having disappeared. The present paper gives an account of experiments which have been made with the object of throwing light on the reactions which occur in the superheater. Mixtures of hydrogen and either ammonia, di- or tri-methylamine were passed through a tube heated to a definite temperature and filled with material which varied in different experiments. The products of reaction were analysed, and conclusions as to the course of the reactions could be drawn from the results.

When a mixture of ammonia and hydrogen is led over wood charcoal at temperatures higher than 700° , hydrogen cyanide and nitrogen are produced, but no methane. Some ammonia and hydrogen remain undecomposed. The proportion of ammonia to hydrogen cyanide varies, so that pure ammonium cyanide is not produced. The yields of hydrogen cyanide and undecomposed ammonia increase with increasing dilution of the ammonia by hydrogen, and also with the rate of flow of gases through the tube. The best yield is obtained at about 1000° . Dilution with coal-gas gives a better yield of hydrogen cyanide than when hydrogen is used as the diluent. The reactivity of the wood charcoal diminishes with continued use. The hydrogen cyanide is formed according to the reversible equation: $\text{NH}_3 + \text{C} \rightleftharpoons \text{HCN} + \text{H}_2$. At the same time the reversible reactions $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$ and $2\text{HCN} \rightleftharpoons \text{N}_2 + \text{H}_2 + 2\text{C}$ also play a part. The two latter reactions are catalytically affected by the material contained in the tube, as was shown by experiments with wood charcoal, chamotte, and a material known as "Marquardt's mass." Glazed material is not nearly so catalytically active as porous material.

At 800 — 1000° trimethylamine is decomposed to the extent of about 98% into hydrogen cyanide and methane, according to the equation $\text{N}(\text{CH}_3)_3 = \text{HCN} + 2\text{CH}_4$. The concentration of the mixed gases—hydrogen and trimethylamine—has no influence on the result, nor has the velocity of flow through the tube much effect. Increasing the velocity slightly increases the yield. If contact substances are avoided and the velocity of flow is not too small, all the hydrogen cyanide produced according to the above equation can be obtained, since even at 1000° the velocity of decomposition of hydrogen cyanide is very small. Raising the temperature above 1000° or allowing the hot gases to come into contact with iron, chamotte, or other porous material, decomposes part of the hydrogen cyanide. Between 800 and 1000° about 2% of the trimethylamine decomposes according to the equation: $\text{N}(\text{CH}_3)_3 + 3\text{H}_2 = \text{NH}_3 + 3\text{CH}_4$. At 720° only 78% of hydrogen cyanide is produced. At 600° no cyanide is formed, but only a base, which is probably tetramethylhydrazine.

At 820 — 1120° dimethylamine decomposes quantitatively according to the equation: $\text{NH}(\text{CH}_3)_2 = \text{HCN} + \text{CH}_4 + \text{H}_2$. If the dimethylamine is diluted with more than 50% of hydrogen, a part of it is decomposed according to the equation: $\text{NH}(\text{CH}_3)_2 + 2\text{H}_2 = \text{NH}_3 +$

2CH_4 . As the percentage of hydrogen increases, the reaction proceeds more and more according to the second equation, until with 97% of hydrogen no hydrogen cyanide is formed, but only ammonia. At 620° no hydrogen cyanide is formed, and at 720° a smaller amount than at higher temperatures.

T. S. P.

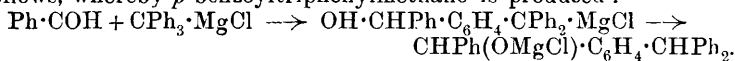
Nitro-derivatives of 3:5-Dibromotoluene. JAN J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 728—730. Compare Nevile and Winther, *Trans.*, 1881, 39, 83; Blanksma, *Abstr.*, 1904, i, 566; 1905, i, 761). —Nitro-derivatives of 3:5-dibromotoluene have been prepared. Diazotisation of 3:5-dibromo-4-nitro-*o*-toluidine yields two products: 3:5-dibromo-4-nitrotoluene, colourless crystals (from light petroleum), m. p. 84° , and converted by nitric acid into Nevile and Winther's 3:5-dibromo-2:4-dinitrotoluene; and a *by-product*, m. p. about 250° , much less soluble in alcohol than the other product of the reaction. A mixture of concentrated nitric and sulphuric acids converts both 3:5-dibromo-4-nitrotoluene and 3:5-dibromo-2:4-dinitrotoluene into 3:5-dibromo-2:4:6-trinitrotoluene.

Diazotisation of 3:5-dibromo-2-nitro-*p*-toluidine produces 3:5-dibromo-2-nitrotoluene, which is separated from a *by-product* of higher melting point by solution in alcohol and crystallisation from light petroleum. Thus purified, it has m. p. 67° . Nitric acid (D 1.52) converts it into a mixture of 3:5-dibromo-2:4-dinitrotoluene and 3:5-dibromo-2:6-dinitrotoluene, the latter not being obtained free from the former, but a mixture of nitric acid and sulphuric acid yields 3:5-dibromo-2:4:6-trinitrotoluene. 3:5-Dibromo-2:6-dinitrotoluene can be prepared by diazotising 3:5-dibromo-2:6-dinitro-*p*-toluidine, extracting with alcohol, and recrystallising from light petroleum. It has m. p. 117° .

On crystallisation from alcohol, a mixture of 3:5-dibromo-2:4-dinitrotoluene and 3:5-dibromo-2:6-dinitrotoluene forms crystals, m. p. 106 — 108° , previously prepared by Nevile and Winther, and identified as mixed crystals by the author. All the possible mono-, di-, and tri-nitro-derivatives of 3:5-dibromotoluene have been prepared.

A. J. W.

Existence of Two Isomeric Magnesium Triphenylmethyl Chlorides. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1909, 42, 3469—3479). —Of the three reactions quoted by Schmidlin for the differentiation of his α - and β -modifications of magnesium triphenylmethyl chloride (*Abstr.*, 1907, i, 26), the reactions with water and with carbon dioxide have been proved fallacious (Tschitschibabin, *ibid.*, i, 1022). Only the reaction with benzaldehyde remains, and the author now shows that this can be explained without the assumption of the existence of two modifications of magnesium triphenylmethyl chloride. He has already suggested (*loc. cit.*) that this substance may react with benzaldehyde normally, yielding β -benzopinacolin, and also abnormally as follows, whereby *p*-benzoyltriphenylmethane is produced:



Illustrations of such abnormal condensation are found in the reaction between formaldehyde and magnesium benzyl chloride, whereby both

benzylcarbinol and *o*-tolylcarbinol are formed (Tiffeneau and Delange, Abstr., 1904, i, 48), and also in the reaction between benzaldehyde and magnesium benzyl chloride, which leads to the formation of phenylbenzylcarbinol, phenyl-*o*-tolylcarbinol, and phenyl-*p*-tolylcarbinol.

The author has also obtained both benzopinacolin and *p*-benzoyltriphenylmethane from solutions of magnesium triphenylmethyl chloride, which should contain, according to Schmidlin, only the β -modification, and also from solutions which should contain only the α -form. Hence he draws the conclusion that there is no evidence for the existence of two isomeric magnesium triphenylmethyl chlorides.

C. S.

Phenanthrene-3-sulphonic Acid and Certain of its Derivatives. HÅKAN SANDQVIST (*Annalen*, 1909, 369, 104—117. Compare Werner, Abstr., 1902, i, 437).—Phenanthrene-3-sulphonic acid crystallises in white leaflets and retains $1\text{H}_2\text{O}$ at $60\text{--}65^\circ$; this hydrate has m. p. $120\text{--}121^\circ$, and yields the anhydrous acid, m. p. $175\text{--}177^\circ$, when heated above 86° ; the latter substance absorbs $2\text{H}_2\text{O}$ from the air and then has m. p. $88\text{--}89^\circ$. The mol. conductivities at 18° of aqueous solutions $v=32, 64, 128, 256, 512$, and 1024 were found to be $313\cdot2, 319\cdot3, 325\cdot2, 328\cdot2, 330\cdot4$, and $335\cdot5$ respectively. The acid does not follow Ostwald's dilution law, or yet agree with the empirical formulæ of van't Hoff and Rudolphi.

The following salts were analysed and their solubilities determined; the value recorded is the weight of anhydrous salt in grams which will dissolve in 100 grams of water at 20° : *potassium*, sol. = $0\cdot342$; *ammonium*, white leaflets, sol. = $0\cdot26$; *sodium* ($1\text{H}_2\text{O}$), irregular, granular crystals, sol. = $1\cdot1$; *calcium* ($2\text{H}_2\text{O}$), faintly yellowish-brown, granular crystals, sol. = $0\cdot11$; *barium* ($3\text{H}_2\text{O}$), white leaflets, sol. = $0\cdot03$; *magnesium* ($4\text{H}_2\text{O}$), large, slender, faintly yellowish-brown leaflets, sol. = $0\cdot116$; *zinc* ($4\text{H}_2\text{O}$), pale yellow, crystalline powder, sol. = $0\cdot19$; *ferrous* ($5\text{H}_2\text{O}$), slightly yellow, crystalline powder, sol. = $0\cdot2$; *lead* ($3\text{H}_2\text{O}$), slightly yellowish-brown, crystalline mass, sol. = $0\cdot08$; *copper* ($4\text{H}_2\text{O}$), pale green spangles, sol. = $0\cdot09$; *silver*, white leaflets, sol. = $0\cdot20$.

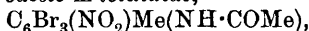
Phenanthrene-3-sulphonyl chloride has m. p. $110\text{--}111^\circ$, sometimes 114° ; when treated with ethyl alcohol, it yields the corresponding ethyl ester, $\text{C}_{14}\text{H}_9\cdot\text{SO}_2\cdot\text{OEt}$, which crystallises in elongated leaflets and needles, m. p. $107\text{--}108^\circ$; the *sulphonyl bromide*, $\text{C}_{14}\text{H}_9\cdot\text{SO}_2\text{Br}$, crystallises in pale yellow, transparent, cubical and rhomboidal plates, m. p. 140° ; the *sulphonamide*, $\text{C}_{14}\text{H}_9\cdot\text{SO}_2\cdot\text{NH}_2$, forms colourless leaflets, m. p. $189\cdot5\text{--}190^\circ$. The sulphonyl chloride when heated with phosphorus pentachloride yields 3-*chlorophenanthrene*, $\text{C}_{14}\text{H}_9\text{Cl}$, aggregates of needles, m. p. 81° and $70\cdot5\text{--}71^\circ$, and a *dichlorophenanthrene*, $\text{C}_{14}\text{H}_8\text{Cl}_2$, white crystals, m. p. 124° .

W. H. G.

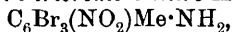
Acetylation with Acetic Anhydride and Sulphuric Acid. JAN J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 717—727).—A number of acetyl derivatives have been prepared by acetylation with acetic anhydride and a drop of concentrated sulphuric acid. For the mono-

acetyl derivatives the reaction was moderated by dissolving the substance in about ten times its weight of glacial acetic acid. The mono- and di-acetyl derivatives of the following have been prepared: 3:5-dibromo-*o*-toluidine, 3:5-dibromo-*p*-toluidine, 2:6-dichloro-4-nitroaniline, 2:6-dibromo-4-nitroaniline, 4:6-dibromo-2-nitroaniline, 2:4:6-tribromo-3-nitroaniline, and *o*-, *m*-, and *p*-nitroanilines. The monoacetyl derivatives of 2:3-, 2:4-, 2:5-, 3:4-, and 3:5-dinitroaniline have been prepared. *o*-Nitrodiaacetanilide forms colourless crystals, m. p. 94°. The diacetyl derivative of 2:4:6-trinitro-*m*-phenylenediamine, $C_6H(NO_2)_3(NH \cdot COMe)_2$, is colourless, does not melt below 300°, but darkens in colour at this temperature. 2:4:6-Tribromoaceto-*m*-toluidide forms colourless crystals, m. p. 205°. 2:4:6-Tribromodiaceto-*m*-toluidide (colourless crystals) has m. p. 103°.

Nitric acid (D 1.52) converts 2:4:6-tribromoaceto-*m*-toluidide into 2:4:6-tribromo-5-nitroaceto-*m*-toluidide,



colourless needles, m. p. 261°, which, with concentrated sulphuric acid at 110°, yields 2:4:6-tribromo-5-nitro-*m*-toluidide,

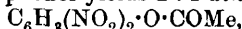


pale yellow needles, m. p. 184°.

2:4:6-Tribromo-5-nitrodiaaceto-*m*-toluidide forms colourless crystals (from alcohol), m. p. 188°. *s*-2:4:6-Tribromoaceto-*xy*lidide forms colourless crystals, m. p. 258°. 2:4:6-Tribromo-3:5-dinitroacetoanilide has m. p. 275°, and the corresponding diacetyl derivative has m. p. 165°.

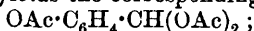
Bromine converts 4-nitro-*o*-toluidine into 3:5-dibromo-4-nitro-*o*-toluidine, $C_6HBr_2(NO_2)Me \cdot NH_2$, yellow crystals, m. p. 104° which yields 3:5-dibromo-4-nitroaceto-*o*-toluidide (colourless crystals, m. p. 201°) and 3:5-dibromo-4-nitrodiaaceto-*o*-toluidide, m. p. 159°. With nitric acid (D 1.52) and concentrated sulphuric acid, 3:5-dibromo-4-nitroaceto-*o*-toluidide yields 3:5-dibromo-4:6-dinitroacetotoluidide, white crystals, m. p. 280°. Bromination converts 2-nitro-*p*-toluidine into 3:5-dibromo-2-nitro-*p*-toluidine, yellow crystals, m. p. 82°, which yields 3:5-dibromo-2-nitroaceto-*p*-toluidide (compare Kuncell, this vol., i, 20).

The acetyl derivatives of *o*- and *p*-nitrophenol, 2:4:6-trinitrophenol, 2:4:6-tribromophenol, and 2:6-dibromo-4-nitrophenol have also been prepared. 2:4-Dinitrophenol yields 2:4-dinitrophenyl acetate,



colourless crystals, m. p. 72°. 2:4-Dibromo-6-nitrophenol yields 2:4-dibromo-6-nitrophenyl acetate, $C_6H_2Br_2(NO_2) \cdot O \cdot COMe$, colourless crystals, m. p. 88°.

Benzaldehyde yields benzylidene diacetate, $C_6H_5 \cdot CH(OAc)_2$; *p*-hydroxybenzaldehyde yields the corresponding triacetate,



furfuraldehyde yields furfurylidene diacetate, $C_4H_3O \cdot CH(OAc)_2$, which has m. p. 52° (from light petroleum). Law (Abstr., 1908, i, 321) gives 45°, but he employed alcohol, which is an unsatisfactory solvent for this compound. Methylfurfuraldehyde yields 2-methylfurfurylidene diacetate, $C_4H_2OMe \cdot CH(OAc)_2$, colourless crystals, m. p. 95°. 4-Hydroxy-2-methylfurfuraldehyde yields the corresponding triacetyl

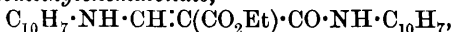
derivative, $\text{OAc}\cdot\text{C}_4\text{OHMe}\cdot\text{CH}(\text{OAc})_2$, colourless crystals from light petroleum, m. p. 73° .

The process furnishes a rapid acetylation method for aldehydes, and for derivatives of aniline and phenol. A. J. W.

Reactions of the Formamidine Derivatives. FRANK B. DAINS and E. W. BROWN (*J. Amer. Chem. Soc.*, 1909, 31, 1148—1157).—It has been shown previously (Abstr., 1902, i, 602) that the disubstituted formamidines react with compounds containing a methylene group to form compounds of the type $\text{R}\cdot\text{NH}\cdot\text{CH}\cdot\text{CX}\cdot\text{Y}$, and that when Y represents a carbethoxy-group, compounds of the type $\text{R}\cdot\text{NH}\cdot\text{CH}\cdot\text{CX}\cdot\text{CO}\cdot\text{NHR}$

are obtained. The completeness of the latter reaction depends on the temperature and the nature of the compound containing the methylene group. Thus with ethyl malonate, a quantitative yield of amide is produced; with ethyl acetoacetate, 50—80% of the amine reacts with the carbethoxy-group, whilst with ethyl cyanoacetate no amide is formed. The former reaction, namely, the replacement of the hydrogen atoms of the methylene group by $\cdot\text{CH}\cdot\text{NHR}$, seems to be affected by the positive or negative nature of the molecule. Thus benzyl cyanide and deoxybenzoin react with greater difficulty than the more negative ethyl malonate or acetoacetate, and the more positive methylpyrazolone fails to combine with diphenylformamidine, whilst phenylmethyl- and diphenyl-pyrazolone unite with it readily.

The following compounds have been obtained by the reaction of formamidines with ethyl malonate. The *a*-naphthylamide of ethyl *a*-naphthylaminomethylenemalonate,



m. p. 162° , yields a bromo-derivative, m. p. 227° . The corresponding *β*-naphthyl compound melts at 172° . When malonanilide is heated with di-*β*-naphthylformamidine, *β*-naphthylamine and *β*-naphthylaminomethylenemalonanilide, $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CH}\cdot\text{C}(\text{CO}\cdot\text{NHPh})_2$, m. p. 289° , are produced. The *m*-toluidide of ethyl *m*-toluidinomethylenemalonate melts at 95° . Methylenedi-*o*-phenetidine, m. p. 81° , obtained by heating ethyl orthoformate with *o*-phenetidine at 140° , yields a platini-chloride, m. p. 178° , and reacts with ethyl malonate, with formation of the *o*-phenetidide of ethyl *o*-phenetidinomethylenemalonate, m. p. 110° .

With ethyl acetoacetate, the following compounds were obtained: *p*-Bromoacetoacetylanilide, m. p. $137\cdot5^\circ$, was prepared by the action of *p*-bromoaniline. Anilinomethyleneacetoacetyl-*p*-bromoanilide and the isomeric *p*-bromoanilinomethyleneacetoacetanilide melt at 158° and 171° respectively. Di-*p*-bromophenylformamidine, m. p. 170° , reacts with ethyl acetoacetate to form *p*-bromoanilinomethyleneacetoacetyl-*p*-bromoanilide, m. p. 190° , together with ethyl *p*-bromoanilinomethyleneacetoacetate, m. p. 107° . *p*-Toluidinomethyleneacetoacetanilide melts at 142° . *ψ*-Cumidinomethyleneacetoacetyl-*ψ*-cumidide and ethyl *ψ*-cumidinomethyleneacetoacetate melt at 183° and 98° respectively. Ethyl *o*-anisidinomethyleneacetoacetate melts at 112° , and *p*-phenetidinomethyleneacetoacetyl-*p*-phenetidide at 138° . *a*-Naphthylaminomethyleneacetoacetyl-*a*-naphthylamide, m. p. 167 — 168° , yields a dibromide, m. p. 226° . Ethyl *a*-naphthylaminomethyleneacetoacetate melts at 92° . *β*-Naphthyl-

aminomethyleneacetoacetyl- β -naphthylamide and ethyl β -naphthylaminomethyleneacetoacetate melt at 184° and 95° respectively.

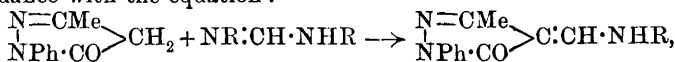
The following compounds of ethyl cyanoacetate are described: Ethyl ψ -cumidinomethylenecyanoacetate, m. p. 196° , ethyl α -naphthylaminomethylenecyanoacetate, m. p. 146° , and ethyl β -naphthylaminomethylenecyanoacetate, m. p. 152° .

With phenylacetoneitrile there were obtained m-toluidinomethylenebenzyl cyanide, m. p. 126° , and β -naphthylaminomethylenebenzyl cyanide, m. p. 194° .

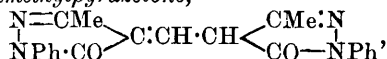
Deoxybenzoin unites with di- α -naphthylformamidine to form α -naphthylaminomethylenedeoxybenzoin, m. p. 161° .

The following compounds were obtained with acetylacetone: o-toluidinomethyleneacetylacetone, m. p. 124° , the corresponding m-toluidino-derivative, m. p. 75° , o-phenetidinomethyleneacetylacetone, m. p. 115 – 116° , and α - and β -naphthylaminomethyleneacetylacetone, melting at 144° and 129° respectively.

Phenylmethylpyrazolone and the formamidines react smoothly in accordance with the equation:



yielding red or yellow substituted aminoethylenepyrazolones. Methylenebisphenylmethylpyrazolone,



m. p. 180° , is sometimes formed in this reaction, this being the first instance in which both the $\text{NR}\cdot$ and $\text{NHR}\cdot$ groups of the substituted formamidines have been replaced in reactions with methylene derivatives. The following compounds are described: 4-Anilinomethylene-1-phenyl-3-methyl-5-pyrazolone, m. p. 154° , 4- β -naphthylaminomethylene-1-phenyl-3-methyl-5-pyrazolone, m. p. 177° , the corresponding α -naphthyl derivative, m. p. 122° , 4-p-bromoanilinomethylene-1-phenyl-3-methyl-5-pyrazolone, m. p. 168° , 4-p-toluidinomethylene-1-phenyl-3-methyl-5-pyrazolone, m. p. 164° , 4- ψ -cumidinomethylene-1-phenyl-3-methyl-5-pyrazolone, m. p. 171° , 4-p-phenetidinomethylene-1-phenyl-3-methyl-5-pyrazolone, 4-anilinomethylene-1:3-diphenyl-5-pyrazolone, m. p. 140° , 4-o-toluidinomethylene-1:3-diphenyl-5-pyrazolone, m. p. 146° , and 4- β -naphthylaminomethylene-1:3-diphenyl-5-pyrazolone, m. p. 192° .

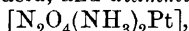
By the action of phenylhydrazine on anilinomethylenebenzoylacetonilide and o-toluidinomethylenebenzoylaceto-o-toluidide, Rüggeberg (*Diss.*, 1904) obtained compounds, m. p. 155° and 160° , which he regarded as aminomethylene derivatives of diphenylpyrazolone, but which do not appear identical with the anilinomethylene- and o-toluidinomethylene-diphenylpyrazolones described previously, which melt at 140° and 146° respectively. On repeating the work with o-toluidinomethylenebenzoylaceto-o-toluidide, it has been found that the compound obtained by Rüggeberg is the o-toluidide of 5-diphenylpyrazolecarboxylic acid, m. p. 165° . When ethyl β -naphthylaminomethyleneacetoacetate is boiled with phenylhydrazine, ethyl 1-phenyl-5-methylpyrazole-4-carboxylate (Claisen, *Abstr.*, 1897, i, 440) is

obtained; the *anilide* of the corresponding acid, m. p. 182°, and the *p-toluidide*, m. p. 177°, *α-naphthylamide*, m. p. 168°, and *β-naphthylamide*, m. p. 170°, are described. E. G.

Acylation of Amines and Phenols. ADOLF KAUFMANN (*Ber.*, 1909, 42, 3480—3483).—Acylated amines or phenols are obtained rapidly and usually almost quantitatively by adding an acid anhydride to the amine or phenol dissolved in a dry, indifferent solvent, such as ether, light petroleum, benzene, toluene, xylene, or nitrobenzene.

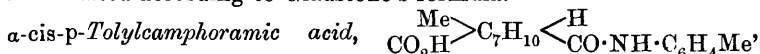
[With RICHARD HÜSSY and A. LUTERBACHER.]—In this way acetanilide, aceto-*o*-toluidide, aceto-*p*-toluidide, *p*-nitroacetanilide, *m*-nitroacetanilide, aceto-*α*-naphthalide, aceto-*β*-naphthalide, acetylanthranilic acid, methylacetanilide, *as*-acetylphenylhydrazine, phenylacetanilide, *p*-acetoxybenzoic acid, *o*-acetoxybenzoic acid, *p*-nitrophenyl acetate, and quinol diacetate have been obtained. In the case of the benzoyl derivatives, the benzoic acid, which is also produced, must be removed by sodium carbonate. Benzanilide and benzoyl-*p*-nitroaniline have been prepared. C. S.

Nitritoplateo-acids. KARL A. HOFMANN and KARL BUCHNER (*Ber.*, 1909, 42, 3392—3394).—When *p*-toluidine acts on nitritoplateo-acid, nitrous acid is abstracted from the latter (compare Abstr., 1908, i, 875), with formation of diazoaminotoluene and *toluidine trinitrito-p-toluidinoplateoate*, (N₃O₆Pt, C₇H₉N)H, C₇H₉N, which separates in faintly yellow, spear-shaped crystals, decomposes with sparking when heated, and is only slowly attacked by boiling 10% potassium hydroxide solution. When treated with concentrated ammonia solution and alcohol, it yields *p*-toluidine, nitrous acid, and *diamminoplatonitrite*,

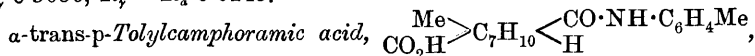


which crystallises in colourless, nacreous leaflets, and, when treated with concentrated hydrochloric acid, yields a toluidinoplateochloride to be described later. T. H. P.

Relations between the Chemical and Physical Characters and the Constitution of Isomeric Amino-derivatives of Camphoric Acid. GINO ABATI and F. DE NOTARIS (*Gazzetta*, 1909, 39, ii, 219—233).—The authors have prepared the four isomeric *p*-tolylcamphoramids and the corresponding three imides, the physical properties of which have been examined. The specific refractions, *R*, are calculated according to Gladstone's formula.



prepared by the interaction of camphoric anhydride (1 mol.) and *p*-toluidine (1 mol.) in toluene solution, forms colourless crystals, m. p. 201—209°, *D*₄²⁰ 1.1704, $[\alpha]_D^{15} + 49.5^\circ$, *R*_a (in ethyl acetate) 0.4791, *R*_y 0.5036, *R*_z − *R*_a 0.0245.



prepared by a method similar to that used by Auwers (Abstr., 1900, i, 84) for obtaining *α-trans*-phenylcamphoramid acid, forms an amorphous powder, m. p. 183°, *D*₄²⁰ 1.1872, $[\alpha]_D^{15} - 3.55^\circ$.

β-cis-*p*-Tolylcamphoramic acid, $\text{CO}_2\text{H} \begin{array}{c} \text{H} \\ \diagup \end{array} \text{C}_7\text{H}_{10} \begin{array}{c} \text{CH}_3 \\ \diagdown \end{array} \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, prepared by the action of alcoholic potassium hydroxide on *s*-*p*-tolylcamphorimide (*vide infra*), forms white crystals, m. p. 190—196°, D_4^{20} 1.2637, $[\alpha]_D^{25} - 64^\circ$.

β-trans-*p*-Tolylcamphoramic acid, $\text{CO}_2\text{H} \begin{array}{c} \text{H} \\ \diagup \end{array} \text{C}_7\text{H}_{10} \begin{array}{c} \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me} \\ \diagdown \end{array} \text{CH}_3$, prepared similarly to the *α*-trans-acid, forms micro-crystals, m. p. 189°, $[\alpha]_D^{25} - 13.7^\circ$.

s-*p*-Tolylcamphorimide, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CO} \\ \diagup \end{array} \text{N} \cdot \text{C}_6\text{H}_4\text{Me} \begin{array}{c} \diagdown \\ \text{CO} \end{array}$, prepared by the interaction of camphoryl chloride and *p*-toluidine in ethereal solution, forms colourless crystals, m. p. 189—190°, D_4^{20} 1.2925, $[\alpha]_D^{25} - 24.5^\circ$, R_a (in benzene) 0.4574—0.4598, R_γ 0.4754—0.4783, $R_\gamma - R_a$ 0.0180—0.0185.

α-*p*-Tolylcamphorisoimide, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \cdot \text{N}(\text{C}_6\text{H}_4\text{Me}) \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{O}$, prepared by the action of phosphoryl chloride or acetyl chloride on the *α*-*cis*-acid, forms crystals, m. p. 131°, D_4^{20} 1.2103—1.2128, $[\alpha]_D^{20} + 16.7^\circ$, R_a (in benzene) 0.4869, R_γ 0.5077, $R_\gamma - R_a$ 0.0208.

β-*p*-Tolylcamphorisoimide, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} \cdot \text{N}(\text{C}_6\text{H}_4\text{Me}) \end{array} \text{O}$, prepared from the *β*-*cis*-acid, has m.p. 146°, D_4^{20} 1.209, $[\alpha]_D^{15} + 7.1^\circ$.

The *p*-tolylcamphoric acids are analogous in both their chemical and their physical properties to the corresponding phenylcamphoramic acids. For example, the m. p.'s of the two series of acids are as follows :

	Phenylcamphoramic.	<i>p</i> -Tolylcamphoramic.
<i>α</i> - <i>cis</i> -Acid.....	203—204°	201—209°
<i>α</i> - <i>trans</i> -Acid	183—183.5	183
<i>β</i> - <i>cis</i> -Acid... ..	196	190—196

T. H. P.

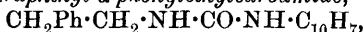
Electrolytic Reduction of the Condensation Products of Aldehydes and Amines. KURT BRAND (*Ber.*, 1909, 42, 3460—3462).—Benzylaniline is obtained in good yield by the electrolytic reduction of benzylideneaniline. The anode is a lead plate which is inclosed in a porous pot in a beaker; the cathode is a lead cylinder. The liquid at the anode is a saturated solution of sodium carbonate, and at the cathode a solution of 18 grams of benzylideneaniline and 15 grams of sodium acetate in 200 c.c. of alcohol and 30 c.c. of water. The reduction is effected at 80° at 6—8 volts and a current density of 0.015 to 0.02 ampere per sq. cm.

p-Methoxybenzylideneaniline is reduced in a similar way to *p*-methoxybenzylaniline. C. S.

Amines. I. Synthesis of Phenylethylmethylamine. TREAT B. JOHNSON and HERBERT H. GUEST (*Amer. Chem. J.*, 1909, 42, 340—353).—This investigation has been undertaken on account of the importance of phenylethylamine and *p*-hydroxyphenylethylamine in

physiological chemistry. In the present paper a description is given of phenylethylmethylamine and its derivatives.

When phenylethylamine is treated with methyl iodide there are produced the *hydriodide*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HI}$, which becomes brown above 190° and decomposes at $235\text{--}236^\circ$, and *phenylethyltrimethylammonium iodide*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NMe}_3\text{I}$, m. p. 227° , which forms colourless plates. β :1-Naphthyl- α -phenylethylcarbamide,

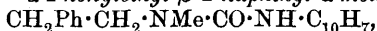


m. p. $209\text{--}210^\circ$, prepared by the action of α -naphthylcarbimide on phenylethylamine, crystallises in needles. *Benzenesulphonylphenylethylamine*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$, m. p. $68\text{--}69^\circ$, forms tabular crystals. *p-Toluenesulphonylphenylethylamine*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$, m. p. $65\text{--}66^\circ$, crystallises in radiating needles. *Benzenesulphonylphenylethylmethylamine*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{SO}_2\text{Ph}$, is obtained as a heavy oil by the action of methyl iodide on the sodium derivative of benzenesulphonylphenylethylamine; when heated with concentrated hydrochloric acid at $150\text{--}160^\circ$, it yields *phenylethylmethylamine*,



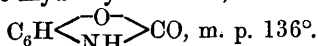
b. p. $112.5\text{--}115^\circ/36\text{--}40$ mm., a strong base which absorbs carbon dioxide from the air and yields precipitates with phosphotungstic acid and bismuth potassium iodide. The double compound of this amine with mercuric chloride melts at $172\text{--}173^\circ$. The *hydrochloride*, m. p. $152\text{--}154^\circ$, crystallises in plates containing $2\text{H}_2\text{O}$. The *picrate*, m. p. 141° , forms prismatic crystals. The *picrolonate*, m. p. $217\text{--}218^\circ$, forms slender prisms or large, tabular crystals. The *platinichloride* and the *hydrogen oxalate* melt at 212° (decomp.) and $183\text{--}184^\circ$ (decomp.) respectively.

α -Phenylethyl- α -methylcarbamide, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{CO}\cdot\text{NH}_2$, m. p. 141° , obtained by the action of potassium cyanate on phenylethylmethylamine, forms colourless plates. β -Phenyl- α -phenylethyl- α -methylcarbamide, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{CO}\cdot\text{NHPh}$, m. p. $104\text{--}105^\circ$, prepared by treating phenylethylmethylamine with phenylcarbimide, crystallises in rectangular plates. α -Phenylethyl- β -2-naphthyl- α -methylcarbamide,



m. p. $105\text{--}106^\circ$, forms rosettes of microscopic needles. β -Phenyl- α -phenylethyl- α -methylthiocarbamide, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{CS}\cdot\text{NHPh}$, m. p. $113\text{--}114^\circ$, crystallises in long prisms. E. G.

Conversion of Aromatic Acid Azoimides into Arylcarbimides. RICHARD STOERMER (*Ber.*, 1909, 42, 3133—3134. Compare Schroeter, this vol., i, 617).—The conversion of aromatic acid azoimides into arylcarbimides has been observed some ten years ago, and the results have been published in Dissertations 1901—1908. Heating the azoimide with dry benzene or toluene is a convenient method for the preparation of certain carbimides on the small scale. The following compounds have been prepared: *m*-phenylenedicarbimide, m. p. 51° ; *o*-methoxyphenylcarbimide, an oil; *m*-nitrophenylcarbimide, m. p. 49° . *o*-Hydroxybenzazide, under similar treatment, yields the urethane,



J. J. S.

New Method of Formation of Phenolic Ethers of Glycerol. FRITZ EHLOTZKY (*Monatsh.*, 1909, 30, 663—671. Compare Shvilkovitch, *Abstr.*, 1908, i, 978; Hantzsch and Vock, *Abstr.*, 1903, i, 664).—The author has prepared the *p*-chlorophenyl, *o*-chlorophenyl, and 5-chloro-*m*-tolyl ethers of glycerol by the interaction of the phenols and glycerol in presence of fused sodium acetate. The yield obtained with *p*-chlorophenol is considerably greater than those given by the other two compounds, whilst with *s*-trichlorophenol no glycerol ether is formed. These results are in agreement with these of V. Meyer and his pupils, who found that the presence of an ortho-substituent usually delays or completely prevents reaction.

p-Chlorophenyl glycerol ether, $C_6H_4Cl \cdot O \cdot C_3H_5(OH)_2$, forms white crystals, m. p. 76° , dissolves in concentrated sulphuric acid with a faint red coloration, which with potassium nitrite solution changes to reddish-violet, and then becomes yellow on supersaturation with potassium hydroxide solution and dilution. The *dibenzoyl* derivative, $C_6H_4Cl \cdot O \cdot C_3H_5(OBz)_2$, separates in a felted mass of white needles, m. p. 83.5° .

p-Chlorophenol forms a *benzoyl*-derivative crystallising in silky leaflets, m. p. 88° .

o-Chlorophenyl glycerol ether, $C_6H_4Cl \cdot O \cdot C_3H_5(OH)_2$, forms white crystals, m. p. 56° , and with concentrated sulphuric acid and potassium nitrite gives a yellow coloration which persists on addition of potassium hydroxide solution to the liquid and dilution. Its *dibenzoyl* derivative, $C_{28}H_{19}O_5Cl$, forms short bundles of white crystals, m. p. 59 — 60° .

5-Chloro-*m*-tolyl glycerol ether, $C_6H_3MeCl \cdot O \cdot C_3H_5(OH)_2$, separates in white, granular crystals, m. p. 83° , and with concentrated sulphuric acid and potassium nitrite gives a dirty green coloration, which is changed to yellow by addition of potassium hydroxide solution and dilution.

None of these three ethers gives a coloration with ferric chloride.

T. H. P.

Derivatives of 1:2-Dimethylbenzene [*o*-Xylene]. EMIL DIEPOLDER (*Ber.*, 1909, 42, 2916—2923).—5-Nitro-*o*-4-xylenol is obtained by nitrating *o*-4-xylenol, dissolved in acetic acid, together with the 3:5-nitro-derivative and a small quantity of tarry matter. It crystallises in thin, yellow rhombs, m. p. 87° , and has an odour similar to *o*-nitrophenol; the *potassium* salt forms bright red prisms in stellar aggregates, whilst the *sodium* salt forms flat, red needles. When heated with ammonia with the addition of ammonium chloride for some time at 140 — 150° , the nitro-compound is converted into 5-nitro-*o*-4-xylydine, which crystallises in microscopic, six-sided prisms, m. p. 140° . The structure of this compound is proved by the fact that on replacing the amino-group by hydrogen the 4-nitro-*o*-xylene, m. p. 29° , described by Jacobsen (*Ber.*, 1884, 17, 160) is obtained.

When *o*-4-xylenol is coupled with benzenediazonium sulphate, a mixture of 83% symmetric and 17% vicinal quinonephenylhydrazone is formed, which is separated by crystallisation from alcohol. The phenylhydrazone of *o*-1:5-xyloquinone, recently described by Auwers

and Heyden (this vol., i, 438) as crystallising in dark orange, glistening needles, more commonly separates in red needles with a violet reflex. The 3-phenylhydrazone of o-3 : 4-xyloquinone crystallises in large, brown plates or prisms.

5-Amino-o-4-xyleneol, obtained by reducing the corresponding nitro-compound, crystallises from ether in glistening plates, and forms colourless rhombs when sublimed. It turns brown above 165°, m. p. 173—175°. The hydrochloride forms silky, glistening needles, m. p. 250°. When oxidised with potassium dichromate in sulphuric acid solution, 1 : 2-dimethyl-4 : 5-benzoquinone is formed. This crystallises in long, red needles, which are greenish-yellow in transmitted light, m. p. 102°. It can also be obtained in yellow plates, which slowly become red and give the red needles when recrystallised. This

corresponds with the isomeric modification :
$$\begin{array}{c} \text{CMe} \cdot \text{CH} \cdot \text{C} \cdot \text{O} \\ | \qquad | \qquad | \\ \text{CMe} \cdot \text{CH} \cdot \text{C} \cdot \text{O} \end{array}$$

2 : 3-Dimethylphenazine, prepared by the interaction of the quinone with o-phenylenediamine, separates in small, yellow crystals, m. p. 173°, which dissolve in concentrated sulphuric acid with a red coloration. E. F. A.

Action of Sulphites on Aromatic Amino- and Hydroxyl Compounds. VII. Application of the Sulphite Reaction to Some *ana*-(1 : 5)-Derivatives of Naphthalene. HANS TH. BUCHERER and A. UHLMANN (*J. pr. Chem.*, 1909, [ii], 80, 201—241. Compare Abstr., 1904, i, 309).—The hitherto unknown 5-amino- α -naphthol-4-sulphonic acid has been prepared, since apparently it fulfils the requirements of an aminonaphtholsulphonic acid suitable for the production of polyazo-dyes like diamine-black, namely, coupling of the acid (2 mols.) with a diazotised *p*-diamine must yield a diazo-derivative in which the sulpho- and the azo-groups are in different rings of the naphthalene nucleus, in order that the existent amino-groups may be capable of diazotisation.

The preparation of the acid was first attempted by sulphonating 1 : 5-naphthylenediamine, but the sulpho-group enters position 2 and not 8, the proof being based on the fact that, after the naphthylenediaminesulphonic acid has been converted into an aminonaphthol-sulphonic acid by the hydrogen sulphite reaction, the sulpho-group is not eliminated by 20% hydrochloric acid, showing that it is not para to the hydroxyl group.

A successful result is obtained by using Nietzki and Zübelen's method (Abstr., 1889, 513), in which naphthionic acid, by the successive operations of acetylation of its sodium salt by acetic anhydride, nitration in concentrated sulphuric acid, and reduction, is converted into 1 : 5-naphthylenediamine-8-sulphonic acid. This acid is changed by the hydrogen sulphite process into 5-amino- α -naphthol-4-sulphonic acid, the orientation of which is proved by its conversion into 5-amino- α -naphthol by 20% hydrochloric acid. The 5-nitro-1-acetylaminonaphthalene-4-sulphonic acid obtained in the preceding operations is reduced by zinc dust and hydrochloric acid below 30° to 5-acetyl-amino- α -naphthylamine-8-sulphonic acid, which is converted by the

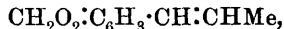
hydrogen sulphite process into 5-*amino- α -naphthol-8-sulphonic acid*. The latter is further changed by the hydrogen sulphite into 1:5-dihydroxynaphthalene-8-sulphonic acid, which is converted by ammonium sulphite and excess of ammonium hydroxide into 1:5-naphthylene-diamine-8-sulphonic acid.

1:5-Dihydroxynaphthalene, sulphonated by concentrated sulphuric acid at 50—60°, yields a mixture of 1:5-dihydroxynaphthalene-2-sulphonic acid and the corresponding 4-sulphonic acid.

5-Amino- α -naphthol-4-sulphonic acid couples with tetrazotised benzidine to form a dark blue dye; when this is diazotised on the fibre and developed with β -naphthol, the dye bleeds freely, and only a pale brown shade is produced. The acid therefore does not fulfil expectations. C. S.

Stereochemistry of Ethylene Derivatives: Two Stereoisomeric *isoSafroles*. PAUL HOERING and FRITZ BAUM (*Ber.*, 1909, 42, 3076—3088).—The allyl side-chain in various unsaturated phenolic ethers is readily transformed into a propylene side-chain by the action of alcoholic potassium hydroxide (compare Eykman, *Abstr.*, 1890, 137, 749). The propylene derivatives thus obtained should exist in two stereoisomeric forms, but so far no such cases of isomerism have been established. In several cases of supposed stereoisomerism, for example, anethole and esdragole, the compounds have been shown to be structural isomerides.

It has been found possible to isolate two *isosafroles*,



from commercial *isosafrole*, which also contains unaltered *safrole*.

β -*isoSafrole*, which is the chief constituent, has b. p. 123°/11.5 mm., $D_{17.5}^{21}$ 1.1227, and n_D^{18} 1.5786, and is most readily isolated in the form of its picrate (m. p. 74°: compare Bruni and Tornani, *Abstr.*, 1904, i, 875), which is decomposed when boiled with solvents in which picric acid is sparingly soluble, or when ammonia is led into its alcoholic solution.

α -*isoSafrole* has b. p. 116.2—116.3°/13.5 mm., or 242.2—242.5°/760 mm., $D_{18.3}^{18}$ 1.1073, and n_D^{18} 1.5678. It is best isolated from the first fractions obtained by repeated fractionation from a Stephan flask. *Safrole* can be removed by shaking an ethereal solution of the *isosafrole* with a 10% aqueous solution of mercuric acetate (Balbiano, this vol., i, 401). Small quantities of β -*isosafrole* can be removed by the addition of picric acid, and then distilling in steam under reduced pressure at 50—55°, when the α -*isosafrole* distils over, whereas the β -compound remains behind in combination with the picric acid.

The two *isosafroles* resemble one another in chemical properties. They yield the same dibromide and also the same glycol when oxidised.

J. J. S.

Oxidation of Dimethyldehydrodiisoeugenol and of Dimethyldehydrodivanillin. HENRI HÉRISSEY and G. DOBY (*J. Pharm. Chim.*, 1909, [vi], 30, 289—297).—An attempt to establish an analogy between dehydrodiisoeugenol and dehydrodivanillin, two compounds resulting from the oxidation of *isoeugenol* and *vanillin*

respectively (Abstr., 1908, i, 783). The phenols were converted into their methyl ethers by the process already described. Oxidation of dehydrodivanillin dimethyl ether by potassium permanganate leads to the production of *dehydrodiveratric acid*,

$\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{CO}_2\text{H}$,
in 93—95% yield. This compound forms needles, m. p. about 308° (decomp.), subliming below this temperature. It is very sparingly soluble in the usual solvents. The *dimethyl* ester, $\text{C}_{20}\text{H}_{22}\text{O}_8$, crystallises from alcohol in long, silky needles, m. p. 130°.

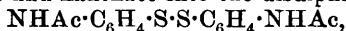
An unexpected result followed when dehydroisoeugenol dimethyl ether was oxidised in the same way, a small yield of veratric acid being obtained. The conclusion is drawn that either the ether does not have the constitution previously ascribed to it, or that the propenyl group exercises an abnormal influence on the course of the oxidation.

W. O. W.

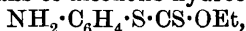
Preparation of Guaiacol-5-sulphonic Acid and its Salts. F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 212389).—This acid is prepared free from the para-isomeride by sulphonating acyl derivatives of guaiacol, hydrolysing the product, and removing excess of sulphuric acid. The sulphonic acid of guaiacol carbonate has m. p. 115—117°. *Potassium benzoylguaiacol-5-sulphonate* forms colourless needles readily soluble in water, but the free acid, being deliquescent, was not readily obtained.

F. M. G. M.

***p*-Aminothiophenol [*p*-Aminophenyl Mercaptan].** THEODOR ZINCKE and P. JÖRG (*Ber.*, 1909, 42, 3362—3374).—In the preparation of *p*-acetylaminophenyl mercaptan (compare Leuckart, Abstr., 1890, 603; Hinsberg, Abstr., 1906, i, 654), it is better not to convert the product, $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CS}\cdot\text{OEt}$, of the interaction of diazotised acetyl-*p*-phenylenediamine and xanthate into the disulphide,

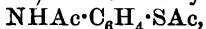


but to convert it by means of alcoholic hydrochloric acid into



which is readily hydrolysed by alcoholic potassium hydroxide and transformed into *p*-aminophenyl mercaptan. Reduction of acetyl-aniline-*p*-sulphonyl chloride by means of zinc dust and hydrochloric acid is a still more simple method of obtaining *p*-acetylaminophenyl mercaptan, which is readily hydrolysed to *p*-aminophenyl mercaptan or its hydrochloride.

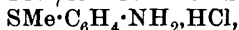
p-Aminophenyl mercaptan solidifies as a white, granular, crystalline mass having a faint smell, m. p. 46°, b. p. 140—145°/15—16 mm.; its hydrochloride forms slender needles; the acetyl derivative has m. p. 150° (Hinsberg, *loc. cit.*, gave 154°). The diacetyl compound,



exists in two forms, the one, m. p. 144°, described by Hinsberg, on heating at 155—160° being converted into a *second*, m. p. 132°, which retains its m. p. after repeated fusion and cooling, but when seeded with the first modification is reconverted into this.

p-Aminophenyl methyl thioether, $\text{SMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, prepared by treating *p*-acetylaminophenyl mercaptan with methyl sulphate and hydrolysing

the *p*-acetylaminophenyl methyl thioether (compare Hinsberg, *loc. cit.*) thus formed by means of alcoholic hydrochloric acid, is an oily liquid with a faint odour, b. p. $140^{\circ}/15-16$ mm. Its *hydrochloride*,



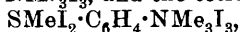
and *sulphate*, $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \frac{1}{2} \text{H}_2\text{SO}_4$, were prepared. *p*-Aminophenyl methyl thioether is very reactive; with quinones it behaves like aniline, and yields intensely-coloured compounds; it can be diazotised, and the diazo-salt couples with β -naphthol and is readily converted into the iodide; the hydrochloride is oxidised by ferric chloride, giving a bluish-violet coloration and then a separation of brownish-violet needles with metallic lustre, which are under investigation.

p-Acetylaminophenyl methyl sulphoxide, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{SOMe}$, prepared by the action of water on the dibromide (*vide infra*) or by oxidising *p*-acetylaminophenyl methyl thioether by means of hydrogen peroxide, crystallises in white needles or plates, m. p. 126° , is converted into *p*-bromoacetanilide by excess of bromine water and with hydrogen bromide yields the *hydrobromide* of *p*-acetylaminophenyl methyl thioether *dibromide*, $(\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{SBr}_2\text{Me})_2 \cdot \text{HBr}$, which forms an orange-yellow, crystalline powder, m. p. about 100° (decomp.). The *dibromide* itself, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{SBr}_2\text{Me}$, obtained by the action of bromine on *p*-acetylaminophenyl methyl thioether in chloroform solution, forms an orange-yellow, crystalline powder, m. p. 104° (decomp.), and when treated with potassium hydroxide liberates iodine with formation of *p*-acetylaminophenyl methyl thioether.

m-Bromo-*p*-acetylaminophenyl methyl thioether, $\text{NHAc} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{SMe}$, prepared by the action of concentrated hydrobromic acid on *p*-acetylaminophenyl methyl sulphoxide, crystallises from benzene in colourless leaflets, m. p. 127° .

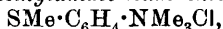
m-Chloro-*p*-aminophenyl methyl thioether, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{SMe}$, obtained together with a blue sulphiminoquinone, $\text{NH} \langle \text{C}_6\text{H}_2 \rangle \text{SMeCl} (?)$, by the action of concentrated hydrochloric acid on *p*-acetylaminophenyl methyl sulphoxide, is a colourless oil with a faint odour; the *hydrochloride*, $\text{C}_7\text{H}_9\text{NSCl}_2$, and the *acetyl* derivative, $\text{C}_9\text{H}_{10}\text{ONSCl}$, m. p. 128° , were prepared.

p-Methylthiophenyltrimethylammonium iodide, $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_3\text{I}$, prepared by heating either *p*-aminophenyl methyl thioether with methyl iodide or *p*-acetylaminophenyl methyl thioether with methyl iodide and methyl alcohol, crystallises in colourless, rhombic plates, m. p. $180-184^{\circ}$ (decomp.), and by addition of iodine is converted into the di-iodide, $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_3\text{I}_2$, and the tetraiodide,



neither of which gave concordant numbers on analysis.

p-Methylthiophenyltrimethylammonium chloride,



prepared from the preceding compound and freshly precipitated silver chloride, forms colourless, unstable needles, m. p. $193-194^{\circ}$. The *platinichloride* was analysed.

p-Dimethylaminophenyl methyl thioether, $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, prepared either by heating *p*-methylthiophenyltrimethylammonium chloride at 200° or by the action of methyl alcoholic hydrogen chloride on

p-aminophenyl methyl thioether, forms white leaflets, m. p. 23°; its *hydrochloride* was analysed.

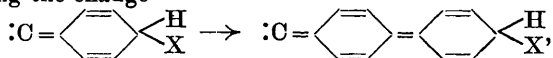
Oxidation of *p*-acetylaminophenyl mercaptan by means of ferric chloride in alcoholic solution yields the α -form of diacetyldiaminodiphenyl disulphide, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$, m. p. 179—180° (Hinsberg, *loc. cit.*, gave 182°), which has been kept for ten months without alteration. T. H. P.

Trithiophloroglucinol. JACQUES POLLAK and J. CARNIOL (*Ber.*, 1909, 42, 3252—3253).—*Trithiophloroglucinol*, $\text{C}_6\text{H}_6\text{S}_3$, prepared by reducing benzene-1 : 3 : 5-trisulphonyl chloride with tin and hydrochloric acid, is a white powder, m. p. 56—58°, having a characteristic odour; it readily undergoes oxidation, and gives an orange-red precipitate with lead acetate. The *triacetate*, $\text{C}_{12}\text{H}_{12}\text{O}_3\text{S}_3$, crystallises in white needles, m. p. 73—74°. The *trimethyl ether*, $\text{C}_9\text{H}_{12}\text{S}_3$, forms slender needles, m. p. 66—68°. W. H. G.

Xylene Thiocyanates. Mlle. MARIE STRZELECKA (*Bull. Acad. sci. Cracow*, 1909, 731—734).—The following substances, obtained from xylyl or xylene bromides and potassium thiocyanate in dilute alcohol, have an unpleasant, piercing odour. *p*-Xylyl thiocyanate, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH}_2 \cdot \text{SCN}$, has m. p. 21.5—22.5. *p*-Xylylene thiocyanate, $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{SCN})_2$, m. p. 134°, has been erroneously described as *p*-xylyl thiocyanate (*Abstr.*, 1902, i, 470). *m*-Xylyl thiocyanate, b. p. 170°/30 mm., is a yellow, oily liquid. *m*-Xylylene thiocyanate, m. p. 60°, crystallises in colourless needles. *o*-Xylyl thiocyanate has m. p. 18—18.5°, and *o*-xylylene thiocyanate has m. p. 79°. C. S.

Analogues of Triphenylmethyl in the Diphenyl Series. WILHELM SCHLENK [with TOBIAS WEICKEL] (*Annalen*, 1909, 368, 295—304).—The effect of gradually replacing the phenyl groups of triphenylcarbinol by diphenyl has been investigated with the object of obtaining information on the cause of the colour of triphenylcarbinol salts.

It is found that the replacement of each phenyl group by the diphenyl residue is accompanied by an increase in the depth of colour; thus, solutions of triphenylcarbinol, 4-phenyltriphenylcarbinol, 4:4'-diphenyltriphenylcarbinol, and 4:4':4"-triphenyltriphenylcarbinol in a mixture of acetic and sulphuric acids are yellow, yellowish-red, red, and bluish-red respectively. The conclusion is drawn, therefore, that the colour of the salts of triphenylcarbinol is not due to a quinonoid structure, since a sudden and marked change of colour representing the change



which must necessarily occur at one stage in the passage of triphenylcarbinol to 4:4':4"-triphenyltriphenylcarbinol, is not observed.

4-Phenyltriphenylcarbinol, $\text{C}_6\text{H}_4\text{Ph} \cdot \text{CPh}_2 \cdot \text{OH}$, prepared by Grignard's method from (1) benzophenone and *p*-iododiphenyl; (2) bromobenzene and methyl diphenyl-*p*-carboxylate, crystallises in needles and plates, m. p. 136°; when acted on by acetyl chloride it yields

4-phenyltriphenylmethyl chloride, $C_6H_4Ph \cdot CPh_2 \cdot Cl$, which crystallises in cubes, m. p. 147.5° .

4:4'-Diphenyltriphenylcarbinol, $CPh(C_6H_4Ph)_2 \cdot OH$, prepared from diphenylbenzophenone and bromobenzene, crystallises in needles, m. p. 151° ; the corresponding chloride, $C_8H_{23}Cl$, has m. p. 131.5° .

4:4':4"-Triphenyltriphenylcarbinol, $C(C_6H_4Ph)_3 \cdot OH$, may be prepared by Grignard's method from (1) methyl diphenyl-*p*-carboxylate and *p*-iododiphenyl; (2) 4:4'-diphenylbenzophenone and *p*-iododiphenyl, and by the method of Friedl and Crafts from diphenyl and carbon tetrachloride; it crystallises in white needles, m. p. $207-208^\circ$. 4:4':4"-Triphenyltriphenylmethyl chloride, $C_{37}H_{27}Cl$, forms white needles, m. p. 195° .

p-Iododiphenyl, $C_{12}H_9I$, prepared by treating diphenyl-4-diazonium chloride with potassium iodide, has m. p. 112° , b. p. $222^\circ/40$ mm., $198^\circ/11$ mm.

Methyl diphenylcarboxylate, $C_{14}H_{12}O_2$, has m. p. 117.5° .

W. H. G.

Preparation of *o*-Dihydroxyphenylethanolamine. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 212206. Compare Barger and Jowett, Trans., 1905, 87, 971).— β -Bromo- α -3:4-trihydroxy- α -phenylethane, $C_6H_3(OH)_2 \cdot CH(OH) \cdot CH_2Br$, an unstable, viscous oil, is obtained by treating $\alpha\beta$ -dibromo-3:4-methylenedioxy- α -phenylethane with phosphorus pentachloride (2 mols.) and heating at 105° during ten to twenty hours. α -3:4-Trihydroxy- α -phenylethylmethylamine, $C_6H_3(OH)_2 \cdot CH(OH) \cdot CH_2 \cdot NHMe$, is obtained when the foregoing compound is treated with seven times its weight of a cold 40% aqueous methylamine solution. The methylamine in this reaction may be replaced by other alkylamines or by ammonium hydroxide.

F. M. G. M.

Preparation of Acid Anhydrides. ADOLF KAUFMANN and A. LUTERBACHER (Ber., 1909, 42, 3483—3485).—A solution of equal molecular quantities of benzoic acid and acetic anhydride in dry benzene is boiled for six hours and fractionally distilled. The last fraction, b. p. $347-348^\circ$, is pure benzoic anhydride in 81.4% yield. By using xylene and $2\frac{1}{2}$ mols. of acetic anhydride, the yield is increased to 86% (compare Autenrieth, Abstr., 1901, i, 185).

C. S.

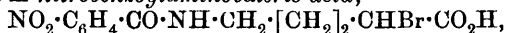
Preparation of Substituted Aromatic Carboxylic Acids from the Corresponding Aldehydes. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 211959).—The oxidation of aromatic aldehydes to the corresponding acids proceeds very smoothly when sodium hypochlorite and excess of alkali are the reagents employed.

m-Nitrobenzaldehyde (151 parts) is slowly added to a solution of sodium hydroxide (40 parts) and sodium hypochlorite (71 parts available chlorine). Care must be taken at first that the reaction does not become violent, but finally the solution is warmed until the hypochlorite is decomposed; on cooling, the greater part of the sodium *m*-nitrobenzoate crystallises out in a pure condition.

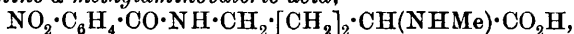
F. M. G. M.

Synthesis of the Two Optically Active Prolines. EMIL FISCHER and GÉZA ZEMPLÉN (*Ber.*, 1909, 42, 2989—2997).—Proline was hitherto only known in the form of the racemic compound, and the *l*-compound obtained by protein hydrolysis. *m*-Nitrobenzoylproline has been synthesised from δ -*m*-nitrobenzoylaminovaleric acid, and resolved into its optically active components by means of cinchonine. These when boiled with hydrochloric acid are decomposed into *m*-nitrobenzoic acid and the optically active prolines, which are similar in properties to the natural *l*-proline. The action of ammonia and of methylamine on α -bromo- δ -*m*-nitrobenzoylaminovaleric acid has been studied, *m*-nitrobenzoylornithine and its methyl derivative being formed respectively.

α -Bromo- δ -m-nitrobenzoylaminovaleric acid,



obtained by acting on δ -*m*-nitrobenzoylaminovaleric acid with bromine and red phosphorus, crystallises in bunches of colourless needles, which sinter about 120°, m. p. 125°. The bromine is eliminated on treatment in the cold with saturated aqueous ammonia, and δ -*m*-nitrobenzoylornithine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot [\text{CH}_2]_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$, obtained in the form of a colourless, crystalline powder, m. p. 250° (decomp.). Aqueous methylamine acts on the bromo-compound to form δ -*m*-nitrobenzoylamino- α -methylaminovaleric acid,



which likewise crystallises in colourless needles; these turn brown at 200°, m. p. 240° (decomp.).

When the bromo-compound is kept at 37° with sodium hydroxide, *dl*-*m*-nitrobenzoylproline, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{N} \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \text{CH}(\text{CO}_2\text{H}) \end{smallmatrix} \text{CH}_2$, is formed.

This crystallises in microscopic, rhombic plates, m. p. 90—92°. The *cinchonine* salt is a colourless, crystalline substance, m. p. 150°, to a brown substance, that of the *d*-isomeride being the first to separate from aqueous solution. When hydrolysed with sodium hydroxide, *d*-*m*-nitrobenzoylproline is obtained. It crystallises in microscopic prisms in stellar aggregates, has m. p. 137—140°, and $[\alpha]_D^{20} + 12.9^\circ$ ($\pm 0.5^\circ$). *d*-Proline is obtained, on heating the above with 10% hydrochloric acid for six hours, mixed with some racemic compound, from which it is separated by treatment of the mixed copper salts with alcohol. It crystallises in prisms, m. p. 215—220° (decomp.), and has $[\alpha]_D + 81.5^\circ$ ($\pm 0.5^\circ$). The cinchonine mother liquors contain the salt of *l*-nitrobenzoylproline, from which *l*-proline can be obtained in the same manner as described for the *d*-isomeride. It has the same crystalline form, m. p. 215—220°, and $[\alpha]_D^{20} - 80.4^\circ$ ($\pm 0.5^\circ$). This is a little higher than the value recorded (-77.4°) for the natural amino-acid.

E. F. A.

Preparation of *o*-Aminobenzonitrile and its Substitution Products. KALLE & Co. (D.R.-P. 212207).—Iron filings (500 parts), 50 c.c. of acetic acid (50%), and water (1000 parts) are mixed and kept at a temperature of 65° during half an hour; *o*-nitrobenzonitrile (148 parts) is then slowly added, and the temperature kept below 70°. When reduction (which proceeds rapidly) is complete, the liquid is

rendered alkaline with sodium carbonate, filtered hot, and a 10% solution of sodium chloride stirred in; on cooling, the *o*-aminobenzo-nitrile separates as colourless leaflets.

F. M. G. M.

Introduction of the Nitroso-group into the Nucleus of *N*-Alkylated Esters of Anthranilic Acid. JOSEF HOUBEN (*Ber.*, 1909, 42, 3188—3196).—A further study of the method of Houben, Brassert, and Ettinger (compare this vol., i, 645) for preparing derivatives of 5-nitrosoanthranilic acid. The author proposes to carry out further investigations of these compounds, as well as of derivatives of *p*-quinoneoximecarboxylic acid, which in regard to the production of dyes behaves as though it were a 5-nitrosalicylic acid. In certain conditions it is possible to introduce the nitroso-group directly into the nucleus of salicylic acid. Direct nitrosylation in the nucleus is impossible in the case of anthranilic acid derivatives, in which both the hydrogen atoms of the amino-group are replaced by alkyl groups, as in dimethylantranilic acid. The author considers that this must be due to some steric rather than chemical influence. It is not a peculiarity of the carboxyl group, since other dialkylamino-compounds with an *ortho*-substituent are also incapable of nitrosylation.

The 5-nitroso-derivative of methylantranilic acid may be prepared with 84% yield by acting on the nitrosoamine with fuming hydrochloric acid; this is in harmony with the idea that the production of the nitroso-derivative depends on the primary formation of the nitrosoamine.

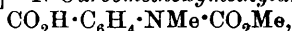
The nitrosylation of phenyl methylantranilate was found to present no difficulty, in spite of the largeness of the group attached to the carboxyl. For the preparation of the phenyl ester it was necessary to devise a special method, since it cannot be obtained from anthranilic acid and phenol.

Attempt to Nitrosylate Methyl Dimethylantranilate. [With LEO ETTINGER].—Neither the ester nor its solutions show any trace of fluorescence; in this they differ from the esters of anthranilic and methylantranilic acids. The desired nitroso-derivative could not be obtained by treatment with sodium nitrite either in dilute or in concentrated hydrochloric acid, or in alcoholic hydrogen chloride. On long standing, a nitroso-compound was obtained as a green, flocculent precipitate, but it was not a derivative of dimethylantranilic acid. Similar experiments with the free acid were also unsuccessful.

Methyl methylethylantranilate is obtained by heating methyl methylantranilate for three to four days with ethyl bromide in a sealed tube at 95°. The white, crystalline product is extracted with ether and decomposed with sodium carbonate in aqueous solution, whereon the ester is obtained as a yellow oil, b. p. 142—143°/16 mm. It does not fluoresce. It does not yield a nitroso-derivative by any of the above methods.

The transformation of *o*-methylnitrosoaminebenzoic acid into 5-nitrosomethylantranilic acid is effected when the nitrosoamine is dissolved in fuming hydrochloric acid; the dark red solution deposits the hydrochloride of the nitroso-acid as a yellow precipitate.

[With R. FREUND.]—*N*-Carbomethoxymethylantranilic acid,



is obtainable from the aromatic amino-acid, methylantranilic acid, by the method which E. Fischer has shown to be applicable to phenolcarboxylic acids (Abstr., 1908, i, 892; 1909, i, 161, 309) and to aliphatic amino-acids (Abstr., 1903, i, 799). Methylantranilic acid is dissolved in the equivalent quantity of potassium carbonate and shaken with methyl chlorocarbonate. The compound forms white crystals, m. p. 137—138°; yield almost theoretical. *N*-Carbethoxymethylantranilic acid, obtained in a similar way, forms white needles, m. p. 118°. When either of these urethanes is heated for some hours with acetic anhydride, or heated alone for a short time at 220°, the *anhydride* of *N*-methyl-isatoic acid, $\text{C}_6\text{H}_4 \cdot \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{O} \end{smallmatrix}$, is obtained in large crystals or in yellow needles, m. p. 177°. When heated with concentrated sulphuric acid, *N*-methylantranilic acid is produced almost quantitatively, and if the temperature is further raised, methylaniline is eventually formed.

[With ERICH KELLNER.]—On heating the above anhydride with phenol, *phenyl N*-methylantranilate is obtained in yellow needles of m. p. 70—71°; yield over 60%. The substance shows a sky-blue fluorescence in solution; it is less basic than the alkyl esters of the same acid. *Phenyl 5*-nitrosomethylantranilate may be obtained by preparing the nitrosoamine of the above phenyl ester and acting on that compound with concentrated hydrochloric acid, but is best prepared (56% yield) by treating the solution of the ester in fuming hydrochloric acid with sodium nitrite. The substance forms lustrous, green needles, and has m. p. 135—136°.

[With WALTER BRASSERT and LEO ETINGER.]—*Methyl 5*-nitroso-*N*-ethylantranilate forms small, green needles of m. p. 91°; yield 48%. *Ethyl N*-ethylantranilate, prepared by esterifying ethylantranilic acid with alcohol and sulphuric acid, is an almost colourless oil, which has b. p. 142°/11 mm. or 150—151°/16 mm. *Ethyl 5*-nitroso-*N*-ethylantranilate forms a felted mass of long, shining green threads, and has m. p. 87—88°; yield 41%.
R. V. S.

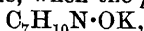
6-Nitro-4-sulpho-3-toluic Acid and Some of its Derivatives.

WILLIAM J. KARSLAKE and R. C. HUSTON (*J. Amer. Chem. Soc.*, 1909, 31, 1057—1060).—It has been shown by Karslake and Bond (this vol., i, 231) that when 6-nitro-*m*-xylene-4-sulphonic acid is oxidised with a cold alkaline solution of potassium permanganate, the potassium salts of 4-nitro-2-sulpho-5-toluic, 6-nitro-4-sulpho-3-toluic, and 6-nitro-4-sulphoisophthalic acids are obtained. As 6-nitro-4-sulpho-3-toluic acid has not been described previously, a further study of this acid and its derivatives has been carried out.

6-*Nitro-4-sulpho-3-toluic acid*, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me}(\text{SO}_3\text{H}) \cdot \text{CO}_2\text{H} \cdot \text{H}_2\text{O}$, m. p. 34—37°, forms long, flat, colourless needles, and, when heated at 110°, is converted into the anhydrous form, m. p. 150·7° (corr.). The chloride, m. p. 90·2° (corr.), and the diamide, m. p. 273—274°, crystallise in prismatic plates. The *dianilide*, m. p. 204·8° (corr.),

forms small, yellow plates. The *di-o*-, *-m*-, and *-p-toluidides* melt at 238.7° (corr.), 208.8° (corr.), and 241.8° (corr.) respectively. The *dimethyl* ester forms white crystals, and chars without melting at 302—305°. The *potassium*, *potassium* hydrogen, *silver*, *sodium*, *sodium hydrogen*, *calcium*, *calcium hydrogen*, *barium*, *barium hydrogen*, *strontium*, *strontium hydrogen*, *ammonium*, *magnesium*, *zinc*, *copper*, and *lead* salts are described. E. G.

Derivatives of Hydroxyhexahydrobenzoic [*cycloHexan-1-ol-1-carboxylic*] Acid. P. JOSEPH TARBOURIECH (*Compt. rend.*, 1909, 149, 604—606).—A study of Bucherer's acid obtained from *cyclohexanone* (Abstr., 1894, i, 366). The nitrile is most conveniently prepared by adding *cyclohexanone* to a very concentrated solution of potassium cyanide, when the *potassium* derivative,



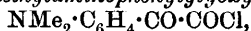
separates; treatment of this with 10% hydrogen chloride yields the nitrile as an oil, b. p. about 110°/18 mm. The *potassium* salt of the acid crystallises in spangles containing 1H₂O.

The *methyl* ester, C₆H₁₁O·CO₂Me, has b. p. 103°/17 mm.; the *ethyl* ester has b. p. 111°/18 mm.; the *isoamyl* ester has b. p. 142°/18 mm.; the *amide* has m. p. 124°. Treatment of the *methyl* ester with *magnesium methyl iodide* leads to the formation of *cyclohexanolpropan-β-ol*, C₆H₁₀(OH)·CMe₂·OH, crystallising in needles, m. p. 83°, and having a camphoraceous odour. On oxidation with chromium trioxide, this yields *propanone* and *cyclohexanone*, whilst under certain conditions it loses water, forming a *pinacolin* with a hydrocarbon.

W. O. W.

Oxalyl Chloride. II. Action of Oxalyl Chloride on Dimethylaniline. HERMANN STAUDINGER and H. STOCKMANN (*Ber.*, 1909, 42, 3485—3496. Compare Abstr., 1908, i, 938).—Since oxalyl chloride is nearly analogous to carbonyl chloride, its behaviour towards dimethylaniline has been examined.

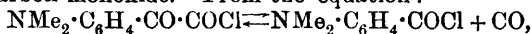
When ethereal solutions of oxalyl chloride (1 mol.) and dimethylaniline (2 mol.) are mixed and kept at 0° for fifteen hours, a quantitative formation of *p-dimethylaminophenylglyoxyl chloride*,



and dimethylaniline hydrochloride occurs. The former compound exists only in solution, and its presence is detected by converting it into *p-dimethylaminophenylglyoxylic acid* and the corresponding *methyl ester* and *anilide*. At higher temperatures, particularly in benzene solution, *p-dimethylaminophenylglyoxyl chloride* decomposes quantitatively into carbon monoxide and *p-dimethylaminobenzoyl chloride*, a portion of which condenses with dimethylaniline to form crystal-violet.

Ethereal or, better, benzene solutions of oxalyl chloride (1 mol.) and dimethylaniline (4 mols.) react in the cold as above, but when they are kept at 0° for fifteen hours and then heated on the water-bath, the initially formed *p-dimethylaminophenylglyoxyl chloride* reacts in two ways: on the one hand, yielding tetramethyl-*p* : *p'*-diaminobenzil, and on

the other, decomposing into carbon monoxide and dimethylaminobenzoyl chloride. This condenses with dimethylaniline to Michler's ketone, which in its turn reacts with dimethylaniline hydrochloride to form crystal-violet under the condensing influence of a part of the dimethylaminobenzoyl chloride, which is thereby converted into dimethylaminobenzoic acid. The products of the whole reaction, therefore, are chiefly crystal-violet and smaller quantities of dimethylaminobenzoic acid and tetramethyl-*p*:*p'*-diaminobenzil. The yield of the last is only 17%, but is increased to 35% by using a large excess of dimethylaniline (10 mols.) to absorb rapidly the liberated hydrogen chloride. A still better way is to work under pressure in an atmosphere of carbon monoxide. From the equation:



it is evident that by increasing the concentration of the carbon monoxide, the dissociation of the dimethylaminophenylglyoxyl chloride must be diminished, and consequently a larger amount of this substance is available for the production of tetramethyldiaminobenzil. It is actually found that the yield of the latter is 50% at 45 atmospheres, and 87% at 150 atmospheres, when oxalyl chloride and dimethylaniline, in the proportion 1:10, are kept at 0° for fifteen hours, and are then heated for six hours on the water-bath in an atmosphere of carbon monoxide.

p-Dimethylaminophenylglyoxylic acid, obtained from the chloride by the action of water, is converted almost quantitatively into *p*-dimethylaminobenzaldehyde when heated with dimethylaniline at 180°.

Tetramethyl-p:*p'*-diaminobenzil, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, m. p. 197—198°, forms small, deep yellow crystals, and yields an *osazone*, m. p. 259—260°. C. S.

Preparation of Substituted Alkylthiolbenzoic Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 212434).—5-Ethoxy-2-methylthiolbenzoic acid, $\text{EtO} \cdot \text{C}_6\text{H}_3(\text{SMe}) \cdot \text{CO}_2\text{H}$, m. p. 135°, sparingly soluble in ether, crystallising from dilute alcohol, is prepared from 2-amino-5-hydroxybenzoic acid as follows. The amino-acid (153 parts) is acetylated, treated in alkaline solution with ethyl sulphate (180 parts), and the acetyl group removed with concentrated sodium hydroxide; the liquid acidified, and the amino-group diazotised. The filtered solution is digested at 20—25° with potassium xanthate (180 parts) until the evolution of nitrogen ceases, sodium hydroxide added, the mixture boiled several hours with 300 parts of sodium methyl sulphate (46%), and the product precipitated with mineral acid. 4-Chloro-2-methylthiolbenzoic acid, m. p. 210—211°, sparingly soluble in cold alcohol, ether, or hot water, readily so in hot alcohol, is prepared from 4-chloro-2-aminobenzoic acid by analogous treatment.

4:2-Dimethylthiolbenzoic acid, $\text{C}_6\text{H}_3(\text{SMe})_2 \cdot \text{CO}_2\text{H}$, m. p. 194°, easily soluble in hot alcohol, sparingly so in the cold solvent, is obtained when 4-acetylamino-2-aminobenzoic acid (from the oxidation and subsequent reduction of 2-nitroaceto-*p*-toluidide) is diazotised and the amino-group replaced by methylthiol as previously described; the acetyl group removed by hydrolysis, and the other amino-group similarly treated. F. M. G. M.

Preparation of Bromoacylsalicylic [*o*-Bromoacyloxybenzoic] Acids. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 212422).—*o*-Halogenacyloxybenzoic acids can be prepared by the interaction of the chlorides, bromides, or anhydrides of the bromoparaffin acids with salicylic acid in the presence of a tertiary aromatic amine such as dimethylaniline.

o-Bromoacetoxybenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$, prepared by the interaction of salicylic acid and bromoacetyl bromide in presence of dimethylaniline in benzene solution, is a colourless, crystalline powder, m. p. 136—137°, with an acid taste, readily soluble in hot benzene or water, sparingly so in the cold. It is decomposed by prolonged heating with water, and when pure gives no coloration with ferric chloride.

o- α -Bromopropionyloxybenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{CHMeBr}$, m. p. 106—107°, has similar properties, and is analogously prepared from α -bromopropionylbromide.

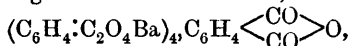
o-Tribromoacetoxybenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{CBr}_3$, m. p. 170—171°, is obtained when tribromoacetyl chloride is employed. These compounds are of therapeutic value. F. M. G. M.

Barium Salts of Phthalic Acid. FRANCIS B. ALLAN (*J. Amer. Chem. Soc.*, 1909, 31, 1061—1065).—A study of the barium phthalates has been made by shaking varying quantities of phthalic acid and barium hydroxide with water until equilibrium occurs, and afterwards analysing the solution. It is shown that the four following barium salts exist, the first three of which have been isolated :

$(\text{C}_6\text{H}_4\cdot\text{C}_2\text{O}_4)_2\text{H}_2\text{Ba}, \text{H}_2\text{O}$;
 $\text{C}_6\text{H}_4\cdot\text{C}_2\text{O}_4\text{Ba}, 1\cdot2\text{H}_2\text{O}$; $(\text{C}_6\text{H}_4\cdot\text{C}_2\text{O}_4\text{Ba})_5, \text{Ba}(\text{OH})_2$; $(\text{C}_6\text{H}_4\cdot\text{C}_2\text{O}_4)_5\text{H}_2\text{Ba}_4$.
 When the first of these salts is heated at 120—150°, a residue is

obtained of the composition $(\text{C}_6\text{H}_4\cdot\text{C}_2\text{O}_4\text{Ba})_4, \text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\rangle\text{O}$. The fourth salt differs from this residue only in containing phthalic acid instead of the anhydride. E. G.

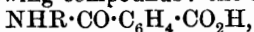
Third Methyl Ester of Phthalic Acid. C. G. ALLIN (*J. Amer. Chem. Soc.*, 1909, 31, 1065—1067).—Experiments have been carried out with the view of ascertaining whether a methyl phthalate could be prepared corresponding with the barium salt,



which is obtained by heating the salt, $(\text{C}_6\text{H}_4\cdot\text{C}_2\text{O}_4)_2\text{H}_2\text{Ba}, \text{H}_2\text{O}$, at 120—140° (Allan, preceding abstract). When the former salt is heated with methyl sulphate at 100° in a sealed tube for forty-five minutes, a methyl ester, $\text{C}_6\text{H}_4(\text{CO}_2\text{Me})_2, \frac{1}{2}\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\rangle\text{O}$, m. p. 187°, is obtained, which forms white crystals. The molecular weight was determined by the ebullioscopic method, acetone being used as the solvent. E. G.

Intramolecular Rearrangement of Phthalamic Acids. IV. J. BISHOP TINGLE and B. F. PARLETT BRENTON (*J. Amer. Chem. Soc.*, 1909, 31, 1157—1164).—In earlier papers (Tingle and Cram, Abstr.,

1907, i, 692; Tingle and Lovelace, Abstr., 1907, i, 1044; Tingle and Rolker, this vol., i, 28) it has been shown that phthalamic acids, $\text{NHR} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, are converted by secondary and tertiary amines into imides, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NR}$, and by primary amines, $\text{NH}_2\text{R}'$, into one or more of the following compounds: the amic acid,



the imides, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NR}$ and $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NR}'$, and the amides, $\text{NHR} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NHR}'$ and $\text{C}_6\text{H}_4(\text{CO} \cdot \text{NHR}')_2$. The investigation has now been extended.

m-Nitrophenylphthalamic acid yields normal salts with butylamine, m. p. 169°, isobutylamine, m. p. 182°, isoamylamine, m. p. 172°, benzylamine, m. p. 166°, benzyloethylamine, m. p. 169°, and dibenzylamine, m. p. 165°. When heated above the m. p., each of these salts decomposes with liberation of the amine and formation of *m*-nitrophenylphthalimide. A salt could not be obtained with either ammonia, diamylamine, or tribenzylamine.

When the benzylamine salt of *p*-tolylphthalamic acid, m. p. 168°, is heated above its m. p., it is converted into benzyl-*p*-tolylphthalimide, $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{Ph}$, m. p. 153°. Benzylamine β -naphthylphthalamate, m. p. 165°, yields dibenzylphthalimide (Tingle and Lovelace, *loc. cit.*), whilst benzylamine phthalate, m. p. 185°, gives benzylphthalimide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{N} \cdot \text{CH}_2\text{Ph}$, m. p. 116°.

p-Chlorophenylphthalamic acid, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, m. p. 180°, is not changed by prolonged heating with 40% alcohol, but is transformed into *p*-chlorophenylphthalimide by pyridine or aniline at 65°, or by β -naphthylamine at 100°.

Attention has also been directed to phthalamic acids containing two similar or dissimilar groups attached to the nitrogen atom. *D*-isobutylphthalamic acid, m. p. 153°, is not changed when boiled with 40% alcohol or heated with pyridine at 65°; aniline reacts with it at 65° with formation of a small quantity of phenylphthalimide, and β -naphthylamine behaves similarly at 100°, yielding β -naphthylphthalimide.

Pyridine reacts with diphenylphthalamic acid to form pyridine phthalate, m. p. 109°. Aniline transforms this acid into phenylphthalimide, whilst β -naphthylamine converts it into phenylphthalimide and β -naphthylphthalamic acid.

Phenyl- β -naphthylphthalamic acid, $\text{C}_{10}\text{H}_7 \cdot \text{NPh} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, m. p. 115°, was prepared without difficulty on two occasions, but, for some unexplained reason, could not be obtained subsequently. E. G.

Dimethylanilinephthalein and Similar Basic Phthaleins. OTTO FISCHER and FRITZ RÖMER (*Ber.*, 1909, 42, 2934—2938).—Dimethylanilinephthalein, prepared by the fusion of phthalic anhydride, dimethylaniline, and zinc chloride, is obtained as a bluish-green mass which becomes colourless on the addition of water. The colour is ascribed to a partial conversion of the lactonic modification into the quinonoid form. Dimethylanilinephthalein is rendered

greenish-blue by a number of reagents (compare Green, Proc., 1908, 24, 206), including hot acetic acid, phenol, cresol, and 2:4-dinitrophenol. The colour in every case vanishes on dilution with water. The quinonoid esters, which are also greenish-blue, are more stable.

When dimethylanilinephthalein, zinc chloride, and methyl alcohol are heated under pressure at 120—125°, a dark blue mass is obtained; this is dissolved in methyl alcohol, sodium picrate added, and the picrate of methyl malachite-green-*o*-carboxylate isolated. It crystallises in lustrous, tin-like, columnar crystals from methyl alcohol or in dark olive-green plates from xylene. The same ester is more conveniently prepared by the interaction of methyl dimethylaminobenzophenone-*o*-carboxylate with dimethylaniline and phosphorus oxychloride.

Dimethylanilineguaiacolphthalein, prepared by the condensation of *p*-dimethylaminobenzophenonecarboxylic acid, and guaiacol in presence of 73% sulphuric acid, crystallises in lustrous, glass-like, tabular crystals, m. p. 172—173°. It dissolves in alkalis with a reddish-violet coloration, and gives the reddish-violet coloration of the quinonoid form when warmed with alcoholic zinc chloride. *Dimethylanilinebenzoylguaiacolphthalein* crystallises in colourless needles, m. p. 155—156°.

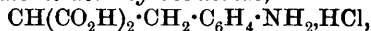
Dimethylanilinephenolphthalein, produced in a similar manner by condensation with phenol in presence of 80% sulphuric acid, forms crystals, which become rose-red on exposure to air; m. p. 122—123°.

Dimethylanilinecatecholphthalein forms colourless, short columns, m. p. 135°, which dissolves with a violet-red coloration in sodium hydroxide, becoming bluer on dilution. Zinc chloride causes a bluish-red coloration.

*Dimethylaniline-*o*-cresolphthalein* crystallises in colourless plates, m. p. 110—112°. E. F. A.

Synthesis of Polypeptides: Derivatives of *p*-Iodophenylalanine. EMIL ABDERHALDEN and G. ALESSANDRO BROSSA (*Ber.*, 1909, 42, 3411—3416).—The authors have prepared *p*-iodophenylalanine (compare Wheeler and Clapp, Abstr., 1908, i, 981) by the following two methods: (1) *p*-Nitrobenzyl chloride was coupled with ethyl sodiomalonate, the ethyl *p*-nitrobenzylmalonate obtained being reduced and hydrolysed to *p*-aminobenzylmalonic acid, into which an iodine atom was introduced by means of the diazo-reaction. The *p*-iodobenzylmalonic acid was then converted into *p*-iodobenzylbromomalonic acid, and this into *p*-iodophenylbromopropionic acid and *p*-iodophenylalanine successively. (2) From synthetic phenylalanine by way of *p*-nitro- and *p*-amino-phenylalanines. The *p*-iodophenylalanine thus prepared was used in the preparation of glycyl-*p*-iodophenylalanine and diglycyl-*p*-iodophenylalanine.

p-Aminobenzylmalonic acid hydrochloride,



has m. p. 178.4° (decomp.), and the free acid, m. p. 213.5° (corr.). When the acid is diazotised and added to cold potassium iodide solution, a crystalline compound, m. p. 192°, separates, which loses nitrogen, yielding *p*-iodobenzylmalonic acid, $\text{C}_6\text{H}_4\text{I} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H})_2$, m. p. 164.4° (corr.).

Chloroacetyl-p-iodophenylalanine, $C_{11}H_{11}O_3NClI$, crystallises in rhombic leaflets, sinters at 142.2° , and decomposes at 233.5° , m. p. 160.4° (corr.).

Glycyl-p-iodophenylalanine, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot C_6H_4I$, crystallises in spherical aggregates of needles, which turn brown at 250° , m. p. 283° (corr.).

Chloroacetylglycyl-p-iodophenylalanine, $C_{13}H_{14}O_4N_2ClI$, has m. p. 176.2° (corr.).

Diglycyl-p-iodophenylalanine,

$NH_2 \cdot CH_2 \cdot CO \cdot NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot C_6H_4I$, crystallises in slender needles, m. p. 240.3° (corr.). T. H. P.

Partial Racemism in Santonin Derivatives. MARIO LEVI-MALVANO and ANTONIO MANNINO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 144—149).—It has been stated by Ladenburg (this vol., i, 252) that partial racemic compounds, as defined by E. Fischer, have never yet been obtained. The authors point out, however, that such a compound was prepared by Andreocci (Abstr., 1899, i, 931) by crystallising from alcohol a mixture of dextro- and lævo-acetyldesmotroposantonins (compare also this vol., i, 32).

The authors have examined the following pairs of compounds for the occurrence of partial racemism, the eutectic points being determined for the ternary systems comprising the two active components and a solvent: (1) acetyldesmotroposantonin and acetylisodesmotroposantonin in naphthalene; (2) desmotroposantonous and *isodesmotroposantonous* acids in acetanilide and in acetic acid; (3) desmotroposantonous and *lævodesmotroposantonous* acids in acetanilide and in acetic acid. The results are as follows:

(1) With these compounds a racemic compound is formed, the eutectic points observed being 55.9° for the racemic compound, 55° for racemic compound + acetyldesmotroposantonin, and 54.9° for racemic compound + acetylisodesmotroposantonin; the racemic compound crystallises from alcohol in prisms, $[\alpha]_D + 108^\circ$.

(2) With the pair of compounds a partly racemic compound is formed in acetic acid, but not in acetanilide solution at the temperatures employed.

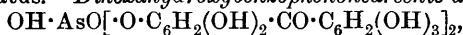
(3) A partly racemic compound is deposited in this case from acetic acid, but not from acetanilide solution.

With *isodesmotroposantonous* and *lævodesmotroposantonous* acids, no racemic compound is formed within the limits of the melting-point curve, but in acetanilide these acids yield a partly racemic compound at about 100° . T. H. P.

Composition and Chemical Constitution of Artificial Tannin. I. PIETRO BIGINELLI (*Gazzetta*, 1909, 39, ii, 268—283).—When gallic and arsenic acids react in moderately concentrated aqueous solution, and the liquid is evaporated on the water-bath at 80 — 90° , very little carbon dioxide is liberated, and the reaction proceeds according to one or other of the two following equations, according to the proportions of the two acids employed: $C_7H_6O_5 + H_3AsO_4 = C_7H_7O_8As + H_2O$; $2C_7H_6O_5 + H_3AsO_4 = C_{14}H_{11}O_{12}As + 2H_2O$.

The first of these compounds, which the author terms arsenic-gallic acid, $\text{AsO}(\text{OH})_2 \cdot \text{O} \cdot \text{C} \begin{smallmatrix} \text{C}(\text{OH}) : \text{CH} \\ \text{C}(\text{OH}) : \text{CH} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$, forms a compound with ether (compare Abstr., 1908, i, 40), and is partly hydrolysed in either aqueous or alcoholic solution, this behaviour being in agreement with the observation that hydrogen sulphide effects precipitation of the arsenic in proportions varying with the dilution. The second acid, *arsenic digallic acid*, $\text{OH} \cdot \text{AsO}[\cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CO}_2\text{H}]_2$, forms a compound with ether and water, $\text{C}_{14}\text{H}_{11}\text{O}_{12}\text{As} \cdot 13\text{Et}_2\text{O} \cdot 7\text{H}_2\text{O}$, and probably forms one of the constituents of Schiff's artificial tannin. By dilute acids and even by acetic acid, these compounds are decomposed into gallic and arsenic acids, so that the formation of acetyl derivatives is possible only under special conditions; this behaviour explains the discrepant observations made by Schiff and others on the acetyl derivatives.

When gallic and arsenic acids are heated together in aqueous solution for a number of hours, especially when the proportion of arsenic acid is relatively small, a part of the gallic acid, which at lower temperatures remains unaltered, undergoes transformation into hexahydroxybenzophenone: $2\text{C}_7\text{H}_6\text{O}_5 - \text{CO}_2 - \text{H}_2\text{O} = \text{C}_{14}\text{H}_{10}\text{O}_7$. It is found, further, that the arsenic acid and hexahydroxybenzophenone react to give compounds, which may also be obtained from the corresponding gallic acid derivatives by heating their solutions for some time in a reflux apparatus. *Di-hexahydroxybenzophenone-arsenic acid*,



was obtained in this way.

Pyrogallol also reacts with arsenic acid, yielding *dipyrogallol-arsenic acid*, $\text{OH} \cdot \text{AsO}[\cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{OH})_2]_2$, which is an amorphous compound, violet and hygroscopic when separated from ethereal solution, and green when deposited from water; it combines with 1 mol. of ether.

It is evident that, for the formation of an artificial tannin by the action of arsenic acid, the presence of a carboxyl group in the compound is unnecessary, three hydroxyl groups in the positions 1 : 2 : 3 being sufficient.

The results of Schiff and others are discussed.

T. H. P.

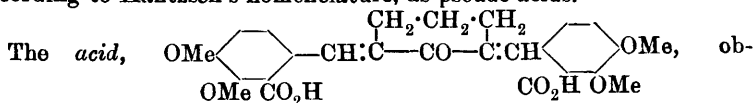
Artificial Tannin. II. PIETRO BIGINELLI (*Gazzetta*, 1909, 39, ii, 283—289. Compare preceding abstract).—Compounds similar to those described in the preceding paper are given by the action of phosphoryl chloride or antimonie acid on gallic acid, the reactions being expressed by the following equations: $3\text{C}_7\text{H}_6\text{O}_5 + \text{POCl}_3 = 3\text{HCl} + \text{PO}[\cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{OH})_2(\text{CO}_2\text{H})]_3$ and either $\text{C}_7\text{H}_6\text{O}_5 + \text{H}_3\text{SbO}_4 = \text{SbO}(\text{OH})_2 \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CO}_2\text{H} + \text{H}_2\text{O}$ or $2\text{C}_7\text{H}_6\text{O}_5 + \text{H}_3\text{SbO}_4 = \text{CH} \cdot \text{SbO}[\text{O} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CO}_2\text{H}]_2 + 2\text{H}_2\text{O}$, according to the proportions of the reacting acids. With pyrogallol, antimonie acid yields the compound, $\text{OH} \cdot \text{SbO}[\cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{OH})_2]_2$, analogous to dipyrogallol-arsenic acid. The compound $\text{PO}(\text{C}_7\text{H}_5\text{O})_3$ combines with $3\text{Et}_2\text{O}$, and the compound $\text{SbO}(\text{C}_7\text{H}_7\text{O}_7)$ with $1\text{Et}_2\text{O}$. Antimonie acid does not react, under the conditions employed, with phloroglucinol or quinol.

T. H. P.

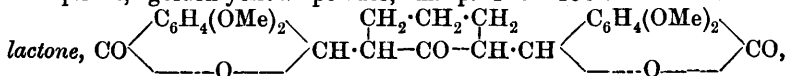
Preparation of Salicylosalicylic [*o*-Salicyloxybenzoic] Acid. C. F. BOEHRINGER & SÖHNE (D.R.-P. 211403).—*Salicylosalicylic acid*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m. p. 147—148°, sparingly soluble in cold alcohol or ether, is obtained when the organic salicylates are treated in an organic solvent with condensing agents, such as phosphorus trichloride, phosphoryl chloride, carbonyl chloride, or thionyl chloride. Salicylic acid (5 parts) and dimethylaniline (5.2 parts) in benzene (1.5 parts) are cooled, and a mixture of phosphorus trichloride (1 part) and benzene (1.5 parts) slowly added. The mixture is left for several days at the ordinary temperature, then acidified with hydrochloric acid, and the unchanged salicylic acid separated with hot water. The product is crystalline, tasteless, and has no irritating action on the stomach, but is rapidly hydrolysed in the intestines.

F. M. G. M.

Condensation of Opianic and Phthalaldehydic Acids with *cyclo*Hexanone and Diethyl Ketone. OTTO MORGENSTERN (*Monatsh.*, 1909, 30, 681—693).—The author has studied the condensation of the symmetrical ketones, *cyclo*hexanone and diethyl ketone, with opianic and phthalaldehydic acids. In the condensations with *cyclo*hexanone, the latter reacts with both the methylene groups adjacent to the carbonyl group, yielding the acids $\text{C}_{26}\text{H}_{26}\text{O}_9$ and $\text{C}_{22}\text{H}_{18}\text{O}_5$, which were transformed into the lactones isomeric with them. These results are in accord with those obtained by Vorländer and Hobohm (*Abstr.*, 1896, i, 603) in studying the action of benzaldehyde on *cyclo*hexanone. The condensation products of *cyclo*hexanone with opianic and phthalaldehydic acids are stable at the ordinary temperature, whilst those formed by non-cyclic ketones readily undergo change into the corresponding lactones. The action of diethyl ketone on opianic and phthalaldehydic acids is similar to that of the other non-cyclic ketones previously studied (compare Hamburger, *Abstr.*, 1899, i, 142; Goldschmiedt and Knöpfer, *Abstr.*, 1900, i, 35; Fulda, *Abstr.*, 1900, i, 36). When titrated with alcoholic alkali hydroxide, all the lactones obtained by the author undergo more or less gradual neutralisation; they must therefore be regarded, according to Hantzsch's nomenclature, as pseudo-acids.



tained by the interaction of *cyclo*hexanone and opianic acid, is an amorphous, golden-yellow powder, m. p. 110—130°. The isomeric



prepared by boiling the acid with water, crystallises in white leaflets, m. p. 196—197°, and forms a yellow *potassium* salt, $\text{C}_{26}\text{H}_{24}\text{O}_9\text{K}_2$, and a *methyl* ester, $\text{C}_{28}\text{H}_{30}\text{O}_9$, m. p. 184—186°, which takes up less bromine than corresponds with the compound $\text{C}_{28}\text{H}_{30}\text{O}_9\text{Br}_4$. The compounds formed by the lactone with hydroxylamine hydrochloride, hydroxylamine in alkaline solution, and phenylhydrazine could not be obtained pure.

The compound, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\overset{\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2}{\text{C}}-\text{CO}-\overset{\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2}{\text{C}}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, formed by cyclohexanone and phthalaldehydic acid, separates in pale brown flocks, and, on boiling with water, is converted into (1) the isomeric lactone, $\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}$
 $\text{O}-\text{CH}-\text{CH}-\text{CO}-\text{CH}-\text{CH}-\text{O}$, which forms white crystals, m. p. 205—206°, and (2) the lactone, $\text{C}_{44}\text{H}_{34}\text{O}_9$, formed by condensation of 2 mols. of the normal lactone with loss of H_2O , which is a white, amorphous powder and unites with less than 2Br.

The acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CMe}\cdot\text{COEt}$, formed by the interaction of phthalaldehydic acid (1 mol.) and diethyl ketone (1 mol.) in presence of sodium hydroxide, readily changes into the corresponding lactone, $\text{CO}\langle\text{C}_6\text{H}_4\rangle\text{CH}\cdot\text{CHMe}\cdot\text{COEt}$, m. p. 109°, which forms a colourless potassium salt. Another lactone, $\text{C}_{45}\text{H}_{40}\text{O}_{10}$, which accompanies the above and is more readily obtained by using 2 mols. of phthalaldehydic acid to 1 mol. of ketone, forms colourless crystals, m. p. 205—207°, and has the normal molecular weight in boiling benzene.

Condensation of opianic acid (1 mol. or 2 mols.) and diethyl ketone (1 mol.) yields a yellow resin, from which no definite compound could be isolated.

T. H. P.

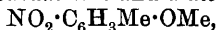
General Reaction of Aldehydes and Ketones. HARTWIG FRANZEN (*Ber.*, 1909, 42, 3293—3295).—Benzaldehyde, when shaken with an aqueous solution of calcium cyanide, yields the calcium derivative of mandelonitrile, $(\text{CN}\cdot\text{CHPh}\cdot\text{O})_2\text{Ca}$. Similar compounds have been prepared by treating salicylaldehyde, *m*-nitrobenzaldehyde, cuminaldehyde, *p*-methylbenzaldehyde, formaldehyde, heptaldehyde, acetone, ethyl acetoacetate, ethyl benzoylacetate, acetylacetone, and acetonylacetone with the cyanides of calcium, strontium, barium, and magnesium. Acetophenone does not appear to form a solid compound with calcium cyanide.

The calcium derivative of mandelonitrile is a fine pale orange-yellow powder, having a slight odour of hydrogen cyanide. It is decomposed by boiling water, but not quantitatively, into calcium cyanide and benzaldehyde.

W. H. G.

4-Amino-3-methoxybenzaldehyde. EUGEN KHOTINSKY and W. JACOPSON-JACOPMANN (*Ber.*, 1909, 42, 3097—3103).—The authors have not been able to obtain pure vanillin from 4-amino-3-methoxybenzaldehyde (compare Tiemann and Ludwig, *Abstr.*, 1883, 189; Ulrich, *ibid.*, 1886, 60). The aldehyde was prepared by Geigy's method (D.R.-P. 86874).

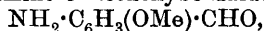
When *m*-cresol is nitrated by Staedel's method (*Abstr.*, 1889, 497; 1891, 186), a mixture of three mononitro-derivatives is obtained. The 6-nitro-derivative is not volatile in steam, whereas the 4- and 2-nitro-compounds are both volatile, but can be separated readily, as the 2-derivative is soluble in water and may be extracted by ether. It forms an intensely red sodium salt and a methyl ether,



in the form of colourless crystals, m. p. 88—89°.

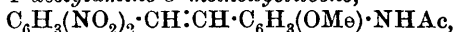
The best yield of 4-nitro-*m*-cresol is obtained when the nitration is conducted at -8 to -5° . Only small amounts of the 4-nitro-compound are formed when Denninger's (Abstr., 1890, 38) or Noelting and Wild's (Abstr., 1885, 973) method is used. In both cases the 6- and 2-nitro-compounds are the chief products.

4-Nitro-*m*-tolyl methyl ether, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OMe}$, obtained by the action of methyl sulphate on sodium 4-nitro-*m*-cresol, forms colourless crystals, m. p. 62° . When treated with sulphur and alcoholic sodium hydroxide, it yields 4-amino-3-methoxybenzaldehyde,



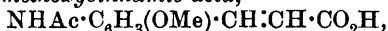
m. p. 102° , which is not volatile in steam. When diazotised and coupled with an alkaline solution of β -naphthol, it yields an *azo-dye*, $\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_2$, m. p. 212° . The *acetyl* derivative, $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$, has m. p. 147° . The *oxime*, $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CH} : \text{N} \cdot \text{OH}$, crystallises from alcohol, and has m. p. 142° ; it yields an *azo-dye*, $\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_3\text{Na}$, m. p. $229-230^{\circ}$.

2 : 4-Dinitro-4'-acetylamino-3'-methoxystilbene,



obtained by condensing the acetylamino-aldehyde with 2 : 4-dinitro-toluene in the presence of piperidine, crystallises from nitrobenzene in brownish-red prisms, m. p. 227° . The corresponding *amino*-compound, obtained by hydrolysis of the *acetyl* derivative with alcoholic hydrochloric acid, crystallises from nitrobenzene and yields an *azo-dye*, $\text{C}_{25}\text{H}_{17}\text{O}_6\text{N}_4\text{Na}$, m. p. 239° , and soluble in sulphuric acid to blue solutions.

4-Acetylamino-3-methoxycinnamic acid,



obtained by Perkin's condensation from the acetylamino-aldehyde, crystallises from alcohol, and has m. p. 100° .

4-Amino-*m*-tolyl methyl ether, $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OMe}$, obtained as a by-product in the preparation of the amino-aldehyde, has b. p. $237-239^{\circ}$. The *acetyl* derivative, $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$, has m. p. 131° , and the *azo-dye*, $\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_2$, obtained by diazotising the amino-methyl ether and coupling with β -naphthol, has m. p. 173° . J. J. S.

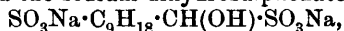
Isomerism of Anils (Schiff's Bases). WILHELM MANCHOT and J. R. FURLONG (*Ber.*, 1909, 42, 3030—3036).—The anils formed by the condensation of aromatic aldehydes with primary aromatic amines should, according to the Hantzsch-Werner theory, exist in two isomeric forms. The existence of these two forms is at present doubtful, the best recorded instance being that of the product from aniline and *p*-homosalicylaldehyde (Anselmino, Abstr., 1907, i, 913). It is, however, doubtful whether this is occasioned by chemical isomerism or physical polymorphism.

The anil from salicylaldehyde and ethyl *p*-aminobenzoate exists in yellow and red modifications. The yellow form is obtained by mixing concentrated alcoholic solutions of the components and quick crystallisation; the red form, on the other hand, results from the slow crystallisation of dilute solutions. The yellow form consists of flat, hexagonal plates, single crystals being colourless; the red modification forms long, prismatic crystals with rectangularly cut ends. The yellow

form melts when quickly heated at 87.5° , the red at 83° without becoming properly liquid; it then becomes yellow, and has m. p. 87.5° .

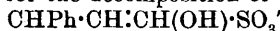
The yellow isomeride is the primary form, and the only one obtainable by direct synthesis. The red isomeride can only be obtained by rearrangement from the yellow form. Accordingly, they are regarded as different chemically. They have the same composition, but differ in solubility. E. F. A.

Combined Sulphurous Acids. IV and V. WILHELM KERF and P. WÖHLER (*Arch. Kais. Ges. Amt.*, 1909, 32, 89—143. Compare Abstr., 1904, i, 713; 1907, i, 1010, 1012).—The behaviour of the three types of salts formed by combination of the unsaturated aldehydes, citronellal and cinnamaldehyde, with sulphurous acid or sodium hydrogen sulphite has been investigated in aqueous solution. In the case of citronellal, the compounds in question are (1) the normal bisulphite compound, $C_9H_{17}\cdot CH(OH)\cdot SO_3Na$, the sodium hydrosulphonate, $SO_3Na\cdot CMe_2\cdot [CH_2]_3\cdot CHMe\cdot CH_2\cdot COH$, formed by addition at the double linking, and the sodium dihydrosulphonate,



formed by addition in both positions. These compounds have already been described by Tiemann (Abstr., 1899, i, 248).

The normal bisulphite compounds do not reach a definite equilibrium when acted on by water, as the bisulphite ion reacts with some of the normal bisulphite compound to form the sodium dihydrosulphonate ion. As, however, the first action is rapid in comparison with the second, it is possible to measure the speed of both reactions, and this has been done for the cinnamaldehyde compounds. The rate of decomposition of the citronellal complex could not be determined, owing to the fact that citronellal accelerates the oxidation of sulphurous acid by the oxygen of the air, a process which disturbs the measurements. The constant for the decomposition of the



ion is 1.02×10^{-3} at 25° .

The dihydrosulphonates of the two aldehydes lose sulphurous acid from the aldehyde group in the normal way in aqueous solution, but the amount lost is much less than in the case of the normal bisulphite compounds. The constant for the citronellal compound is 0.8×10^{-6} , and for the cinnamaldehyde compound 4.06×10^{-6} . Hence the addition of bisulphite at the double bond greatly diminishes the tendency for it to be eliminated from the aldehyde group. As may be anticipated, the compound $SO_3Na\cdot C_9H_{17}\cdot COH$ is stable in aqueous solution. The pharmacological action of the complex sulphurous acids is discussed in the light of these results.

The bisulphite compound with furfuraldehyde has also been prepared, and its behaviour in aqueous solution examined. The average value of the constant, obtained by experiments in $N/1$, $N/10$, and $N/30$ molar aqueous solution, is 0.72×10^{-3} . The equilibrium is established almost instantaneously in aqueous solution, but much more slowly in acid solution, and, in the latter case, the amount of decomposition is greater. This is doubtless owing to the presence of the non-ionised furfuraldehydesulphurous acid, which is decomposed to a greater extent

than the anion. Furfuraldehyde does not combine with sulphurous acid at the double linking.

The mode of occurrence of sulphurous acid in the residual solution obtained in the extraction of cellulose from wood by means of sulphurous acid has been investigated. G. S.

p-Benzoyltriphenylmethane and *p*-Benzoyldiphenylmethane. *p*-Benzoyltriphenylcarbinol and Benzoylbenzophenone. MAURICE DELACRE (*Bull. Soc. chim.*, 1909, [iv], 5, 952—958, 958—962).—Bourcet has prepared *p*-benzoyltriphenylmethane by condensing benzene with phenyl ω -dibromo-*p*-tolyl ketone (Abstr., 1897, i, 566), and this method of preparation has been confirmed by Schmidlin (Abstr., 1907, i, 26, 601). The author has repeated this work and obtained somewhat different results. Three products result from the condensation: (1) a hydrocarbon of about C_{14} complexity, boiling at 240° ; (2) *p*-benzoyldiphenylmethane, and (3) *p*-benzoyltriphenylmethane.

The last-mentioned substance occurs in two forms, the one in vitreous crystals, the other in silky spangles, both of which melt at 161° , as against 164° recorded by Bourcet (*loc. cit.*), but show slight differences in solubility. A mixture of both forms, obtained by crystallising from acetic acid, gradually changes wholly into the spangle form. On oxidation with chromic acid, *p*-benzoyltriphenylmethane yields *p*-benzoyltriphenylcarbinol, which crystallises either with 1 mol. of acetic acid, and then melts at 80° , or anhydrous, and then has m. p. 116° (not 157° as stated by Bourcet, *loc. cit.*). By the further action of the oxidising agent on the carbinol, some *p*-benzoylbenzophenone is formed. The latter is also produced by the oxidation of benzoyldiphenylmethane, obtained as described above. T. A. H.

Nature of Quinhydrones and Triphenylmethane Dyes. WILHELM SCHLENK [with ANGELO KNORR] (*Annalen*, 1909, 368, 277—295).—I. *New Types of Quinhydrone-like Compounds.*—*p*-Benzoquinone and its tetrachloro-derivative unite with quinol dimethyl ether when melted together, forming brownish-red and intensely violet-blue quinhydrone-like compounds respectively, which are so unstable that they dissociate into their components at the ordinary temperature.

p-Benzoquinonedi-imine and benzidine combine in ethereal solution, forming the *quinhydrone-base*, $C_6H_4(NH)_2 \cdot C_{12}H_8(NH_2)_2$, which crystallises in long, ruby-red needles, commences to decompose at about 128° , and is completely molten at 145° .

The following quinone-diamines are prepared by bringing the components together in a suitable solvent; with the exception of the compound from *p*-benzoquinone and *p*-phenylenediamine, they contain the components in equimolecular proportions.

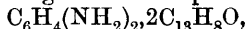
Tetrachloro-*p*-benzoquinone forms *quinone-diamines* with the following bases: (1) *p*-phenylenediamine, bluish-black, glistening needles; (2) tetramethyl-*p*-phenylenediamine, glistening, dark red needles with a bronzy reflex, m. p. about 80° ; (3) 3:3'-dibromo-*o*-tolidine, bluish-black needles, m. p. 225 — 228° ; (4) 3:3'-dichloro-*o*-tolidine, black,

glistening needles; (5) tetramethylbenzidine, nodules of violet-black, hexagonal leaflets.

Tetrabromo-*p*-benzoquinone forms *quinone-diamines* with 3:3'-dibromo-*o*-tolidine, greenish-black, glistening needles, m. p. 190°, and with tetramethylbenzidine, violet-black leaflets.

The *quinone-diamine*, $5C_6H_4O_2 \cdot 2C_6H_4(NH_2)_2$, obtained from *p*-benzoquinone and *p*-phenylenediamine, forms dark blue crystals, m. p. about 83°.

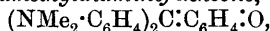
Fluorenone, having a semi-quinonoid structure, combines with *p*-phenylenediamine, forming an *additive* product,



which crystallises in small, brick-red needles, and with benzidine, yielding the *additive* product, $C_{12}H_8(NH_2)_2 \cdot 2C_{13}H_8O$, which crystallises in glistening, yellow prisms and slender leaflets, m. p. 126—127°.

II. *Constitution of Quinhydrone-like Compounds*.—This part of the paper is mainly polemical against Willstätter and Piccard (Abstr., 1908, i, 475). The formulæ assigned by these authors to Wurster's dye salts and quinhydrone are considered very improbable, for many complex partial-quinonoid immonium salts, likewise the quinhydrone-like *additive* product of 2 mols. of *p*-phenylenediamine with 5 mols. of *p*-benzoquinone, cannot be formulated in the same manner. The quinhydrones and similar compounds are *additive* products, which at present cannot be represented by structural formulæ.

III. *Constitution of Triphenylmethane Dyes*.—The theories advanced by von Baeyer (Abstr., 1907, i, 757) and by Willstätter and Piccard (*loc. cit.*) to account for the colour of triphenylmethane dyes are improbable, since *tetramethyldiaminofuchsone*,



is as intensely coloured as magenta. It crystallises in brick-red prisms, and is prepared by condensing Michler's ketone by Grignard's method with *p*-iodoanisole and removing the methoxy-group from the methoxy-malachite green thus formed by means of a mixture of glacial acetic acid and 60% sulphuric acid.

W. H. G.

Quinonoid Derivatives of Diphenyl. II. WILHELM SCHLENK [with HUGO KELLER and ANGELO KNORR] (*Annalen*, 1909, 368, 271—277).—*Quinonechloroimines*.—In continuation of the investigation recorded previously (this vol., i, 36), it is shown that an analogy exists between the 1:2-positions in benzene and the 2:2'-positions in diphenyl, since 2:2'-diaminodiphenyl when treated with hydrochloric acid and sodium hypochlorite in dilute aqueous solutions yields 2:2'-*diphenoquinonedichlorodi-imine*, $C_{12}H_8N_2Cl_2$, a chocolate-brown, amorphous powder, which explodes slightly when heated. 2:4'-*Diphenoquinonedichlorodi-imine*, $C_{12}H_8N_2Cl_2$, prepared by the same method from the corresponding diamine, is a light brown, amorphous powder, which explodes slightly when heated.

Partial-quinonoid Immonium Salts.—The term partial-quinonoid ("theilchinoid") is employed instead of *meri*-quinonoid, since the author cannot agree with the views of Willstätter and Piccard (compare Abstr., 1908, i, 915) associated with this term.

It is found that derivatives of benzidine having only weakly basic

properties, such as 2 : 2'-dinitrobenzidine, 3 : 3'-dinitrobenzidine, 4 : 4'-dinitro-*o*-tolidine, and diacetylbenzidine, do not yield partial-quinonoid salts when oxidised. Further, as a general rule, only those benzidine bases yield partial-quinonoid salts which give rise to substantive, cotton azo-dyes.

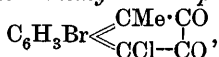
Coerulignone.—It is shown by titration with stannous chloride that, contrary to the statement of Moir (Proc., 1906, 22, 110), *coerulignone* (cediret) is a quinone and not a quinhydrone. W. H. G.

The Constitution of Thiophenoquinone. THEODOR POSNER (*J. pr. Chem.*, 1909, [ii], 80, 270—282).—Polemical. A reply to Michael (this vol., i, 494). J. V. E.

2 : 3-Quinone of 1-Methylnaphthalene. KARL FRIES and J. EMPSON (*Ber.*, 1909, 42, 3375—3381).—4-Chloro-6-bromo-3-hydroxy-1-methyl-2-naphthaquinone, $C_6H_3Br \begin{smallmatrix} CMe(NO_2) \cdot CO \\ \diagdown \\ CCl = C \cdot OH \end{smallmatrix}$, prepared by the action of nitrous acid on 4-chloro-6-bromo-2 : 3-dihydroxy-1-methylnaphthalene (see following abstract), crystallises from benzene in nodular masses, m. p. 110—112° (decomp.).

4-Chloro-6-bromo-1 : 2-dinitro-2 : 3 : 3-tetrahydroxy-1-methylnaphthalene, $C_6H_3Br \begin{smallmatrix} CMe(NO_2) \cdot C(OH)_2 \\ \diagdown \\ CCl(NO_2) - C(OH)_2 \end{smallmatrix}$, prepared by the action of nitric acid on 4-chloro-6-bromo-2 : 3-dihydroxy-1-methylnaphthalene (compare Zincke and Fries, Abstr., 1904, i, 1008), forms white crystals, m. p. 102° (decomp.).

The action of iodine on the lead salt of 4-chloro-6-bromo-2 : 3-dihydroxy-1-methylnaphthalene gives a yellow, amorphous compound, $(C_{11}H_6O_2ClBr)_3$, m. p. 210°, which, when heated in acetic acid solution, gives 4-chloro-6-bromo-1-methyl-2 : 3-naphthaquinone,



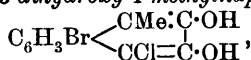
which crystallises from acetic acid in rosettes of yellow prisms or flat needles decomposing at about 220°, and has the theoretical molecular weight in boiling ethyl acetate and double this value in boiling benzene. Treatment of this compound with *o*-phenylenediamine in alcohol or benzene yields 6-chloro-8-bromo-11-methyl- $\beta\beta$ -naphthaphenazine (see following abstract). T. H. P.

2 : 3-Diketo-derivative of Tetrahydro-1-methylnaphthalene. KARL FRIES and ERNST HEMPELMANN (*Ber.*, 1909, 42, 3381—3388. Compare preceding abstract).—A better method for the reduction of 6-bromo-3-nitro-1 : 2-methylnaphtha- ψ -quinol (compare Fries and Hübner, Abstr., 1906, i, 190) to 6-bromo-3-amino-1-methyl- β -naphthol is by means of stannous chloride in presence of hydrochloric and acetic acids.

1 : 4 : 4-Trichloro-6-bromo-2 : 3-diketo-1-methyltetrahydronaphthalene, $C_6H_3Br \begin{smallmatrix} CClMe \cdot CO \\ \diagdown \\ CCl_2 - CO \end{smallmatrix}$, prepared by chlorinating 6-bromo-3-amino-1-

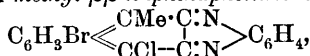
methyl- β -naphthol, separates in nodular crystals, m. p. 132—138° (decomp.).

4-Chloro-6-bromo-2 : 3-dihydroxy-1-methylnaphthalene,



obtained on reducing the preceding compound, crystallises in slender, silky needles, m. p. 184°, and in alcoholic or acetic acid solution gives a deep blue coloration with ferric chloride; its *diacetyl* derivative has m. p. 184°.

6-Chloro-8-bromo-11-methyl- $\beta\beta$ -naphthaphenazine,

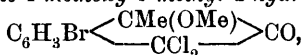


prepared from 1 : 4 : 4-trichloro-6-bromo-1-methyl-2 : 3-diketotetrahydronaphthalene and *o*-phenylenediamine, separates in slender, carmine-red needles, decomposing at 230—270°.

The action of calcium hypochlorite on 1 : 4 : 4-trichloro-6-bromo-2 : 3-diketo-1-methyltetrahydronaphthalene yields (1) 1:3:3-trichloro-5-bromo-1-methyl-2-hydrindone, $\text{C}_6\text{H}_3\text{Br} \begin{array}{c} \text{CMeCl} \\ \diagdown \quad \diagup \\ \text{CCl}_2 \end{array} > \text{CO}$, which crystallises in thick plates, m. p. 75°; (2) 4-bromo-1-methylphthalide-1-carboxylic acid, $\text{C}_6\text{H}_3\text{Br} \begin{array}{c} \text{CMe}(\text{CO}_2\text{H}) \\ \diagdown \quad \diagup \\ \text{CO} \end{array} > \text{O}$, which crystallises in small prisms, m. p. 132—135°.

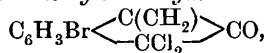
4-Bromo-1-methylphthalide, $\text{C}_6\text{H}_3\text{Br} \begin{array}{c} \text{CHMe} \\ \diagdown \quad \diagup \\ \text{CO} \end{array} > \text{O}$, obtained by heating the preceding compound at 200°, crystallises in long prisms, m. p. 62°.

3 : 3-Dichloro-5-bromo-1-methoxy-1-methyl-2-hydrindone,



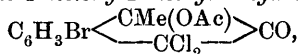
prepared by the action of sodium methoxide on 1 : 3 : 3-trichloro-5-bromo-1-methyl-2-hydrindone, is very unstable and forms small, shining scales, m. p. 108°.

3 : 3-Dichloro-5-bromo-1-methylene-2-hydrindone,



separates from an acetic acid solution of the preceding compound and crystallises in faintly yellow prisms, m. p. 200°.

3 : 3-Dichloro-5-bromo-1-acetoxy-1-methyl-2-hydrindone,



separated from the acetic acid mother liquor from the preceding compound, crystallises in thin plates, m. p. 126—133°. T. H. P.

Preparation of Acetylaminoanthraquinones. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 211958).—Aminoanthraquinones can be readily acetylated in the presence of fuming sulphuric acid (23% SO_3). Aminoanthraquinone (10 parts) is dissolved in 100 parts of fuming sulphuric acid, and acetic anhydride (10 parts) stirred in, the temperature being maintained at 30—40° until the reaction is complete; this is indicated by the formation of a yellow precipitate on the addition of water, and the absence of a red coloration. F. M. G. M.

Side-Chain Halogen Substituted Methylanthraquinone.

MAX H. ISLER (*J. pr. Chem.*, 1909, [ii], 80, 287—288. Compare this vol., i, 563).—In criticising the recent publication of Otto Fischer (*loc. cit.*), numerous references unmentioned by this author are given to previously published work on the preparation of methylanthraquinones in which halogen is a substituent in the side-chain.

The opinion is expressed that Fischer's ω -substituted methylanthraquinone is probably a ring substituted methylanthraquinone.

J. V. E.

Preparation of 1:2-Dihydroxyanthraquinone-3:5- and 3:8-disulphonic Acids. R. WEDEKIND & Co. (D.R.-P. 210863. Compare this vol., i, 496).—By the sulphonation of alizarin-3-sulphonic acid in presence of mercury, the same two disulphonic acids are produced as are formed by sulphonating alizarin directly in presence of mercury. The latter are therefore the 3:5- and the 3:8-disulphonic acids. It is not necessary first to isolate the alizarin-3-sulphonic acid for their preparation, but when the formation of the monosulphonic acid is complete, mercury is added to the sulphonation mixture, which is then further heated. The salts of the 3:5-acid are more sparingly soluble than those of the 3:8-compound.

With dilute sulphuric acid at 170° , the sulphonic group in position 3 is eliminated, and 1:2-dihydroxyanthraquinone-5- and -8-sulphonic acids are formed. 1:2:5-Trihydroxyanthraquinone has m. p. 278° , and 1:2:8-trihydroxyanthraquinone, m. p. 239 — 240° , instead of 272 — 274° and 230° respectively as previously recorded.

F. M. G. M.

The Resolution of *d,l*-Camphorsulphonic Acid into its Optically Active Components. BRUNO REWALD (*Ber.*, 1909, 42, 3136—3138).—This resolution of the camphorsulphonic acid prepared from synthetic camphor furnishes an additional argument for the view that the latter is the racemic form of the natural product. The resolution was effected by means of brucine. Brucine *d*-camphorsulphonate first separates in aggregations of rhombohedral crystals; the *l*-salt is more soluble, and forms small needles. From the salts, the free acids were obtained by decomposing with baryta. *d*-Camphorsulphonic acid, m. p. 193 — 195° (decomp.), has (in agreement with Reychler's value for the acid from natural camphor) $[\alpha]_D^{20} + 22.06^{\circ}$. The rotation of the acid from pure *d*-camphor was determined afresh, and found to be $[\alpha]_D^{20} + 22.60^{\circ}$.

l-Camphorsulphonic acid has m. p. 193 — 195° (decomp.); $[\alpha]_D^{20} - 20.75^{\circ}$.

R. V. S.

Terpenes and Ethereal Oils. CI. OTTO WALLACH (*Annalen*, 1909, 369, 63—103. Compare this vol. i., 726).—I. *The Fenchone Series*.—The author's formula for fenchone is finally abandoned, since the reactions described in this communication cannot be explained by its aid. It is possible by making use of Semmler's formula to deduce structural formulae for the compounds described later, but these are by no means definitely established.

[With HEINRICH WIENHAUS.]—Contrary to Semmler's statement

(compare Abstr., 1908, i, 37), fenchone reacts as completely, although not so readily, with sodium as camphor. The chief product of the reaction is the pinacone of fenchone, $C_{20}H_{34}O_2$, which has been described previously (Abstr., 1898, i, 486); it has b. p. 219—220°/13 mm., and crystallises in stout prisms and plates, m. p. 97°, and in slender needles, m. p. 94°. The pinacone from *d*-fenchone has $[\alpha]_D^{15} + 45.00^\circ$ (in ethyl acetate), $+ 32.26^\circ$ (in benzene), $[\alpha]_D^{18} + 32.08^\circ$ (in benzene); the pinacone from *l*-fenchone has $[\alpha]_D^{20} - 44.78^\circ$ (in ethyl acetate), $- 36.70^\circ$ (in benzene); the *racemic* compound has m. p. 104—105°. If air be not excluded during the reaction, an *acid*, which dissolves in aqueous alkalis to a yellowish-red solution, and small quantities of fencholic acid are formed.

Fencholic acid is identical with Semmler's dihydrofencholenic acid (b) (compare Abstr., 1906, i, 681), but is so named in order to emphasise its analogy to campholic acid. It is readily prepared by heating fenchone with solid potassium hydroxide under pressure at 220—240°; the product obtained thus is a mixture of two isomerides, one of which is present, however, in extremely small quantities; it forms large, hard crystals, m. p. 18—19°, b. p. 255—256°/760 mm., 151—152°/17 mm., D_{20}^{20} 0.9700, n_D^{20} 1.4563, n_D^{20} (in 1-dcm. tube) $+ 3.92^\circ$ to $+ 4.28^\circ$. The *chloride*, $C_9H_{17}\cdot CO\cdot Cl$, obtained by the action of phosphorus trichloride on the acid, has b. p. 100°/15 mm., 218—219°/750 mm., D_{20}^{20} 1.0045, n_D^{20} 1.4606, $[\alpha]_D^{19} - 2.43^\circ$; the following compounds are obtained from it by the usual methods: *ethyl fencholate*, a colourless liquid with a fruity odour, b. p. 222—223°, D_{19}^{19} 0.913, n_D^{19} 1.4392; *isoamyl fencholate*, $C_{15}H_{28}O_2$, a colourless liquid, b. p. 262—269°, D_{19}^{19} 0.903, n_D^{19} 1.4436; *fencholanilide*, $C_9H_{17}\cdot CO\cdot NHPh$, large prisms, m. p. 79—80°.

[With FRIEDRICH RITTER.]—When fencholamide (1 mol.) is acted on by bromine (1 mol.) and subsequently treated with an aqueous solution of potassium hydroxide (2 mols.), it yields *fenchylcarbimide*, $C_9H_{17}\cdot N\cdot CO$, a slightly yellow oil, b. p. 201°, $[\alpha]_D^{19} + 3.04^\circ$, D_{19}^{19} 0.9210, n_D^{19} 1.4461 (compare Bouveault and Levallois, Abstr., 1908, i, 193). The carbimide reacts (1) with ammonia, forming *fenchylcarbamide*, $NH_2\cdot CO\cdot NH\cdot C_9H_{17}$, m. p. 129—130°; (2) with fenchylamine, yielding difenchylcarbamide, m. p. 169° (compare Bouveault and Levallois, *loc. cit.*); (3) with piperidine, yielding the *carbamide* derivative, $C_5H_{10}N\cdot CO\cdot NH\cdot C_9H_{17}$, colourless needles, m. p. 96°.

Fenchylamine, $C_9H_{17}\cdot NH_2$, prepared by hydrolysing the carbimide with hot concentrated hydrochloric acid, is a colourless, limpid liquid, b. p. 173°, D_{21}^{21} 0.832, n_D^{21} 0.4450, which absorbs carbon dioxide readily, and forms a *hydrochloride*, m. p. 169—170°, $[\alpha]_D + 2.95^\circ$ (in water), and a *platinichloride* crystallising in leaflets. The hydrochloride decomposes when heated, yielding a hydrocarbon, C_9H_{16} , which is also formed together with other hydrocarbons by the dry distillation of sodium fencholate, and is identical with that described by Bouveault and Levallois (*loc. cit.*). The hydrocarbon yields a crystalline *nitrosochloride*, $(C_9H_{16}NOCl)_2$, m. p. 115°, which when acted on by piperidine yields the crystalline *nitrolpiperidide*, $C_9H_{16}NO\cdot C_5NH_{10}$, m. p. 159—159°. A *ketone*, $C_9H_{14}O$, is obtained by hydrolysing the oily *oxime* which results from the action of sodium acetate on the nitrosochloride

just described; it is a colourless liquid, b. p. 204—206°, with an odour like carvone; the *semicarbazone*, $C_9H_{14}N \cdot NH \cdot CO \cdot NH_2$, crystallises in glistening leaflets, m. p. 149—150°.

[With WERNER LANGE.]—The oxidation of fencholic acid with potassium permanganate leads to the formation of (1) a *hydroxy-acid*, $C_{10}H_{18}O_3$, which crystallises in prisms, m. p. 80—81°; the corresponding *lactone*, $C_{10}H_{16}O_2$, has m. p. 11°, b. p. 134—135°/20 mm., 251—252°/760 mm.; (2) an isomeric *hydroxy-acid*, $C_{10}H_{18}O_3$, m. p. 110—112°, obtained only in very small quantities; (3) a *dihydroxy-acid*, $C_{10}H_{18}O_4$, compact crystals, m. p. 130—133°; the *lactone*, $C_{10}H_{16}O_3$, crystallises in prisms, m. p. 189—190°; (4) a *dihydroxy-acid*, $C_{10}H_{18}O_4$, m. p. 130°; the *lactone*, $C_{10}H_{16}O_3$, crystallises in needles, m. p. 70—71°.

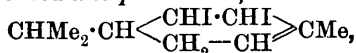
[With ALFRED HOMBERGER.]—*iso*Fenchone when treated with potassium hydroxide yields *isofencholic acid*, $C_{10}H_{18}O_2$, m. p. 33—34°; the *amide*, $C_9H_{17} \cdot CO \cdot NH_2$, has m. p. 65—66°; the *anilide* crystallises in needles, m. p. 100—101°.

II. *Behaviour of Monocyclic Ketones towards Potassium Hydroxide.*—The tendency of *cyclohexanone* and its homologues when heated with potassium hydroxide under pressure at 180—190° is to form condensation products rather than substances produced by fission of the ring.

[With MAX BEHNKE.]—*cycloHexanone* when heated with potassium hydroxide yields *cyclohexenyl-2-cyclohexanone* (compare Abstr., 1907, i, 220), *dodecahydrotriphenylene* (compare Mannich, Abstr., 1907, i, 205), a *substance*, $C_{18}H_{26}O$, crystallising in large prisms, m. p. 122—125°, an *acid*, $C_{12}H_{20}O_2$, b. p. 180—190°/19 mm., the *amide* of which, $C_{12}H_{21}ON$, crystallises in silvery leaflets, m. p. 96—97°, and an *acid*, $C_{18}H_{28}O_2$, b. p. 230—240°/19 mm.

2-Methylcyclohexanone yields an *acid*, $C_{14}H_{24}O_2$, b. p. 170—195°/18 mm.; the *3-methyl* compound yields an *acid*, $C_{14}H_{24}O_2$, b. p. 185—195°/18 mm., and an *acid*, $C_{21}H_{34}O_2$, b. p. 230—240°/25 mm.; the *4-methyl* compound yields an *acid*, $C_{14}H_{24}O_2$, b. p. 170—195°/18 mm., and an *acid*, $C_{21}H_{34}O_2$, b. p. 230—240°/20 mm. W. H. G.

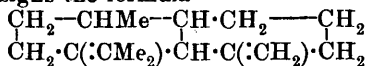
Additive Product of Iodine and Essential Oil of Turpentine. CARLO CASANOVA (*Boll. chim. farm.*, 1909, 48, 684—685).—The action of iodine on turpentine oil proceeds energetically, and results in the formation of *p*-cymene: $C_{10}H_{16} + I_2 = 2HI + C_6H_4MePr$. If, however, the reaction takes place in presence of excess of the turpentine oil or with the addition of a diluent, such as almond oil, no hydrogen iodide is evolved, and by treating the mixture with alcohol, the author has separated a *terpene iodide*,



as a dense, yellowish-red, unstable liquid, b. p. 170°, at which temperature decomposition into hydrogen iodide, iodine, and *p*-cymene occurs; by the action of air or of light, the iodide decomposes with liberation of iodine. T. H. P.

Sesquiterpenes. III. ERNST DEUSSEN (*Annalen*, 1909, 369 41—62. Compare Deussen and Lewinsohn, Abstr., 1908, i, 353; Deussen, this vol., i, 171).—The author, from the results of his

investigations on the oxidation of β -caryophyllene and because it forms a blue nitrosite, assigns the formula



to this sesquiterpene.

[With A. LOESCHE and A. KLEMM.]—I. "*Caryophyllene*" from Oil of Clove-stalks.—It is proposed to name the nitrosate, m. p. 148—149°, described originally by Wallach and Tuttle, α -caryophyllene nitrosate; the correct m. p. is 162°; when treated with benzylamine it yields α -caryophyllenenitrolbenzylamine. The nitrosate, m. p. 131—132°, obtained by Deussen and Lewinsohn (Abstr., 1907, i, 945) from the blue caryophyllene nitrosite (β -caryophyllene nitrosite) is now designated *d*-caryophyllene nitrosate. The colourless isomeride, m. p. 139°, derived from β -caryophyllene nitrosite is named β -caryophyllene *isonitrosite*. The substance, m. p. 162—163°, obtained by the action of alcoholic potassium hydroxide on β -caryophyllene nitrosite cannot have the formula given previously (*loc. cit.*); it is either $\text{C}_{15}\text{H}_{25}\text{O}_2\text{N}$ or $\text{C}_{15}\text{H}_{23}\text{O}_2\text{N}$.

The α -compound obtained by Schreiner and Kremers (Abstr., 1900, i, 106) by the action of light on β -caryophyllene nitrosite is *d*-caryophyllene nitrosate, whilst the β -compound is identical with the substance, $\text{C}_{15}\text{H}_{24}\text{O}_6\text{N}_4$, m. p. 159°, formed by the action of hot light petroleum on the blue nitrosite.

A substance, $\text{C}_{15}\text{H}_{23}\text{O}_2\text{N}$ or $\text{C}_{15}\text{H}_{25}\text{O}_2\text{N}$, has been isolated from the mother liquor obtained in the preparation of α -caryophyllene nitrosochloride; it crystallises in slender needles, m. p. 125—125.5°, $[\alpha]_D + 24^\circ$ (in benzene), and does not decolorise bromine.

α -Caryophyllene nitrosochloride when treated with sodium ethoxide or propoxide in alcoholic solution yields a *nitrosocaryophyllene*, $\text{C}_{15}\text{H}_{23}\text{ON}$, crystallising in rhombic plates, m. p. 128—129°, whilst with sodium methoxide it yields the optically inactive compound, m. p. 116° (*loc. cit.*), which is now shown to have the formula $\text{C}_{15}\text{H}_{25}\text{ON}_2$.

β -Caryophyllene nitrosochloride, m. p. 159°, when heated with alcohol passes into the nitrosochloride, m. p. 122° (α -isocaryophyllene nitrosochloride), derived from the sesquiterpene (*isocaryophyllene*) obtained during the preparation of β -caryophyllene nitrosite (*loc. cit.*); the nitrosochloride, m. p. 146° (β -isocaryophyllene nitrosochloride), when similarly treated also passes into the isomeride, m. p. 122°. The three nitrosochlorides when acted on by sodium methoxide yield a substance, $\text{C}_{15}\text{H}_{25}\text{O}_2\text{N}$, m. p. 162—164°, probably identical with that obtained in the preparation of α -caryophyllene nitrosochloride (Abstr., 1907, i, 945).

A new *sesquiterpene*, $\text{C}_{15}\text{H}_{24}$, has been isolated from the "first runnings" obtained in the preparation of caryophyllene alcohol; it is a colourless oil, b. p. 126—127°/24 mm., $D_{19}^{20} 0.9227$, $n_D^{20} - 24^\circ$, $n_D^{20} 1.49533$.

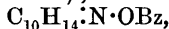
*iso*Caryophyllene when oxidised with potassium permanganate yields $\alpha\alpha$ -dimethylsuccinic acid and the liquid ketonic or aldehydic acid, b. p. 196—198°/23 mm., described previously (Abstr., 1908, i, 171). The glycol formed by the oxidation of "caryophyllene" probably has the formula $\text{C}_{14}\text{H}_{22}\text{O}_4$, since it yields a crystalline *oxime*, $\text{C}_{14}\text{H}_{23}\text{O}_4\text{N}$, m. p. 187—188° (compare Haarmann, this vol., i, 400).

II. [With HANS PHILIPP.]—Gurjun balsam oil when oxidised with potassium permanganate in acetone yields a *ketone* or *aldehyde*, $C_{15}H_{24}O$, b. p. 170° – $180^{\circ}/12$ mm., which forms a crystalline *semi-carbazone*, $C_{16}H_{27}ON_3$, m. p. 234° (decomp.).

III. [With A. KLEMM.]—A simple apparatus for use in the preparation of nitrosochlorides of mono- and sesqui-terpenes is described. The mixture of terpene, alcohol, ethyl acetate, and ethyl nitrite, contained in a tall glass vessel cooled by a freezing mixture, is stirred mechanically, and hydrochloric acid, likewise kept cold, is allowed to flow into the mixture drop by drop.

Monoterpenes. I. [With A. HAHN.]—*d*-Limonene nitrosochloride when treated with sodium methoxide yields a mixture of *l*-carvoxime (α -carvoxime) and a new β -carvoxime, which may be separated through the benzoyl derivatives.

β -Carvoxime, $C_{10}H_{14}N\cdot OH$, crystallises in glistening needles, m. p. 57 – 58° , $[\alpha]_D + 68\cdot3^{\circ}$ (in benzene); the benzoyl derivative,



has m. p. 77° , $[\alpha]_D + 75\cdot3^{\circ}$.

II. [With HANS PHILIPP.]—Pinene nitrosochloride is converted by sodium methoxide into nitrosopinene and a *substance*, $C_{11}H_{19}O_2N$, probably formed by the replacement of chlorine by methoxyl; it has m. p. 101 – 102° .
W. H. G.

Essential Oils. HEINRICH HAENSEL (*Bericht von H. Haensel*, April–September, 1909. Compare this vol., i, 312).—A résumé of information on essential oils accumulated during the half-year April to September, 1909. The data recorded are mostly commercial, but the following are of scientific interest. The optical rotations quoted are for direct readings in a 100 mm. tube, except where otherwise stated.

Birch bud oil contains 73.2% of betulol, of which 29.6% occurs in the form of the acetate, and the rest free (compare von Soden and Elze, *Abstr.*, 1905, i, 451). *Ranunculus ficaria* herb in the flowering stage, free from roots, yielded 0.02% of a dark brown oil, which deposited solid matter on standing, and had a tobacco-like odour. The filtered oil, D^{24}_{20} 0.9101, b. p. 150 – 310° , reduced ammoniacal silver solution. The solid deposit contained palmitic acid.

A sample of opoponax resin gave 3.46% of oil, having D^{19}_{20} 0.8931, optical rotation in a 50 mm. tube $-10\cdot3^{\circ}$, soluble in 8.5 volumes of 95% alcohol.

The “terpenes,” separated in preparing “terpeneless orange oil” from oil distilled from unripe fruits, boiled at 171 – 175° , and contained *d*-limonene, but no camphene or pinene could be detected.

“Macassar” sandalwood yielded an oil having D^{19}_{20} 0.9723, $\alpha_D - 16\cdot92^{\circ}$, saponification number 7.7, and acetyl ester number 206.6, corresponding with 96% of santalol. New Caledonian sandalwood furnished an oil having D^{20}_{20} 0.9665, $\alpha_D 21\cdot69^{\circ}$ (direction not stated), saponification number 6.1, acetyl ester number 205.6, corresponding to 95.5% of santalol. Both these oils are soluble in two or more volumes of 70% alcohol.

Asparagus root oil gave 0.0108% of sour, strong-smelling, dark

brown oil, having D^{23} 0.8777, saponification number 101, acid number 33, and yielding palmitic acid on saponification.

The roots of *Valeriana celtica* yielded 0.1% of thick yellow oil, D^{20} 0.9693, $\alpha_D - 42^\circ$, saponification number 62.5, acetyl ester number 71.9, which was miscible in all proportions with 90% alcohol, and boiled from 165—210°/45 mm. The portion boiling above 190° had D 0.9359 and $\alpha_D - 30.88^\circ$, and appeared to be a sesquiterpene. On saponification the oil yielded some palmitic acid.

The physical constants of "terpeneless oils," prepared from many well-known essential oils, are also quoted. T. A. H.

Essential Oils. SCHIMMEL & Co. (*Bericht*, October, 1909).—The "terpene portion" of ajowan seed oil contains *p*-cymene, α -pinene, dipentene, and γ -terpinene.

Artemisia herba-alba, var. *densiflora* herb, yielded 0.58% of oil, having D^{15} 0.8994, $\alpha_D + 14.5'$, n_D^{20} 1.46684, acid number 4.6, ester number 35.0, and acetyl ester number 163.3. It is soluble in 1.8 parts of 70% alcohol, with the separation of some paraffin (compare this vol., i, 317).

Fiji "bay" oils had D^{15} 0.9605—0.9893, $\alpha_D - 1^\circ$ to $-2^\circ 10'$, phenols 23—24%, and were soluble in 0.3 or more volumes of 90% alcohol. These oils were probably "light" bay oils only.

Ocimum basilicum oil, from Anjouan, had D^{15} 0.9608, $\alpha_D + 0^\circ 40'$, and n_D^{20} 1.51425, and was soluble in five or more volumes of 80% alcohol (compare van Romburgh, *Abstr.*, 1901, i, 220; this vol., i, 597).

Birch bud oil, of this season's distillation, deposited crystals at $+8^\circ$, had D^{15} 0.9730, $\alpha_D - 5^\circ 34'$, n_D^{20} 1.50153, acid number 2.8, ester number 51.4, and acetyl ester number 150. The oil gave a clear solution with 0.25 volume of 90% alcohol, and deposited paraffin on further dilution.

A portion of camphor oil having b. p. 106—120°/7 mm., D^{15} 0.9378, $\alpha_D + 11^\circ$, n_D^{20} 1.50188, contained bisabolene (Tucholka, *Abstr.*, 1897, ii, 584), but no cadinene.

Chrysanthemum sinense, var. *japonicum* flowers (?), yielded 0.8% of a yellowish-brown oil containing *i*-camphor and *l*-camphene (Keimatsu, *J. Ph. Soc. Japan*, 1909, 1).

African copaiba balsam oil gave results agreeing with those recorded by von Soden (this vol., i, 401), but whilst the original oil was strongly dextrorotatory, the cadinene isolated from the oil by way of the trihydrochloride proved to be levorotatory, and it is not certain whether the cadinene occurs in the oil in the *d*- or *l*-form.

Coriander oil, in which *d*-pinene and *d*-linalool had been recorded already, contained *d*- α -pinene, *i*- α -pinene, β -pinene, phellandrene (?), cymene, dipentene, α -terpinene, γ -terpinene, terpinolene (?), *n*-dec-aldehyde, geraniol, *l*-borneol, and acetic esters of the three alcohols.

Cumin fruit oil contained in the hydrocarbon portion, *d*- and *i*- α -pinenes, β -pinene, *p*-cymene (Wolpian's hydrocuminene was probably a mixture of these hydrocarbons), β -phellandrene, and dipentene. The aldehyde portion contained, in addition to cuminaldehyde, probably a *hydrocuminaldehyde*, since from the semicarbazones a portion melting at 200—201° was isolated and from the oximes a fraction having

m. p. 72—76°. The alcohol portion consisted of cumin alcohol and a small quantity of an unidentified alcohol.

The hydrocarbon portion of lemon oil consists mainly of *d*-limonene with a considerable quantity of *l*- β -pinene, and small amounts of *l*- and *i*- α -pinenes, *l*-camphene, β -phellandrene, and γ -terpinene. No *p*-cymene could be detected. The sesquiterpene portion consists of cadinene(?) and bisabolene (Burgess and Page's "limene," Trans., 1904, 85, 414; compare Tucholka, Abstr., 1897, ii, 584).

Sweet orange oil, from Jamaica, had D^{15} 0.8481 to 0.8488, $\alpha_D^{20} + 97^{\circ}47'$ to $+98^{\circ}2'$, and bitter orange oil from the same locality had D^{15} 0.8517 to 0.8521, and $\alpha_D^{20} + 96^{\circ}20'$ to $+96^{\circ}58'$.

Eucalyptus oil, from the Transvaal, had D^{15} 0.9236, $\alpha_D + 1^{\circ}45'$, n_D^{20} 1.46337, contained 65% cineol, no phellandrene, and was soluble in 2.8 and more volumes of 70% alcohol.

It is suggested that Wallach and Grosse's sesquiterpene from pine needle oil (*Annalen*, 1909, 368, 19) may be bisabolene (see above).

Chamomile florets yielded 0.35% of viscous, deep blue oil, having D^{15} 0.954, $\alpha_D \pm 0$, n_D^{21} 1.363734, and saponification number 74.4. The flower heads gave 0.51% of thick, greenish oil, having D^{15} 0.949, $\alpha_D \pm 0$, n_D^{21} 1.363716, and saponification number 33.7.

Lantana camara oil, prepared in the Philippines, had D^{20} 0.9132, $\alpha_D^{30} + 11^{\circ}5'$, n_D^{30} 1.4913 (Bacon, *Philippine J. Sci.*, 1909, 4, 127; compare this vol., i, 114).

French Lavender plants, grown during three years at Miltitz near Leipzig, yielded an oil having D^{15} 0.8888, $\alpha_D - 8^{\circ}40'$, n_D^{20} 1.46010, and contained 55.1% of linalyl acetate.

Lemon grass oil, from the Comores Islands, had D^{15} 0.8914, and contained 83% citral. Samples from Jalpaiguri, in North Bengal, had D^{15} 0.8924 to 0.8954, $\alpha_D - 0^{\circ}28'$ to $-0^{\circ}49'$, and citral 87 to 90% (acid sulphite process). All three were of the "insoluble" type.

The following limiting values for "hand-pressed lime oil" are suggested: D^{15} 0.878 to 0.901, $\alpha_D + 32^{\circ}50'$ to $+37^{\circ}50'$, n_D^{20} 1.482 to 1.486, acid number 3, ester number 18 to 30, non-volatile residue 10 to 14%, cloudy solution in 4 to 10 volumes of 90% alcohol.

Rosaceous fruit kernels gave the following yields of volatile oil: cherry, 0.7%; apricot, 1.6%; plum, 0.3 to 0.46%; bitter almonds, 0.81%; the aldehyde content of these varied from 61.8 to 88.7%.

Piper camphoriferum leaves gave 1.11% oil, having D^{20} 0.9500 and $\alpha_D + 19^{\circ}21'$, and contained camphor, borneol, terpenes, and a sesquiterpene. *Piper lineatum* leaves furnished 0.44% oil, b. p. 140—160°/15 mm., D 0.958, and $\alpha_D + 8^{\circ}45'$. Camphor and phenyl ethers were absent. *Piper angustifolium*, var. *ossanum*, leaves furnished 0.87% oil containing camphor and borneol. "Matico" leaves, consisting mainly of *Piper acutifolium*, var. *subverbascifolium*, mixed with a few leaves of *P. asperifolium* and *P. molliconum*, gave 0.8% oil, having D^{20} 1.10, $\alpha_D + 24'$, methoxyl 21.8 to 22.1%. It contained pinene, sesquiterpene, dillisoapiol, and dillapiol (compare this vol., i, 316).

Rabak observed that leaves of *Mentha arvensis*, var. *glabrata*, grown in S. Dakota, gave 0.8% oil, having D 0.9267, $\alpha_D + 16^{\circ}27'$, acid number 2.6, ester number 13.1.

Schinus molle leaves, from Algeria, Grasse and Mexico, examined by

Roure-Bertrand fls, furnished an oil having D^{15} 0.8492 to 0.8696, $\alpha_D + 42^\circ 30'$ to $+ 65^\circ 20'$, n_D^{20} 1.47616 to 1.47909, acid number 0.7 to 2.1, ester number 3.4 to 25.2, and acetyl ester number 29.4 to 56.5.

Celery oil, from herb and seed of wild celery, grown in S. France, was yellow, had a characteristic celery odour, and had D^{15} 0.8713, α_D $58^\circ 30'$, n_D^{20} 1.47715, acid number 1.8, ester number 41.5, and did not give a clear solution with 95% alcohol.

Sium cicutae-folium herb, grown in S. Dakota, gave, according to Rabak, 0.5% oil, of yellow colour with an odour recalling those of caraway and turpentine oil. It had D^{22} 0.8447, $\alpha_D + 63^\circ 40'$, ester number 33, no free alcohols, gave a cloudy solution with 6 volumes of 90% alcohol, and probably contained *d*-limonene.

Juniper berry oil contained, in addition to pinene and cadinene already recorded, 4-terpinenol and a second alcohol, possessing an odour suggestive of borneol and geraniol, and having b. p. $105-110^\circ/8$ mm., $218-226^\circ/760$ mm., D^{15} 0.9476, $\alpha_D - 4^\circ 30'$, and n_D^{20} 1.48248. The *phthalate* boiled from $95-130^\circ$ in the purest state obtained, so that a mixture of alcohols may be present. Other unidentified constituents of the oil occur in the fraction having b. p. $72-88^\circ/8$ mm.

Curcuma zedoaria roots gave 0.065% of a bluish-green oil, smelling of camphor and having D^{20} 0.933, n_D^{30} 1.4920, $\alpha_D^{30} < + 1.5^\circ$. A quantity of a volatile crystalline substance was also obtained.

Lebanon cedar (*Cedrus Libani*) wood gave 3.5% of lemon-yellow oil of balsamic odour, and reminiscent of methyl heptenone and thujone. It had D^{15} 0.9427, $[\alpha]_D + 80^\circ 20'$, n_D^{20} 1.51254, acid number 0.5, ester number 3.0, acetyl ester number 19.8, and dissolved in five to six volumes of 95% alcohol.

Bolivian copaiba balsam, from *Copaiba paupera*, had D^{15} 0.998, $\alpha_D^{15} + 36^\circ$, n_D^{20} 1.522, acid number (indirect) 89.7, saponification number (cold) 97.25. On distillation it furnished 23% oil, having D^{15} 0.916, $\alpha_D + 18^\circ$, n_D^{20} 1.5048, and of which 70% distilled from $250-270^\circ$, and probably contained cadinene and caryophyllene (Hartwich, *Schweiz. Woch. Chem. Pharm.*, 1909, 47, 373).

Tahiti vanilla yielded, according to Walbaum, besides vanillin, an oil heavier than water and boiling at $105-118^\circ/6$ mm., and containing anisaldehyde, anisic alcohol, and anisic acid.

A résumé of recent work on the constituents of essential oils, new analytical processes, and a bibliography of recent works relating to the chemistry, botany, and pharmacology of the subject are also given.

T. A. H.

Turpentine of Aleppo Pine. MAURICE VÈZES (*Bull. Soc. chim.*, 1909, [iv], 5, 931—933).—Three samples of turpentine from the Aleppo pine (*Pinus halepensis*), collected in France and in the Province of Oran in Algeria, have furnished the following percentage results on analysis. Turpentine oil 14.7—27.0, dry residue (rosin) 66.7—78.3, solid impurities 0.8—6.6, water and loss 2.1—5.5 (compare Tschirch and Schulz, *Abstr.*, 1907, i, 544). The turpentine oils obtained by the steam distillation of five samples of the oleo-resin had D^{25} 0.8552—0.8568, $[\alpha]_D + 46.6^\circ$ to $+ 47.6^\circ$ and n_D^{25} 1.4638—1.4652. On redistillation, 80% of each of the oils passed over at $155-156^\circ$, and

these fractions had D_{25}^{25} 0.8541—0.8547, $[\alpha]_D + 47.4^\circ$ to $+ 48.4^\circ$, and n_D^{25} 1.4633—1.4639 (compare Tsakalotos, *Archimedes*, 1908, No. 1). It is concluded that at least 80% of the oil consists of *d*-pinene.

T. A. H.

Chemical Examination of Jalap. FREDERICK B. POWER and HAROLD ROGERSON (*Pharm. J.*, 1909, [iv], 29, 7—8).—Jalap consists of the dried tuberous roots of *Exogonium purga*, and on extraction with alcohol yields a product which, after washing with water, constitutes the "jalap resin" of medicine. This has been generally assumed by investigators to consist of two amorphous glucosidic constituents, one soluble in ether, the other insoluble, the latter being called "convolvulin." Numerous divergent formulæ have been assigned to convolvulin (compare Taverne, *Abstr.*, 1895, i, 119; Kromer, *Abstr.*, 1893, i, 423; 1894, i, 540, and 1896, i, 385; Höhnelt, *Abstr.*, 1897, i, 228). The present investigation shows that jalap resin is much more complex than has been supposed previously, that its physiologically active components are all indefinite and amorphous, as are also the most important products of their hydrolysis, and that consequently there is no justification for assigning empirical formulæ to these substances.

The jalap used was exhausted with hot alcohol, and from the extract so prepared the following products were obtained by (a) steam distillation, (b) extraction with water, and (c) successive extraction with light petroleum, ether, chloroform, ethyl acetate, and alcohol.

A small quantity of volatile oil, b. p. 80—160°/60 mm., D_{20}^{20} 0.8868, $[\alpha]_D$ 0, possessing a smoky, disagreeable odour, and a yellow colour which gradually darkened.

The aqueous extract contained colouring matter and a sugar which yielded *d*-phenylglucosazone.

The residue ("jalap resin") yielded 1.9% to light petroleum. This dissolved portion was physiologically inactive and contained free palmitic and stearic acids, and on hydrolysis yielded formic, butyric, and higher volatile acids, palmitic acid, and a mixture of unsaturated acids, including much linoleic acid. The unsaponifiable portion included a *phytosterol*, $C_{27}H_{46}O$, m. p. 134—135°, $[\alpha]_D - 32.4^\circ$, cetyl alcohol, and a *substance*, $C_{18}H_{36}O$, m. p. 56—57°, which gave the phytosterol reaction.

The ether extract amounted to 9.7% of the resin; it was purgative, and contained a small amount of *ipurganol*, $C_{21}H_{32}O_2(OH)_2$, m. p. 222—225°, $[\alpha]_D - 44.9^\circ$, which crystallised in colourless needles and gave the colour reactions of the phytosterols; its *diacetyl* derivative has m. p. 166—167° and $[\alpha]_D - 36.0^\circ$. The residue of the ether extract, after hydrolysis by alkalis, gave a little phytosterol, cetyl alcohol, volatile acids, and amorphous products.

The chloroform extract amounted to 24.1% of the resin, and was purgative. It yielded a little β -methylæsculetin, and, after hydrolysis, furnished formic, butyric, and *d*- α -methylbutyric acids and convolvulinic acid, $C_{15}H_{30}O_8$, and possibly a higher homologue of the latter. Some dextrose was also formed, so that a portion of the extract was glucosidic.

The ethyl acetate extract, which was also purgative, formed 22% of the resin, and, on hydrolysis with dilute alcoholic sulphuric acid, yielded products similar to those got from the ether extract.

The alcoholic extract amounted to 38.8% of the resin, and was purgative. It was an almost white powder, m. p. 150—160°, $[\alpha]_D - 37.1^\circ$. On fusion with potassium hydroxide, it yielded formic, acetic, butyric, valeric, and higher volatile acids, together with azelaic and sebacic acids. On hydrolysis with barium hydroxide, it furnished formic, butyric, and α -methylbutyric acids, together with amorphous "hydrolysed resin"; the latter proved to be inactive physiologically, and was of complex composition, since it could be separated into various products by successive extraction with (I) ether, (II) chloroform, (III) ethyl acetate, and (IV) alcohol. These on hydrolysis with dilute sulphuric acid all yielded formic, butyric, and other acids and sugar. No. III gave also α -methylbutyric acid, and No. IV furnished convolvulinolic acid and ipurololic acid; the latter has been obtained already from the stems of *Ipomoea purpurea* (Power and Rogerson, Abstr., 1908, ii, 725). No. IV also furnished sebacic acid on oxidation with nitric acid. Each of the four extracts of the hydrolysed resin appeared to be only partly glucosidic, and to contain a soluble organic acid which was unaffected by dilute sulphuric acid.

T. A. H.

Preparation, Behaviour, and Quantitative Estimation of Pure Urobilin and of Urobilinogen. D. CHARNAS (*Biochem. Zeitsch.*, 1909, 20, 401—430).—In the spectro-photometric investigation of urobilin, its extraordinary instability has hitherto not been sufficiently taken into account; the "acid" and "alkaline" modifications do not exist. Urobilin can only be prepared pure by exposing urobilinogen to light. The latter substance is prepared from urobilin by reduction with sodium amalgam, or, better, by alkaline fermentation of the urine, and is then purified. Pure urobilin has three times the absorptive power for light possessed by hydrobilirubin, so that the two substances cannot be identical. The spectro-photometric estimation of urobilin is carried out by means of Ehrlich's colour reaction with dimethylaminobenzaldehyde.

G. B.

Uromelanin. The Decomposition Product of the Colouring Matter of Urine. ST. DOMBROWSKI (*Zeitsch. physiol. Chem.*, 1909, 62, 358—366. Compare Gawinskiy, this vol., ii, 331).—Analyses have been made of the uromelanin obtained by boiling urochrome with hydrochloric acid. The black precipitate was washed with water, dried, and extracted with alcohol, carbon disulphide, and ether. The analyses agree with the formula $C_{47}H_{44}O_{13}N_7S$, and differ but little from the numbers given by Nencki's proteinochromogen. Since urochrome contains sulphur and uropyrrol does not, it is impossible that urochrome can be an anhydride of the latter.

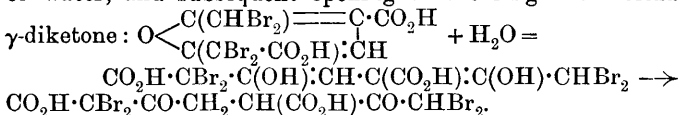
J. J. S.

Constitution of Aniline-black. HANS T. BUCHERER (*Ber.*, 1909, 42, 2931—2933. Compare Willstätter and Dorogi, this vol., i, 535).—Willstätter and Dorogi have established that aniline-black can

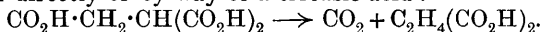
be converted into benzoquinone with a yield of 95.44% of the theoretical, and in consequence of this, regard aniline-black as possessing an open-chain indamine structure. The author cites the great stability of emeraldine and aniline-black towards acids as opposed to this view, and considers the azine formula to be more probable in spite of the conversion of aniline-black into quinone. E. F. A.

Action of Zinc Dust on Tannin. LEO F. ILJIN (*J. pr. Chem.*, 1909, [ii], 80, 332—336).—When an approximately 10% aqueous solution of tannin is boiled with zinc dust for 15—20 hours, gallic acid is produced together with an amorphous substance, $C_{56}H_{48}O_{34}$, which resembles tannin in appearance, has $[\alpha]_D^{18.4} + 24.1^\circ$ in 95% alcohol, gives coloured precipitates with many metallic salts, does not reduce Fehling's solution, and yields gallic acid when heated with 20% sulphuric acid in a current of hydrogen. C. S.

Peculiarities in the Decomposition of Furan Derivatives. HYPOLYT A. TREPHILIEFF and B. V. MANGUBI (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 875—885. Compare Abstr., 1907, i, 1063; 1908, i, 735).—The action of water on the tetrabromo-derivative of methronic acid results in the formation of succinic acid. The first phase of the action probably consists in the union of the furan ring with a molecule of water, and subsequent opening of the ring with formation of a



Removal of the side groups from this compound then yields succinic acid, either directly or by way of a tribasic acid:



The action of bromine water on bromo-derivatives of furan containing a methyl group in the 3-position yields a tetrabromopropane and methylsuccinic acid, whilst when the methyl group is in the 2-position, as in methronic acid, only oxalic acid is obtained.

The action of bromine water on 3-carboxy-2-methylfuran-4-acetic acid (compare Feist, Abstr., 1899, i, 675) yields 5-bromo-4-methylfuran-2:3-dicarboxylic acid, $O < \begin{array}{c} CBr \\ | \\ C(CO_2H) : C \cdot CO_2H \end{array} = \begin{array}{c} CMe \\ | \\ C \cdot CO_2H \end{array}$ m. p. 149—151°.

The interaction of methronic acid and bromine water in the cold yields two compounds in which the furan ring is probably not opened: (1) the compound, $C_7H_2O_4Br_4$, m. p. 129—130°, and (2) the compound, $C_7H_2O_4Br_3$, m. p. 138—139°. T. H. P.

Methoxy-2-phenylcoumarones. SIGMUND MOTYLEWSKI (*Ber.*, 1909, 42, 3148—3152).—The author extends to purely aromatic *o*-hydroxyketones the method of Kostanecki and Tambor (compare this vol., i, 319) for obtaining 2-substituted coumarones from *o*-hydroxyketones.

Benzoresorcinol monomethyl ether (2-hydroxy-4-methoxybenzophenone: compare König and Kostanecki, Abstr., 1907, i, 62) and

ethyl bromoacetate, when heated on the water-bath for twelve hours with an alcoholic solution of sodium, yield *ethyl 5-methoxy-2-benzoyl-phenoxyacetate*. After saponification with alcoholic potash, the unattacked ether is removed by means of carbon dioxide, and, on acidifying, the free acid is precipitated. The product is rendered impure by the presence of 5-methoxy-2-phenylcoumarilic acid, formed by intramolecular condensation from the 5-methoxy-2-benzoylphenoxyacetic acid primarily produced. The two are separated by fractional crystallisation from dilute alcohol, in which the latter acid is the more soluble. The *5-methoxy-2-benzoylphenoxyacetic acid* forms small, hexagonal laminæ, m. p. 114—115°. *5-Methoxy-2-phenylcoumarilic acid* forms rhombic laminæ or needles, m. p. 198° (decomp.). *5-Methoxy-2-phenylcoumarone* is formed by dry distillation of 5-methoxy-2-phenylcoumarilic acid, and also from 5-methoxy-2-benzoylphenoxyacetic acid by the action of acetic anhydride and sodium acetate. It forms colourless needles of m. p. 41—42°, and dissolves in concentrated sulphuric acid, giving a yellow colour. The products of the action of ethyl bromoacetate on hydrocotoin (benzophloroglucinol dimethyl ether or 2-hydroxy-4 : 6-dimethoxybenzophenone) are similar. *3 : 5-Dimethoxy-2-phenylcoumarilic acid* crystallises in colourless needles, m. p. 215°, with evolution of carbon dioxide. *3 : 5-Dimethoxy-2-benzoylphenoxyacetic acid* forms small, colourless laminæ, m. p. 140—141°. *3 : 5-Dimethoxy-2-phenylcoumarone* crystallises from alcohol in small, colourless laminæ or needles, m. p. 83—84°, and is slightly volatile in steam. Concentrated sulphuric acid dissolves it with production of a brownish-yellow colour. The fact that hydrocotoin enters into this reaction shows that it has the constitution above stated (compare Pollak, Abstr., 1898, i, 304).

The production of a corresponding coumarone from alizarin-yellow-A, which is obtained from benzoic acid and pyrogallol, shows that the substance is 2 : 3 : 4-trihydroxybenzophenone (compare E. Fischer, this vol., i, 309). On methylating benzopyrogallol (alizarin-yellow), a *monomethyl ether* is obtained, which crystallises from alcohol in yellow laminæ, m. p. 164—165°. On further methylating this substance, *2-hydroxy-3 : 4-dimethoxybenzophenone* is produced as white laminæ, m. p. 120—121°. This yields directly by the above reaction, not the expected *5 : 6-dimethoxy-2-benzoylphenoxyacetic acid*, but *5 : 6-dimethoxy-2-phenylcoumarone*, which crystallises from alcohol in colourless laminæ, m. p. 83—84°, slightly volatile in steam. In concentrated sulphuric acid, it dissolves, giving a yellow coloration; on adding a trace of ferric chloride to the solution, the colour becomes green, and finally violet.

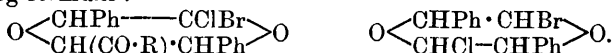
R. V. S.

Constitution of the So-called Halogendiphenacyls. OSKAR WIDMAN (*Ber.*, 1909, 42, 3261—3270).—Many objections are raised against the formulæ assigned by Paal and Schultze (compare Abstr., 1903, i, 707) to the α - and β -halogendiphenacyls. It is shown that these compounds cannot contain hydroxyl or ketonic groups, or yet ethylene linkings, since they do not interact with acetic anhydride, phenylcarbimide, phenylhydrazine, hydrazine hydrate, hydroxylamine, bromine in chloroform, or potassium permanganate in glacial acetic acid.

The chemical properties of the α - and β -isomerides (for example, the so-called α - and β -bromodiphenaclys) are most clearly represented by

the formula $\text{O} \begin{array}{c} \text{CHPh} \cdot \text{CBr} \cdot \text{O} \\ \text{---} \text{CH} \text{---} \text{CHPh} \end{array}$; thus, when reduced by magnesium

powder or sodium amalgam, they yield diphenacyl or diphenyltetramethylene glycol respectively, and when treated with acyl chlorides or bromides under pressure at 100° , or with hydrogen bromide or chloride in glacial acetic acid, yield additive products, which probably have the following formulæ:

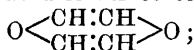


In agreement with the last formula, it is shown that the additive product of β -bromophenacyl with hydrogen chloride when acted on by sodium ethoxide in alcohol, yields a mixture of α - and β -bromodiphenacyl, and when heated with red phosphorus and hydriodic acid yields acetophenone.

A substance having the constitution represented by the formula just assigned to the halogendiphenaclys must be capable of existing in a *cis*- and *trans*-form, in agreement with which is the fact that the chloro-, bromo-, and iodo-compounds are known in two isomeric forms which may be converted, either directly or indirectly, one into the other. It is not yet possible to state which isomeride has the *cis*- and which the *anti*-configuration.

The β -iododiphenacyl described by Paal and Schultze (*loc. cit.*) is undoubtedly a mixture of the α - and δ -compounds, the latter being the true β -modification.

The α - and β -halogendiphenaclys and their additive products are to be regarded, therefore, as derivatives of 1:4-dioxine,

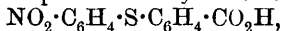


thus, the α - and β -bromodiphenaclys are (*cis*-, *trans*-)-3-bromo-2:5-diphenyl-2:5-dihydrodioxines.

W. H. G.

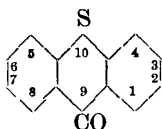
Derivatives of Thiosalicylic Acid and of Thioxanthone. FRITZ MAYER (*Ber.*, 1909, 42, 3046—3067. Compare this vol., i, 405).

—Various nitrophenyl-sulphide-carboxylic acids,



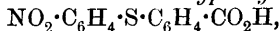
have been synthesised, but they do not yield nitrothioxanthenes when heated with sulphuric acid. The corresponding amino-compounds, however, readily lose water, yielding aminothioxanthenes. The nitrothioxanthenes can be prepared from the chlorides of the nitrophenyl-sulphide-carboxylic acids; they crystallise remarkably well, and their solutions in sulphuric acid have but a slight fluorescence. The aminothioxanthenes (numbering as in annexed formula), on the other hand, exhibit a strong green fluorescence. 2-Aminothioxanthone, which is analogous to β -aminoanthraquinone, does not yield an indanthrene derivative when fused with potassium hydroxide, or a flavanthrene derivative with antimony pentachloride in nitrobenzene solution.

When subjected to Skraup's synthesis, however, it yields a thioxanthoquinoline (compare Graebe, *Abstr.*, 1884, 759)

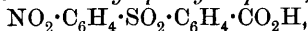


When oxidised with chromic acid, the nitrothioxanthenes yield the sulphones, $\text{C}_6\text{H}_4\langle\text{SO}_2\rangle\text{C}_6\text{H}_3\cdot\text{NO}_2$; so far, the formation of sulphoxides has not been observed.

p-Nitrothioanisole has m. p. 71—72°, not 67° as stated by Blanksma (Abstr., 1902, i, 282). 4-Nitro-2'-carboxyphenyl sulphide,

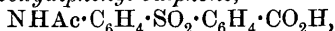


obtained by coupling a diazotised solution of anthranilic acid with a hot solution of sodium *p*-nitrophenylmercaptide, crystallises from alcohol in flat, yellow prisms, m. p. 229—231° after softening at 210°. The sodium salt forms deep red solutions; the methyl ester, $\text{C}_{14}\text{H}_{11}\text{O}_4\text{NS}$, has m. p. 131·5°; the ethyl ester, $\text{C}_{15}\text{H}_{13}\text{O}_4\text{NS}$, forms yellow needles, m. p. 127°. 4-Nitro-2'-carboxyphenylsulphoxide, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, obtained by oxidising the sulphide with nitric acid or chromic acid, has m. p. 216—217°, and is identical with Weedon and Doughty's acid (Abstr., 1905, i, 345). The methyl ester, $\text{C}_{14}\text{H}_{11}\text{O}_5\text{NS}$, crystallises from acetic acid and light petroleum in slender needles, m. p. 143·5°, and the ethyl ester, $\text{C}_{15}\text{H}_{13}\text{O}_5\text{NS}$, has m. p. 107—107·5°. When the sulphide is oxidised with potassium permanganate, 4-nitro-2'-carboxydiphenylsulphone,



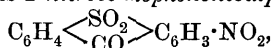
is formed. It crystallises from glacial acetic acid in compact, pale yellow cubes, m. p. 196·5°. The methyl ester has m. p. 136°, and the ethyl ester, m. p. 101°.

4-Amino-2'-carboxyphenyl sulphide, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, obtained by reducing the nitro-compound with tin and alcoholic hydrogen chloride, crystallises from dilute alcohol in colourless plates, m. p. 193°. The hydrochloride forms colourless, felted needles, which decompose at 260°; the acetyl derivative, $\text{C}_{15}\text{H}_{13}\text{O}_3\text{NS}$, forms slender needles, m. p. 236—237°, and when oxidised with chromic acid yields 4-acetylamino-2'-carboxydiphenyl sulphone,



which has m. p. 215°.

2-Nitrothioxanthone, $\text{C}_6\text{H}_4\langle\text{S}\rangle\text{C}_6\text{H}_3\cdot\text{NO}_2$, obtained by the action of phosphorus pentachloride on the sulphide, crystallises from glacial acetic acid in pale brown plates, m. p. 219—221°, and when oxidised with chromic acid yields 2-nitrobenzophenonesulphone,



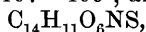
which crystallises from acetic acid in flat plates, m. p. 254—255°.

2-Aminothioxanthone, $\text{C}_{13}\text{H}_9\text{ONS}$, obtained by reducing the nitro-compound, or by the action of sulphuric acid on the aminocarboxy-sulphide, crystallises from nitrobenzene in yellowish-brown plates, m. p. 221—222°. The hydrochloride, $\text{C}_{13}\text{H}_9\text{ONS}\cdot\text{HCl}$, decomposes at 230°. The acetyl derivative, $\text{C}_{15}\text{H}_{11}\text{O}_2\text{NS}$, crystallises in glistening plates, m. p. 236—237°. When 4-nitro-2'-carboxydiphenylsulphoxide is heated with phosphorus pentachloride or thionyl chloride, 2-nitrothioxanthone is formed, and not nitrobenzophenone sulphoxide.

Thioxanthone-1 : 2-(or 2 : 3)-quinoline, $\text{C}_{16}\text{H}_9\text{ONS}$, crystallises from

light petroleum in glistening, yellow needles, m. p. 167°. The *hydrochloride*, $C_{16}H_9ONS.HCl$, crystallises from glacial acetic acid in needles, which decompose at 240—260°, and are hydrolysed by water.

2-Nitro-2'-carboxyphenyl sulphide, $C_{13}H_9O_4NS$, is prepared most readily by condensing methyl thiosalicylate with *o*-chloronitrobenzene, sodium methoxide, and a little copper powder at 140°, and hydrolysing the resulting ester. It crystallises from glacial acetic acid in yellow, nodular masses, m. p. 165—166°. The *methyl* ester, $C_{14}H_{11}O_4NS$, forms yellow crystals, m. p. 92°, and the *ethyl* ester has m. p. 75—76°. *2-Nitro-2'-carboxydiphenylsulphoxide*, $C_{13}H_9O_5NS$, obtained by oxidising an ester of the sulphide and subsequent hydrolysis, crystallises from glacial acetic acid in glistening, pale yellow plates, m. p. 277°. The *methyl* ester, $C_{14}H_{11}O_5NS$, has m. p. 147—148°, and the *ethyl* ester, m. p. 120°. The corresponding *sulphone*, $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot C_6H_4 \cdot CO_2H$, forms slender needles, m. p. 197—199°, and its *methyl* ester,



has m. p. 127°.

2-Amino-2'-carboxyphenyl sulphide, $NH_2 \cdot C_6H_4 \cdot S \cdot C_6H_4 \cdot CO_2H$, prepared by reducing the nitro-derivative with ammonia and ferrous sulphate, crystallises from glacial acetic acid in colourless nodules, m. p. 156—157.5°. The *acetyl* derivative, $C_{15}H_{13}O_3NS$, has m. p. 188—196°.

4-Nitrothioxanthone crystallises from benzene in yellow needles, m. p. 215°, and when oxidised with an excess of chromic acid yields *4-nitrobenzophenone sulphone*, $C_{13}H_7O_5NS$, which crystallises in brilliant, colourless needles, m. p. 240°. *4-Aminothioxanthone*, $C_{13}H_9ONS$, crystallises from benzene in glistening plates, m. p. 202—203°; the *acetyl* derivative, $C_{15}H_{11}O_2NS$, has m. p. 233—234°.

3-Nitro-2'-carboxyphenyl sulphide, prepared by condensing methyl thiosalicylate and *m*-iodonitrobenzene with sodium methoxide and copper powder at 160—170°, and hydrolysing the resulting ester, crystallises from glacial acetic acid, and has m. p. 168—169°. The *methyl* ester crystallises in yellow, rectangular plates, m. p. 112—114°, and when oxidised yields the *sulphoxide*, $NO_2 \cdot C_6H_4 \cdot SO \cdot C_6H_4 \cdot CO_2Me$, which crystallises from glacial acetic acid in colourless needles, m. p. 137—138°. The corresponding *acid*, $C_{13}H_9O_5NS$, has m. p. 222—223°, and the *carboxysulphone*, $C_{13}H_9O_6NS$, m. p. 190°. *3-Amino-2'-carboxyphenyl sulphide* crystallises from alcohol in pale yellow needles, m. p. 159—160°.

1-Nitrothioxanthone crystallises from benzene in pale yellow needles, m. p. 237°, and the corresponding *amino*-compound in greyish-brown needles, m. p. 249—250°. The *acetylamino*-compound has m. p. 273°.

3-Nitro-6-carboxyphenyl sulphide, $CO_2H \cdot C_6H_3(NO_2) \cdot SPh$, prepared by diazotising 4-nitro-2-aminobenzoic acid and coupling with an alkaline solution of phenyl mercaptan, crystallises in yellow nodules, m. p. 210—211°. The corresponding *amino-acid*, $C_{13}H_{11}O_2NS$, crystallises from methyl alcohol in compact cubes or glistening plates, m. p. 200—201°.

3-Nitrothioxanthone forms glistening prisms, m. p. 247°; the *3-amino*-compound has m. p. 246°, and its *acetyl* derivative, m. p. 267°.

o-Nitrophenyl mercaptan has m. p. 56° , not 46° as stated by Blanksma (*loc. cit.*), and its *methyl* ether, m. p. 63 — 64° . J. J. S.

Sulphides from the Ester of 2:6-Dithiolketopenthiophen-3:5-dicarboxylate. VI. HERMANN APITZSCH and C. KELBER (*Ber.*, 1909, 42, 2940—2943).—By the oxidation of ethyl 2:6-dithiol-4-ketopenthiophen-3:5-dicarboxylate, a termolecular sulphide is formed (this vol., i, 46, 47). By carrying out the oxidation with iodine quantitatively, it has been possible to establish the structure of this sulphide, $C_{33}H_{30}O_{15}S_9$, as $\left(\begin{array}{c} CO_2Et \cdot C - CO - C \cdot CO_2Et \\ -SC - S - CS- \end{array} \right)_3$.

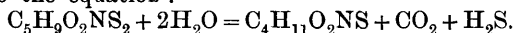
This termolecular sulphide is easily decomposed by alkalis into the original unimolecular mercaptan. A sulphinic acid is also formed, as shown by the formation of sulphurous acid when the alkaline solution is rendered acid.

When the dithiolketopenthiophendicarboxylate is oxidised with amyl nitrite, a *disulphide*, $C_{22}H_{30}O_{10}S_4(SH)_2$, is formed. This separates in radial bunches of thin, orange-red needles, m. p. 158 — 159° .

E. F. A.

Cheiroline. WILHELM SCHNEIDER (*Ber.*, 1909, 43, 3416—3420).—The numbers given by Wagner (*Abstr.*, 1908, i, 202) and by the author (this vol., i, 118) for the proportion of sulphur in cheiroline are considerably lower than the true number, owing to the fact that a portion of the sulphur of this compound is combined in such a manner that its complete oxidation to sulphuric acid by means of fuming nitric acid in a sealed tube takes place only after protracted heating at a temperature not lower than 300° . The mean proportion of sulphur found in this way is 35.7%. Repetition of the estimation of carbon, hydrogen, and nitrogen by very slow combustion in a tube having double the ordinary length, and packed in the first half with copper oxide and in the second with lead chromate, gives numbers which correspond closely with the formula $C_5H_9O_2NS_2$ (mol. wt. 179), which is also in agreement with the molecular weights in freezing (186 — 260) and boiling benzene (220 — 271).

This new formula for cheiroline affords a ready explanation of the resolution of this compound by means of dilute sodium hydroxide solution, which must be regarded as a simple hydrolysis taking place according to the equation:

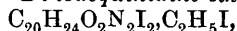


In wallflower seeds, cheiroline appears to exist in the form of a glucoside. T. H. P.

Iodine Derivatives of Cinchona Alkaloids. TAD. KOZŃIEWSKI (*Bull. Acad. Sci. Cracow*, 1909, 734—746).—By adding a solution of iodine in carbon disulphide to a hot alcoholic solution of the alkaloids, *di-iodocinchonine*, $C_{19}H_{22}ON_2I_2$, orange-yellow crystals, m. p. 147 — 149° , and *di-iodoquinidine*, $C_{20}H_{24}O_2N_2I_2$, m. p. 157 — 159° , can be obtained; these substances are analogous to the strychnine and brucine derivatives previously described (*Abstr.*, 1908, i, 1007). With

an excess of iodine, the much more soluble hydriodide is formed, $C_{19}H_{22}ON_2I_2, HI, H_2O$ (= cinchonine periodide).

The di-iodo-derivatives yield with methyl iodide, *di-iodocinchonine methiodide*, $C_{19}H_{22}ON_2I_2, CH_3I$, m. p. 193—195°, and *di-iodoquinidine methiodide*, $C_{20}H_{24}O_2N_2I_2, CH_3I$, m. p. 194—197°, which can also be obtained by adding an iodine solution to cinchonine and quinidine methiodide respectively. *Di-iodoquinidine ethiodide*,



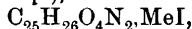
has also been prepared.

G. B.

Formation of *i*-Nicotine from Methyl- δ -3-pyridylbutylamine (Dihydrometanicotine). KARL LÖFFLER and SAMY KOBER (*Ber.*, 1909, 42, 3431—3438).—The reaction for the preparation of 1-alkyl-pyrrolidines (this vol., i, 830) has been applied to the production of *i*-nicotine from dihydrometanicotine. Metanicotine, obtained from nicotine by Pinner's method (*Abstr.*, 1894, i, 388), is heated with fuming hydriodic acid and amorphous phosphorus at 100° for fifteen hours, and the resulting iodo-compound is treated for twenty-four hours with zinc dust in a freezing mixture, 25% hydrochloric acid being added subsequently, and, after one day, the mixture is heated on the water-bath. The *dihydrometanicotine*, $C_5NH_4 \cdot C_4H_8 \cdot NHMe$, is then liberated by sodium hydroxide and purified through the *picrate*, m. p. 161—162°. The base itself has b. p. 258—259° and D_4^{20} 0.959, and forms an *aurichloride*, m. p. 138°, and a *platinichloride*, m. p. 198—199° (decomp.). By treatment with sodium hypobromite, it yields the *N*-brominated derivative, an unstable, yellow oil, which is converted into nicotine by concentrated sulphuric acid under definite conditions. C. S.

ψ -Codeine. LUDWIG KNORR, HOWARD BUTLER, and HEINRICH HÖRLEIN (*Annalen*, 1909, 368, 305—323. Compare *Abstr.*, 1907, i, 151, 789, 956; 1908, i, 41, 42, 361).—A further contribution to the chemistry of ψ -codeine.

Benzoyl- ψ -codeine hydrochloride, $C_{25}H_{25}O_4N, HCl$, crystallises in small, white needles, m. p. 174—184°; the *methiodide*, $C_{25}H_{25}O_4N, MeI$, forms small, silky needles, m. p. 206—208° (decomp.). ψ -Codeine yields with phenylcarbimide the *anilino-carboxylic ester*, the *hydrochloride* of which, $C_{25}H_{26}O_4N_2, HCl, Et \cdot OH$, crystallises in stellate aggregates of prisms, m. p. 73—94° (decomp.), whilst the *methiodide*,



has m. p. 243—244°. *Chloro- ψ -codeine*, $C_{18}H_{20}O_3NCl$, prepared by the addition of potassium chlorate to a solution of the base in dilute hydrochloric acid, forms glistening, white needles, m. p. 203—204°, $[\alpha]_D^{15} - 100.8^\circ$ (in 99% alcohol). *Bromo- ψ -codeine*, $C_{18}H_{20}O_3NBr$, crystallises with 1 $Et \cdot OH$ in small, silky, white needles, m. p. 190—192°, $[\alpha]_D^{15} - 75.2^\circ$ (in 99% alcohol). *Nitro- ψ -codeine*, $C_{18}H_{20}O_5N_2$, crystallises in rectangular leaflets, m. p. about 235° (decomp.), $[\alpha]_D^{15} - 49.9^\circ$ (in chloroform).

The action of phosphorus pentachloride on ψ -codeine leads to the formation of a mixture of α -chlorocodide and ψ -chlorocodide; the *methiodide* of the latter, $C_{18}H_{20}O_2NCl, MeI$, crystallises in glistening leaflets and cubes, m. p. 185—186° (decomp.), $[\alpha]_D^{15} - 227.4^\circ$ (0.102 gram in 20 c.c. of alcohol + water, 1:3), -229° (0.197 gram in 20 c.c.

of the same solvent). ψ -Codeine when treated with phosphorus tribromide yields bromocodide (compare Schryver and Lees, *Trans.*, 1901, 79, 575).

ϵ -Methylmorphimethine (compare Abstr., 1907, i, 151) crystallises in tetragonal pyramids, m. p. $129-130^\circ$, $[\alpha]_D^{15} - 120.1^\circ$ (in 99% alcohol); the hydrochloride has $[\alpha]_D^{15} - 154^\circ$ (in water); the methiodide has $[\alpha]_D^{15} - 111^\circ$ (in water); acetyl- ϵ -methylmorphimethine methiodide has $[\alpha]_D^{15} - 45^\circ$ (in water). Attempts to obtain a sixth methylmorphimethine by treating the ϵ -isomeride with aqueous and alcoholic potassium hydroxide were unsuccessful. ϵ -Methylmorphimethine is decomposed by acetic anhydride at 180° , yielding acetylmethylmorphol and ethanoldimethylamine, whilst the methiodide when treated with alcoholic potassium hydroxide at 160° , yields morphenol and trimethylamine (compare Vongerichten, *Abstr.*, 1901, i, 742).

W. H. G.

Strychnine Alkaloids. VI. Preparation of Brucinesulphonic Acids and Cause of the Nitric Acid Reaction for Brucine. HERMANN LEUCHS and WALTER GEIGER (*Ber.*, 1909, 42, 3067—3075).—Brucine, when treated in the same manner as strychnine (this vol., i, 671), gives rise to three isomeric sulphonic acids. It is considered that the base contains the grouping $R'CHR''-CH_2R''$, and that the three acids are formed by the replacement of the three hydrogen atoms; two of the acids are therefore stereoisomeric. The sulphonic acids are feeble acids, their alkali salts being decomposed by carbon dioxide, and the basic character of the alkaloid is so completely destroyed that the compounds do not form salts with acids.

The product obtained by the action of manganese dioxide and sulphurous acid at $70-80^\circ$, and subsequent cooling with ice, is a mixture of sulphonic acids I. and II.; the filtrate from these, when kept for several weeks, yielded the acid III. The acids I. and II. can be separated by fractional solution in, and crystallisation from, hot water.

Brucinesulphonic acid I., $C_{23}H_{26}O_7N_2S$, crystallises from hot water, in which it is moderately soluble (1:12), in long, colourless crystals, which change colour at 280° , but are not molten at 300° . Its solution in sodium hydroxide has $[\alpha]_D^{20} - 242^\circ$. The *sulphonic acid* II. is less soluble in hot water (1:55), and crystallises in flat, rectangular plates; it turns brown at 200° , and has m. p. 260° (decomp.) and $[\alpha]_D^{20} + 29^\circ$ in sodium hydroxide solution. The *sulphonic acid* III. crystallises from hot water in pointed, broad prisms; it turns brown at 180° , and has m. p. 245° (decomp.) and $[\alpha]_D^{20} + 156.8^\circ$. It has the same solubility as acid II. in water.

The sulphonic acid I. reacts readily with dilute nitric acid, yielding short, bright red prisms of the *quinone*, $C_{21}H_{20}O_7N_2S, 3H_2O$, which is only sparingly soluble in the usual organic solvents, but which dissolves readily in alkalis. When reduced with sulphurous acid, it yields the *quinol*, $C_{21}H_{22}O_7N_2S, 3H_2O$, which crystallises from water in colourless needles. The quinone is undoubtedly formed from brucinesulphonic acid by the elimination of methyl from two $O\cdot CH_3$ groups and the oxidation to an orthoquinone, $OC \begin{array}{c} \diagup CO\cdot CR' \\ \diagdown CR''\cdot CR''' \end{array} N\cdot COR$.

A by-product formed during the preparation of the quinone is *didemethylnitrobrucine sulphonic acid hydrate* I.,

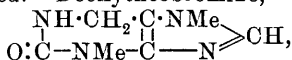


which crystallises from hot water in glistening, yellow needles. This compound is analogous to Moufang and Tafel's cacothelein (Abstr., 1899, i, 309).

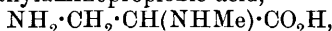
The unstable red compound obtained by the action of nitric acid on brucine is undoubtedly a quinone analogous to the quinonesulphonic acid described above.

J. J. S.

Diamino-acids from Deoxyxanthines. JULIUS TAFEL and EDWARD P. FRANKLAND (*Ber.*, 1909, 42, 3138—3146).—In their investigation on deoxycaffeine, Baillie and Tafel observed the production of barium carbonate and barium formate when the substance was boiled with barium hydroxide (Abstr., 1900, i, 121). Continuing the examination of this hydrolysis in the case of deoxycaffeine and of deoxytheobromine, the authors have now isolated the diamino-acids which are also produced. Deoxytheobromine,



yields β -amino- α -methylaminopropionic acid,



whilst from deoxycaffeine, $\begin{array}{c} \text{NMe}\cdot\text{CH}_2\cdot\text{C}\cdot\text{NMe} \\ | \quad | \\ \text{O}\cdot\text{C}-\text{NMe}-\text{C}-\text{N}\geq\text{CH}, \end{array}$ $\alpha\beta$ -dimethylaminopropionic acid, $\text{NHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{NHMe})\cdot\text{CO}_2\text{H}$, is obtained. The new acids resemble diaminopropionic acid, especially in the power of forming, with one equivalent of an acid, salts which are stable towards water and insoluble in alcohol.

Hydrolysis of Deoxytheobromine with Baryta.—The method of preparation previously given for deoxytheobromine may be simplified by directly neutralising with ammonia after the reduction. Yield 90%. The hydrolysis is effected by boiling with 10 parts of barium hydroxide in 50 parts of water for five hours. β -Amino- α -methylaminopropionic acid crystallises in well-developed prisms, m. p., on rapid heating, towards 160° (decomp.). The monohydrochloride forms flat, rhombic plates; it turns brown above 200° , m. p. $210\text{--}212^\circ$ (decomp.). The dihydrochloride, prepared by treating the acid with concentrated hydrochloric acid, forms crystals resembling saltpetre, m. p. $190\text{--}192^\circ$ (decomp.). When warmed with water, it yields the monohydrochloride. The sulphate, $\text{C}_4\text{H}_{10}\text{O}_2\text{N}_2\cdot\text{H}_2\text{SO}_4$, crystallises in well-formed tetrahedra, which soften at 165° , m. p. $185\text{--}188^\circ$ (decomp.). The nitrate, $\text{C}_4\text{H}_{10}\text{O}_2\text{N}_2\cdot\text{HNO}_3$, crystallises from water in prisms, m. p. about 185° (decomp.). The ethyl ester hydrochloride is prepared by boiling the hydrochloride of the acid with alcoholic hydrochloric acid for eighteen hours. The acid itself is only very slowly attacked under these conditions. Crystalline solid, m. p. about 176° (decomp.). The dibenzoyl derivative is an imperfectly crystalline powder, m. p. $202\text{--}204^\circ$. β -Amino- α -methylnitrosoaminopropionic acid is prepared by acting on the monohydrochloride of the acid with silver nitrite; it crystallises in small tetrahedra, which are anhydrous; it decomposes at $210\text{--}212^\circ$. The nitrosoamine gives Liebermann's reaction very

distinctly. On heating with dilute hydrochloric acid, the above-described dihydrochloride of α -methylamino- β -aminopropionic acid is produced.

Hydrolysis of Deoxycaffeine with Baryta.—The hydrolysis is best effected at a lower temperature (80°), and requires longer heating (fifty hours) than that of deoxytheobromine. Free $\alpha\beta$ -dimethylamino-propionic acid shows much less inclination to crystallise than the monomethylated acid. The monohydrochloride crystallises from water and methyl alcohol in stellar aggregates of prisms, and has m. p. about 180° (decomp.). It was not found possible to prepare from it a dihydrochloride. The ethyl ester hydrochloride is prepared by warming a concentrated aqueous solution of the monohydrochloride with alcoholic hydrochloric acid for a few minutes; on cooling, the substance separates out as a granular, crystalline precipitate. When heated it melts partly at 120 – 125° , solidifies again, and finally decomposes towards 180° . Mononitrosoamines of $\alpha\beta$ -dimethylaminopropionic acid were obtained by the action of silver nitrite as above. One crystallised in rectangular plates (from water) and had m. p. 270° (decomp.), and showed Liebermann's reaction. The other crystallised from water in needles, m. p. 186° . These are probably the two isomerides which would be expected. The dinitrosoamine was obtained as an acid syrup, which showed Liebermann's reaction.

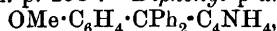
R. V. S.

New Preparation of 1-Alkylpyrrolidines. KARL LÖFFLER and CURT FREYTAG (*Ber.*, 1909, 42, 3427–3431).—A method which seems to be general for the preparation of 1-alkylpyrrolidines from aliphatic amines of the type of methylbutylamine or methylisoamylamine is the following. Methylbutylamine is shaken with a strongly cooled solution of sodium hypobromite. The resulting *N*-bromomethylbutylamine is added slowly to concentrated sulphuric acid, and the mixture is heated, at first for three hours on the water-bath and finally at 135° for thirty minutes. The base, liberated by sodium hydroxide and purified through the picrate, m. p. 221° , is proved to be 1-methylpyrrolidine.

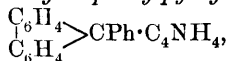
C. S.

Condensation of Aromatic Carbinols with Pyrrole. EUGEN KHOTINSKY and RAPHAEL PATZEWITCH (*Ber.*, 1909, 42, 3104–3106).—Tertiary carbinols of the type of triphenylcarbinol condense with pyrrole in the presence of acetic acid. Anthranol and primary and secondary alcohols do not condense with pyrrole.

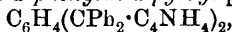
Triphenylpyrrylmethane, $\text{C}_6\text{H}_5\cdot\text{C}_4\text{NH}_4$, obtained by boiling a glacial acetic acid solution of triphenylcarbinol and pyrrole, is sparingly soluble in most solvents, but crystallises from ethylene bromide or nitrobenzene and has m. p. 253° . *Diphenyl-p-anisylpyrrylmethane*,



has m. p. 172 – 176° ; *diphenylenephenylpyrrylmethane*,



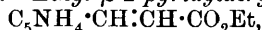
has m. p. 210° , and *tetra- ω -phenyldi- ω -pyrryl-p-xylene*,



obtained from tetraphenylxylene glycol and pyrrole, has no definite m. p. All condensation products give the pine wood reaction.

J. J. S.

2-γ-Hydroxypropylpiperidine and a New Synthesis of Piperolidine (δ-Coniceine). KARL LÖFFLER and MAX FLÜGEL (*Ber.*, 1909, 42, 3420—3427).—*Ethyl β-2-pyridylacrylate*,



b. p. 161°/25 mm., is obtained by the action of hydrogen chloride on a hot alcoholic solution of the hydrochloride of pyridylacrylic acid and subsequent treatment by potassium carbonate. It forms an *aurichloride*, $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}\cdot\text{HAuCl}_4$, m. p. 149°, and a *platinichloride*,



m. p. 114°. It is reduced by sodium and hot ethyl alcohol to 2-γ-hydroxypropylpiperidine, $\text{C}_5\text{NH}_{10}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, b. p. 248°, D_4^{15} 1·0043, which is best purified as the *hydrochloride*, $\text{C}_8\text{H}_{17}\text{ON}\cdot\text{HCl}$, m. p. 128°. The *mercurichloride*, $\text{C}_8\text{H}_{17}\text{ON}\cdot\text{HCl}\cdot 6\text{HgCl}_2$, has m. p. 182—183°. Piperolidine is obtained when 2-γ-hydroxypropylpiperidine is heated for six hours with fuming hydriodic acid and amorphous phosphorus in a sealed tube at 125°, and the isolated product is heated on the water-bath with an alkali for thirty minutes.

When 2-γ-hydroxypropylpiperidine is heated with phosphoric oxide at 135° for three hours, or with glacial acetic and concentrated sulphuric acids at 160—165° for three to four hours, a mixture of piperolidine and 2-allylpiperidine, containing chiefly the former, is obtained, which is separated by means of the picrates. The production of piperolidine in these two reactions illustrates the greater ease of formation of five- than of four-membered rings, since 2-β-hydroxypropylpiperidine does not yield 2-methylconidine under these conditions. Moreover, the 2-allylpiperidine, $\text{C}_5\text{NH}_{10}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$, b. p. 170—171°, D_4^{15} 0·8823 (*hydrochloride*, m. p. 202—203°; *aurichloride*, m. p. 101°; *platinichloride*, m. p. 174°), is not identical with either of the unsaturated bases obtained by dehydrating 2-β-hydroxypropylpiperidine (this vol., i, 180), thus furnishing another proof that these two bases are stereoisomerides and not structurally different (this vol., i, 324).

C. S.

A New Instance of Nitrogen Isomerism in the Piperidine Series. ALBERT LADENBURG and W. SOBECKI (*Ber.*, 1909, 42, 3152—3156).—The indications of the existence of isomeric forms which were met with in the case of coniine (Abstr., 1906, i, 692; 1907, i, 956) and of stilbazoline (Abstr., 1904, i, 92, 1048) have now again shown themselves in the case of benzyl-α-pipecoline. Active *d*-benzylpipecoline has a different rotatory power according to the mode of preparation employed. Pure *r*-pipecoline and benzyl chloride react with development of heat, forming *r*-benzylpipecoline, which has b. p. 160—162°/47 mm. or 267° (corr.) at atmospheric pressure. The resolution of the base was effected by means of the hydrogen tartrate. After nine recrystallisations of the hydrogen tartrate, the liberated base had $\alpha_D^{21} +48\cdot5^\circ$ when examined in a tube 49·65 mm. long. Optically active *d*-pipecoline was also benzylated in the same way, and

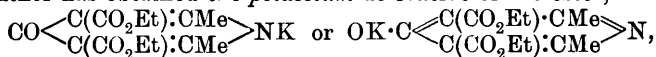
the active benzylpipercoline purified first by fractionation and then by recrystallisation of the hydrogen tartrate. After four recrystallisations, the liberated base had $\alpha_D^{21} + 50.1^\circ$ when examined in the above tube. The difference in rotatory power was not accompanied by any marked differences in other respects.

d-Benzylpipercoline from *r*-pipercoline has D^{21} 0.9527 and n_D 1.5187. The hydrogen tartrate has m. p. $67-69^\circ$. The aurichloride has m. p. $110-112^\circ$.

d-Benzylpipercoline from *d*-pipercoline has D^{21} 0.9525 and n_D 1.5182. The hydrogen tartrate has m. p. $67-69^\circ$, and the aurichloride has m. p. $112-114^\circ$. R. V. S.

The Relationship of Pyridine to the Sugars. CARL NEUBERG (*Biochem. Zeitsch.*, 1909, 20, 526-530).—Attention is called to the frequent conversion, especially in plants, of sugars into cyclic substances, and of cyclic substances into sugars. Pyridine can be converted into a carbohydrate-like substance from which furfuraldehyde can be obtained by distillation with sulphuric acid, from which distillate it was isolated in the form of its *p*-nitrophenylhydrazine derivative. The conversion of the pyridine into the carbohydrate-like substance was brought about by hydrogen peroxide in the presence of sulphuric acid and ferrous sulphate. The yield was very small. S. B. S.

Characteristics of Ethyl Lutidonedicarboxylate. TH. SABANÉEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 789-791).—By dissolving ethyl lutidonedicarboxylate in dilute potassium hydroxide solution and precipitating with excess of concentrated potassium hydroxide solution, the author has obtained the *potassium* derivative of the ester,



which is not methylated by the ordinary methods, and gives an almost quantitative yield of lutidonedicarboxylic acid when heated with ethyl iodide and ethyl alcohol in a sealed tube at 150° . This hydrolysing action of a mixture of ethyl iodide and ethyl alcohol is also shown with ethyl diphenylpyridonedicarboxylate, which is converted into the corresponding acid. Under similar conditions, ethyl dimethylpyrone-dicarboxylate gives a good yield of dimethylpyrone. T. H. P.

Constitution of Anthranil. VI. GUSTAV HELLER (*J. pr. Chem.*, 1909, [ii], 80, 320-331).—In connexion with the non-production of anthranil from anthroxanic acid (*Abstr.*, 1908, i, 267), Bamberger's criticism (this vol., i, 509) and comparison of anthroxanic acid with isooxazolecarboxylic acids are not justifiable, since the stabilities of monocyclic and dicyclic molecules are not strictly comparable. Bamberger and Elger's experiment, the heating of anthroxanic acid and water at 150° , has been repeated, with utterly different results. The product is not anthranil, as they claim, but aniline. Its production is explained by the elimination of carbon dioxide from the anthroxanic acid with the formation of anthroxan, which absorbs water, yielding anthranilic acid, from which the aniline is produced by loss of

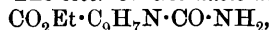
carbon dioxide. Anthranil and water at 153—156° do not yield aniline (this fact is additional evidence of the different constitutions of anthranil and anthroxan), but a yellow, crystalline condensation product, m. p. 245°.

Bamberger and Lublin's experiment with methylantranil (methyl-anthroxan), 23% hydrochloric acid, and sodium nitrite (*loc. cit.*) has been repeated; methylantranil dichloride (methylanthroxan dichloride) and a diazo-salt are produced, but not *o*-acetylphenylnitrosohydroxylamine. The paper concludes with a short discussion of the constitution of anthranil and the possibility of tautomerism. C. S.

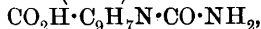
1-Methylindole-2:3-dicarboxylic Acid and 2-Amino-1-methylindole-3-carboxylic Acid. GEORG REIF (*Ber.*, 1909, 42, 3036—3045).—According to Piccinini and Salmonini (*Abstr.*, 1902, i, 491), it is not possible to transform indolecarboxylic acid into aminoindole by the Hofmann-Curtius reaction. It is now shown that an aminocarboxylic acid can be obtained by this reaction from 1-indole-2:3-dicarboxylic acid.

Ethyl 1-methylindole-2:3-dicarboxylate, $C_6H_4 \begin{smallmatrix} \text{C}(\text{CO}_2\text{H}) \\ \text{NMe} \end{smallmatrix} > \text{C} \cdot \text{CO}_2\text{H}$,

is readily obtained by Fischer's method (*Abstr.*, 1886, 805) from the phenylmethylhydrazone of ethyl oxalacetate, and can be purified by distillation in steam. It forms a reddish-brown oil, and has an obnoxious odour. When hydrolysed with 20% alcoholic potassium hydroxide, a precipitate of *potassium ethyl methylindoledicarboxylate*, $\text{CO}_2\text{K} \cdot \text{C}_9\text{H}_7\text{N} \cdot \text{CO}_2\text{Et}$, is formed. The acid ester, $\text{CO}_2\text{H} \cdot \text{C}_9\text{H}_7\text{N} \cdot \text{CO}_2\text{Et}$, crystallises from dilute alcohol in brilliant needles, has m. p. 158° (corr.) when heated quickly, and does not give the pine-wood reaction. The *dicarboxylic acid*, $\text{C}_9\text{H}_7\text{N}(\text{CO}_2\text{H})_2$, obtained by hydrolysing the monopotassium salt with aqueous potassium hydroxide, crystallises from dilute alcohol in large prisms, and when heated quickly has m. p. 218° (corr.); at the same time carbon dioxide is evolved and 1-methylindole formed. The *acid chloride*, $\text{C}_9\text{H}_7\text{N}(\text{COCl})_2$, prepared by shaking the acid with light petroleum and phosphorus pentachloride, crystallises from benzene in small needles; it turns yellow at 82°, melts at a higher temperature, and is readily decomposed by water. The *amide*, $\text{C}_9\text{H}_7\text{N}(\text{CO} \cdot \text{NH}_2)_2$, crystallises from hot water in slender needles with a silky lustre. When rapidly heated, it sinters at 259° and melts at 267° (decomp., corr.). The *ester of the amic acid*,



crystallises from benzene or light petroleum in long needles, m. p. 201° (decomp., corr.). The *anhydride*, $\text{C}_9\text{H}_7\text{N} \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{O}$, obtained by the action of acetyl chloride or acetic anhydride on the acid, crystallises from ethyl acetate in large, glistening, rhombohedral prisms, sintering at 209° and melting at 212° (corr.). The *amic acid*,



obtained in the form of its *ammonium* salt by the action of ammonia on a benzene solution of the anhydride, crystallises in small prisms, m. p. 204° (decomp., corr.), and when its solution in sodium hydroxide is treated with sodium hypochlorite (Graëbe, *Abstr.*, 1902, i, 663), it

yields an *acid product*, $C_9H_7\begin{matrix} \diagup N=C\cdot OH \\ \diagdown CO\cdot O \end{matrix}$, which crystallises from dilute acetone in slender, glistening needles, m. p. 260° (decomp.). This product, analogous to isatoic anhydride (Mohr, this vol., i, 420), dissolves readily in alkalis and ammonia, and when boiled with 5% sodium hydroxide solution yields 2-(or 3)*amino-1-methylindole-3-(or 2)-carboxylic acid*, $NH_2\cdot C_9H_7N\cdot CO_2H$, which crystallises from acetone in long needles, m. p. $65-69^\circ$ (decomp., corr.), and is extremely unstable, rapidly changing colour in contact with the air. It gives a bluish-brown coloration with an aqueous bleaching powder solution, and its alcoholic solution gives a blue coloration with a few drops of ferric chloride. With *p*-dimethylaminobenzaldehyde, it gives a reddish-coloured additive compound analogous to the product obtained by Pawleski (Abstr., 1908, i, 638) from anthranilic acid. J. J. S.

The Red Urinary Pigment Derived from Indole. II. ALBERICO BENEDICENTI (*Zeitsch. physiol. Chem.*, 1909, 62, 390-398. Compare Abstr., 1908, ii, 1057).—It is shown that methylketole (2-methylindole), when administered to animals, does not pass in an unaltered condition into the urine, but is transformed into a chromogen, which yields a red pigment when oxidised with hydrochloric acid and calcium hypochlorite. The same chromogen appears to be formed when 2-methylindole is brought into contact with urine *in vitro*, and numerous other *C*-alkylated indoles behave in the same manner as 2-methylindole.

The pigment obtained by oxidising 2-methylindole with hydrochloric acid and hypochlorite has been investigated. The formation of the red compound is preceded by the production of a green coloration, which changes rapidly into the red compound unless the temperature is kept low. Most oxidising agents form the green compound as an intermediate substance, but ferric chloride appears to produce the red pigment directly.

The crude red compound is washed and dried, then extracted with hot benzene to remove methylindole, and finally dissolved in acetic acid and precipitated with water. The last traces of chlorine can only be removed by solution in alcohol and treatment with small amounts of sodium. The analyses of the purified product agree with the formula $C_{12}H_{13}ON$, and in many respects it resembles Niggeler's Indigo-red. It is not an oxidation product of indoxyl, and has phenolic properties. A *dinitro*-derivative, $C_{12}H_{11}(NO_2)_2ON$, has been obtained as a yellow, amorphous powder.

It is probable that the red compound is identical with the red pigment of urine. J. J. S.

Acetylchloroacetyltetrahydroquinoline. FRANZ KUNCKELL and ERNST VOLLHASE (*Ber.*, 1909, 42, 3196-3199).—The work of one of the authors on the preparation of amino-ketones by means of the Friedel and Crafts reaction between chloroacetyl chloride and acylamines (Abstr., 1900, i, 664; 1901, i, 213) is now extended to tetrahydroquinoline and diphenylamine. The amines themselves do

not enter into the reaction, but their acetyl derivatives do so readily. Diphenylamine will form the subject of a further communication.

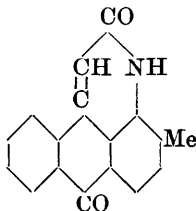
Acetylchloroacetyltetrahydroquinoline, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{C}_9\text{H}_9\text{OAc}$, is obtained in a 60% yield, and forms white needles, which have m. p. 137° . *Acetylbromoacetyltetrahydroquinoline*, from bromoacetyl bromide and acetyltetrahydroquinoline, forms white, silky needles, m. p. 134° . To remove the acetyl group, the acetylchloroacetyltetrahydroquinoline was heated with 20% hydrochloric acid on the water-bath until dissolved; on neutralising with ammonium carbonate, *chloroacetyltetrahydroquinoline* was precipitated. It crystallises in yellow leaflets, which have m. p. $123\text{--}124^\circ$. A *hydrochloride* or *hydrobromide* of the compound could not be prepared. Oxidation of acetylchloroacetyltetrahydroquinoline with hydrogen peroxide yielded an *acetyltetrahydroquinolinecarboxylic acid*, which crystallises in small, yellowish-white needles, m. p. 187° .

Acetylchloroacetyl-6-methyltetrahydroquinoline crystallises in white needles, m. p. 132° . *Acetylbromoacetyl-6-methyltetrahydroquinoline* also forms white needles, m. p. 128° . R. V. S.

Action of Benzoyl Chloride on Hydroxyquinolines.

ALEXANDER ELLINGER and OTTO RIESER (*Ber.*, 1909, 43, 3336—3339).—When kynurine (4-hydroxyquinoline) or 2-hydroxy-4-methylquinoline (compare Knorr and Klotz, *Abstr.*, 1887, 278) is boiled for several hours with excess of benzoyl chloride, no benzoyl derivative is obtained, the reaction which occurs consisting in the substitution of the hydroxyl group by chlorine. Thus, ψ -hydroxyquinoline yields ψ -chloroquinoline, the platinichloride of which has m. p. $280\text{--}281^\circ$ (Skraup, *Abstr.*, 1890, 174, gave m. p. $278\text{--}279^\circ$). Similarly, 2-hydroxy-4-methylquinoline gives 2-chloro-4-methylquinoline, the platinichloride of which has m. p. 55° (Knorr, *loc. cit.*, gave 59°); in this case, the yield is small, owing more to the presence of the methyl group than to the 2-position of the hydroxyl, since, under similar conditions, 4-hydroxy-2-methylquinoline gives only traces of a volatile base. T. H. P.

[Preparation of 2-Methylantrapyridone.]

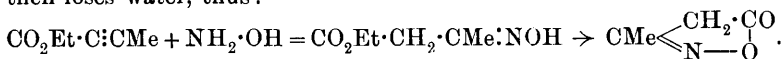


BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 212204).—2-Methylantrapyridone (annexed formula) (yellow crystals from acetic acid) is prepared by heating together 1-acetylamino-2-methylantraquinone and acetic anhydride for half an hour at 210° . The halogenated aminoanthraquinones can also be employed for this condensation. The products are crystalline, soluble in the ordinary high boiling organic solvents, and the solutions show greenish-yellow fluorescence. F. M. G. M.

Addition of Hydroxylamine to Acetylene Derivatives.

E. OLIVERI-MANDALÀ (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 141—144. Compare Claisen, *Abstr.*, 1904, i, 14; Ruhemann and Cunningham, *Trans.*, 1899, 778, 954).—The action of hydroxylamine on ethyl

tetrolate in alcoholic solution rendered slightly alkaline with sodium hydroxide yields, as the sole separable product, the methylisooxazolone obtained by Hantzsch (Abstr., 1891, 739) by the action of an alkaline solution of hydroxylamine on ethyl acetoacetate. The first stage in the reaction consists in the addition of the hydroxylamine to the tetrolic ester with formation of ethyl oximinoacetoacetate, which then loses water, thus:



It is worthy of note that hydroxylamine is added to two carbon atoms united by a triple linking in the same manner as to a carbon atom and a nitrogen atom joined by a triple linking. T. H. P.

New Series of Leuco-bases and of Colouring Matters Derived from Diphenylethylene. PAUL LEMOULT (*Compt. rend.*, 1909, 149, 606—608).—The alkyl derivatives of diphenylethylene described by Busignies (this vol., i, 736) are leuco-bases of the same type as the corresponding derivatives of diphenylmethane. In solutions acidified with acetic acid, they rapidly absorb oxygen from the air and develop distinctive colorations. By adding an alkali nitrite to an acidified solution of the base, intense colorations are obtained varying from green in the case of tetramethyl- and tetraethyl-diaminodiphenylethylene to blue in the case of the corresponding propylene derivatives. The dialkylmonoamino-bases give orange-yellow solutions under these conditions. When dyed on cotton mordanted with tannin, the shades produced resemble those obtained with derivatives of di- or tri-phenylmethane.

The author considers the development of the colouring matter to be due, not to decomposition of the bases, but to their specific constitution. W. O. W.

Hydrazine Derivatives of Triphenylmethane. Constitution of Triphenylmethyl. HEINRICH WIELAND (*Ber.*, 1909, 42, 3020—3030).—In spite of the use of all manner of oxidising agents it was not found possible to convert hydrazotriphenylmethane into azotriphenylmethane, $\text{CPh}_3\cdot\text{N}:\text{N}\cdot\text{CPh}_3$. It appears that azotriphenylmethane, even at 0° , spontaneously dissociates into nitrogen and triphenylmethyl. The latter was isolated as triphenylmethyl peroxide with a yield of 60%, or as the perhaloids of ω -bromo- or ω -iodotriphenylmethane when bromine or iodine were used as oxidising agents.

Hydrazotriphenylmethane, $\text{CPh}_3\cdot\text{NH}\cdot\text{NH}\cdot\text{CPh}_3$, prepared by the action of hydrazine hydrate on ω -chlorotriphenylmethane, forms long, colourless, glistening, rectangular plates, m. p. 209° (partial decomp.). It dissolves in sulphuric acid with an orange-yellow coloration. It is readily reduced, but remarkably stable towards atmospheric oxygen or mild oxidising agents; more powerful oxidising agents convert it into triphenylmethyl.

Triphenylmethylhydrazine, $\text{CPh}_3\cdot\text{NH}\cdot\text{NH}_2$, is formed at the same time as the hydrazo-compound; the *hydrochloride* crystallises in colourless, rhombic plates, m. p. 133° . The free base crystallises only with difficulty in needles, m. p. 108 — 112° (decomp.), and readily decomposes

when boiled in solvents; the *acetate* separates in stellar aggregates of colourless needles, m. p. 197° (decomp.).

By the reduction of triphenylmethylhydrazine with sodium nitrite, *triphenylmethylazoimide*, $\text{CPh}_3 \cdot \text{N} \begin{smallmatrix} \diagup \text{N} \\ \diagdown \text{N} \end{smallmatrix}$, is formed. This crystallises very well in large, colourless, dice-like rhombohedra, m. p. 64°, decomp. 180°. This azoimide is very stable; it dissolves in concentrated sulphuric acid with a golden-yellow colour, and is not affected by boiling with water.

Schmidlin (Abstr., 1908, i, 150) has shown that triphenylmethyl exists in a colourless and a coloured form. In solution the colourless form in part passes over into the yellow isomeride; equilibrium exists between the two forms, the proportion of each being dependent on the temperature and the nature of the solvent. It is claimed that the yellow isomeride possesses the true triphenylmethyl structure. Gomberg's molecular-weight determinations indicated the double molecular weight, but applied to solutions in which not more than about 5% of the yellow isomeride can have been present. In naphthalene, however, where the amount of the yellow unimolecular form is much larger, a much lower molecular weight was found.

E. F. A.

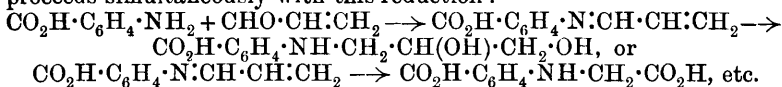
Mobility of the Amino-group. GALEAZZO PICCININI (*Ber.*, 1909, 42, 3219—3233).—In a former paper (Abstr., 1908, i, 908) the author has described two amino-bases, 3-amino-2-keto-4:6:6-trimethyltetrahydropyridine and 3-amino-2-keto-1:4:6:6-tetramethyltetrahydropyridine, which, when acted on with water at the ordinary temperature, exchange the group $-\text{NH}_2$ for $-\text{OH}$. A similar looseness of the carbon-nitrogen linking can be observed in most compounds of the type $\text{R} \cdot \text{C}(\text{NH}_2) \cdot \text{E}$, where E may be any negative element of valency greater than one. In order to compare the mobility of the amino-group in different compounds, it is necessary to follow carefully the hydrolysis in the different cases to obtain a measure of the influence of substituents, etc. To this end the reaction has been followed by physical-chemical methods in the case of the above compounds.

The method adopted was to enclose known quantities of the base and water in sealed tubes in a thermostat at 25°. At intervals a tube was removed and the amount of ammonia which had been formed was estimated. In aqueous solution at 25° the conversion of amine into hydroxy-compound reached an equilibrium when the ammonia formed was not removed. The reversibility of the reaction was further shown by the preparation of one of the bases, 3-amino-2-keto-4:6:6-trimethyltetrahydropyridine, from the corresponding hydroxy-compound by the action of aqueous or alcoholic ammonia. Alkali hydroxides do not affect the course of the reaction. In acid solution (hydrochloric acid) the reaction is greatly accelerated; the hydrochlorides decompose completely, even in dilute solution, according to the formula for unimolecular reactions which proceed completely. The constant of the reaction is greatest when the concentration is 1—2 gram-molecules of hydrochloride per litre.

When the amount of acid in the solution is increased above the equivalent quantity, the value of the reaction constant decreases, whatever the concentration of the hydrochloride in the solution. The reaction constant is increased by rise of temperature: K at $50^\circ/K$ at $25^\circ = 10$; K at $100^\circ/K$ at $25^\circ = 100$. The *N*-methylated base is the more quickly hydrolysed. The author considers that the observed influence of change of concentration, alkali, acid, etc., on the progress of the reaction receives a satisfactory explanation if it is supposed that the hydrolysis is a hydrolysis of the ion of the base, and not of the undissociated molecules themselves. In this connexion, experiments in other solvents are to be undertaken. A similar study of the nitroanilines and of picramide is also in progress. R. V. S.

Mechanism of the Formation of Indigotin from Anthranilic Acid and Polyhydroxy-compounds. New Synthesis of Indigotin. IWAN VON OSTROMISLENSKY and A. PAMFILOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 784—789).—The mechanism of the formation of indigotin by heating anthranilic acid with potassium hydroxide in presence of glycerol may be explained by the following scheme: $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} + \text{C}_3\text{H}_5(\text{OH})_3 \rightarrow$
 $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH} \rightarrow$
 $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H} \rightarrow$
 $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH} \rightarrow$
 $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \rightarrow \text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{NH} \\ \text{CO} \end{smallmatrix} \right\rangle \text{CH}_2 \rightarrow \text{indigotin}.$

When acraldehyde is employed in place of glycerol, the reduction of the group $\cdot\text{N}:\text{CH}\cdot$ to $\cdot\text{NH}\cdot\text{CH}_2\cdot$ is effected by the hydrogen always formed in oxidation processes brought about by potassium hydroxide, owing to the dissociation of water, this hydrogen, in a nascent state, acting on the initial products of the process; oxidation of $\cdot\text{CH}:\text{CH}_2$ proceeds simultaneously with this reduction:

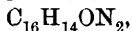


According to the above views, it should be possible to prepare indigotin from *o*-aminobenzyl alcohol, the group $\text{CH}_2\cdot\text{OH}$ undergoing oxidation to CO_2H ; this the authors find to be the case. A mixture of *o*-aminobenzyl alcohol, potassium hydroxide, and glycerol, heated in an atmosphere of nitrogen to $280\text{--}300^\circ$, yields indigotin, the amount of which is increased on passing air through the mixture; the yield is appreciably greater than that obtained under the same conditions from anthranilic acid, and, as the indigotin begins to form in about two minutes, the reaction may serve as a lecture experiment. As *o*-aminobenzyl alcohol has b. p. $270\text{--}280^\circ$, the yield of indigotin would doubtless be increased if the heating were carried out in a reflux apparatus, or, better still, an autoclave.

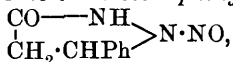
T. H. P.

Formation of Nitrosopyrazolidones and Pyrazolones from Hydrazides of Unsaturated Acids. ERNST MUCKERMANN (*Ber.*, 1909, 42, 3449—3460).—*Cinnamoyl hydrazide*,
 $\text{CHPh}:\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$,

m. p. 101°, is obtained by the prolonged heating of ethyl cinnamate, alcohol, and hydrazine hydrate. With alcoholic hydrogen chloride at 0°, it forms a *hydrochloride*, $C_9H_{10}ON_2 \cdot HCl$, m. p. 201° (decomp.), whilst with benzaldehyde it yields the *benzylidine* derivative,



m. p. 180°. An aqueous solution of the hydrochloride at 0° is converted by sodium nitrite into 1-nitroso-5-phenyl-3-pyrazolidone,



m. p. 127—128° (decomp.), which responds to Liebermann's reaction, is very soluble in alkalis, yields heavy precipitates with many metallic salts, is converted by bromination in acetic acid into Rothenburg's 4:4-dibromo-3-phenyl-5-pyrazolone (m. p. 198°, not 189°), yields cinnamic acid by treatment with boiling concentrated hydrochloric acid, and Rothenburg's 4-oximino-3-phenyl-5-pyrazolone with boiling dilute sulphuric acid.

Crotonyl hydrazide, $\text{CHMe} \cdot \text{CH} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$, is a syrup which is obtained in a similar way, and yields a similar series of derivatives. The *hydrochloride* has m. p. 173° (decomp.), and the *benzylidine* compound, m. p. 72°. 1-Nitroso-5-methyl-3-pyrazolidone, m. p. 131° (decomp.), closely resembles the corresponding phenyl derivative in its preparation and properties. C. S.

Bromination of Diphenylglyoxalone. HEINRICH BILTZ (*Annalen*, 1909, 368, 262—270. Compare Abstr., 1908, i, 573, 575).—A solution of 4:5-diphenylglyoxalone in concentrated sulphuric acid, when treated with bromine and kept in a desiccator, deposits 4:5-di-p-bromophenylglyoxalone disulphate, $C_{15}H_{10}ON_2Br_2 \cdot 2H_2SO_4$, as colourless, hexagonal prisms, m. p. 70—80°, which, when boiled with water, yields 4:5-di-p-bromophenylglyoxalone. By using certain proportions of the reagents and pouring the solution on to ice, it is possible to obtain good yields of 4:5-dihydroxy-4:5-diphenyldihydroglyoxalone (*loc. cit.*), which forms slender, flexible needles, m. p. 250° (decomp.). W. H. G.

Pyrimidines. XLVI. Dimethyl Derivatives of 2-Aminopyrimidine. Preparation of 2-Methylamino-5-methylpyrimidine. TREAT B. JOHNSON and KENNETH G. MACKENZIE (*Amer. Chem. J.*, 1909, 42, 353—370).—Suzuki, Aso, and Mitarai (*Bull. Coll. Agric. Tōkyō*, 1907, 7, 477), in an investigation of the constituents of soja source, have described two products of the composition $C_6H_9N_3$ and $C_4H_{12}N_2$, and have stated that the former compound is probably an amino-dimethylpyrimidine.

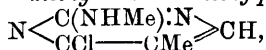
The present authors are making a study of the pyrimidines of the formula $C_6H_9N_3$, and have now described 2-methylamino-5-methylpyrimidine and some derivatives of 2-methylamino-4-methylpyrimidine. It has been pointed out by Johnson (Abstr., 1907, i, 879) that when 2-methylthiol-5-methyl-6-pyrimidone-4-carboxylic acid, obtained by the condensation of ψ -methylthiocarbamide with the sodium derivative of ethyl oxalylpropionate, is heated above its m. p., it is converted into 2-methylthiol-5-methyl-6-pyrimidone. It is now shown that this

compound, on hydrolysis, gives a quantitative yield of thymine, and the investigation has been extended.

2-Methylamino-5-methyl-6-pyrimidone, $\text{NH} \begin{smallmatrix} \text{C}(\text{NHMe})\text{:N} \\ \text{CO} \text{---} \text{CMe} \end{smallmatrix} \text{CH}$, m. p.

213°, obtained by the action of methylamine on 2-methylthiol-5-methyl-6-pyrimidone, forms colourless crystals containing $1\text{H}_2\text{O}$, and gives a claret-red colour with diazobenzenesulphonic acid in presence of sodium hydroxide. The *sulphate* melts at 202°, and the *picrate* at 240° (decomp.); the *platinichloride* was also prepared.

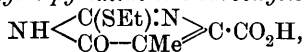
When 2-methylamino-5-methyl-6-pyrimidone is heated with phosphoryl chloride, 6-chloro-2-methylamino-5-methylpyrimidine,



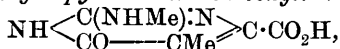
m. p. 131°, is produced, which forms prismatic crystals, sublimes at 100°, and when treated with zinc dust is converted into 2-methylamino-5-methylpyrimidine, $\text{N} \begin{smallmatrix} \text{C}(\text{NHMe})\text{:N} \\ \text{CH} \text{---} \text{CMe} \end{smallmatrix} \text{CH}$, m. p. 102°, which crystallises in prisms, and is not identical with the base obtained by Suzuki, Aso, and Mitarai (*loc. cit.*). 2-Methylamino-5-methylpyrimidine does not give an immediate coloration on addition of diazobenzenesulphonic acid, but, after a time, a deep red colour is developed; its *picrate* does not melt, but decomposes above 150°; the *hydrochloride*, m. p. 162—163°, crystallises in prisms.

2-Methylamino-4-methyl-6-pyrimidone (Jaeger, Abstr., 1891, 1007), m. p. 201—202°, has been prepared by heating 2-methylthiol-4-methyl-6-pyrimidone with excess of methylamine at 140—150°. When this compound is heated with phosphoryl chloride, 6-chloro-2-methylamino-4-methylpyrimidine, $\text{N} \begin{smallmatrix} \text{C}(\text{NHMe})\text{:N} \\ \text{CCl} \text{---} \text{CH} \end{smallmatrix} \text{CMe}$, m. p. 135°, is produced, which forms colourless needles, and slowly sublimes above 100°. If this chloropyrimidine is treated with zinc dust, a double compound of 2-methylamino-4-methylpyrimidine and zinc chloride, $2\text{C}_6\text{H}_9\text{N}_3 \cdot \text{ZnCl}_2$, m. p. 170—172°, is produced, which forms red crystals. The presence of 2-methylamino-4-methylpyrimidine in the reaction product was established by means of the *picrate*, m. p. 150—155°, which forms irregular prisms.

2-Ethylthiol-5-methyl-6-pyrimidone-4-carboxylic acid,



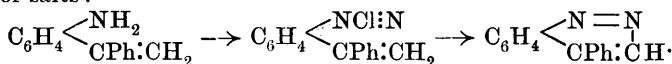
m. p. 220°, obtained by the condensation of ψ -ethylthiocarbamide with the sodium derivative of ethyl methylloxalacetate, forms needles or prisms; the *ethyl ester*, m. p. 172—173°, crystallises in prisms. If 2-ethylthiol-5-methyl-6-pyrimidone-4-carboxylic acid is heated at 220—230°, it undergoes decomposition with formation of 2-ethylthiol-5-methyl-6-pyrimidone (Wheeler and Johnson, Abstr., 1904, i, 624), which, when heated with concentrated hydrochloric acid for several hours, is converted into thymine. By the action of methylamine on 2-ethylthiol-5-methyl-6-pyrimidone-4-carboxylic acid at 140—150°, 2-methylamino-5-methyl-6-pyrimidone-4-carboxylic acid,



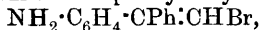
m. p. 270—280° (decomp.), is produced, which forms long, slender crystals. The *hydrochloride* crystallises in prisms and decomposes at 276—283°; the *methylamine* salt forms granular crystals, and decomposes at 274°.

E. G.

New Synthesis of Cinnoline Derivatives. RICHARD STOERMER and H. FINCKE (*Ber.*, 1909, 42, 3115—3132. Compare von Richter, *Abstr.*, 1883, 1105; Busch and Klett, *ibid.*, 1892, 1494; Busch and Rast, 1897, i, 300).—When attempts are made to replace by hydroxyl the amino-groups in certain *o*-amino-*as*-diphenylethylene derivatives, almost quantitative yields of cinnoline derivatives are obtained in the form of salts:

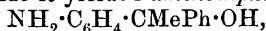


When α -bromo- β -*o*-amino-*as*-diphenylethylene,

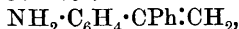


is used, phenylcinnoline and not a bromo-derivative is formed. *o*-Aminodiphenylmethylcarbinol, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPhMe} \cdot \text{OH}$, does not yield a cinnoline derivative.

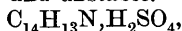
o-Aminobenzophenone is best prepared by a modification of Ullmann and Bleier's method (*Abstr.*, 1903, i, 176). When condensed with magnesium methyl iodide it yields *o*-aminodiphenylmethylcarbinol,



which crystallises from a mixture of benzene and light petroleum in colourless prisms, m. p. 84—85°. *o*-Amino-*as*-diphenylethylene,



obtained by boiling the carbinol for one hour with 35% sulphuric acid, forms colourless crystals, m. p. 76—77.5°. The *hydrochloride* is sparingly soluble; the *platinichloride* melts and decomposes at 195°, and the *aurichloride* is oily and unstable. The *sulphate*,

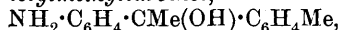


forms sparingly soluble, pale yellow, crystalline plates, m. p. 166—168°; the *picrate*, $\text{C}_{20}\text{H}_{16}\text{O}_7\text{N}_4$, forms brilliant, yellow crystals, m. p. 149°, and the *acetyl* derivative, which can be obtained either from the olefine directly or by heating the carbinol for some time with sodium acetate and acetic anhydride, separates from alcohol in colourless crystals, m. p. 122°. *o*-Acetylaminodiphenylmethylcarbinyl acetate, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CMePh} \cdot \text{OAc}$, forms colourless crystals, m. p. 160—162°. α -Bromo- β -*o*-acetylaminodiphenylethylene, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh} \cdot \text{CHBr}$, obtained by the action of an acetic acid solution of bromine on acetylaminodiphenylethylene, separates from alcohol in colourless crystals, m. p. 146°, and when hydrolysed with fuming hydrochloric acid yields α -bromo- β -*o*-aminodiphenylethylene, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh} \cdot \text{CHBr}$, as colourless crystals, m. p. 87—88°; its *platinichloride*,



has m. p. 209° (decomp.).

o-Aminophenyl-*p*-tolylmethylcarbinol,



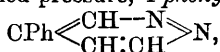
forms colourless crystals, m. p. 92—93°, and *o*-aminophenyl-*p*-tolylethylene, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4\text{Me}) \cdot \text{CH}_2$, is an oil, b. p. 224—226°/50 mm. The *sulphate*, $2\text{C}_{15}\text{H}_{15}\text{N}_2, \text{H}_2\text{SO}_4$, forms colourless plates, m. p.

141—142°. *o*-Aminodiphenylethylcarbinol, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{Et})\text{Ph} \cdot \text{OH}$, obtained from *o*-aminobenzophenone and magnesium ethyl iodide, crystallises from alcohol in colourless plates, m. p. 101—102°, and when boiled with 30% sulphuric acid yields *o*-aminodiphenylpropylene, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh} : \text{CHMe}$, which separates from light petroleum as colourless crystals, m. p. 50—52°. The *hydrochloride*, $\text{C}_{15}\text{H}_{15}\text{N} \cdot \text{HCl}$, formed colourless plates, m. p. 205—208°; the *platinichloride* forms yellow crystals, m. p. 191° (decomp.), and the *aurichloride*, a red, crystalline powder, m. p. 125° (decomp.).

4-Phenylcinnoline, $\text{C}_6\text{H}_4 \cdot \begin{smallmatrix} \text{N}=\text{N} \\ \diagup \quad \diagdown \\ \text{CPh} : \text{CH} \end{smallmatrix}$, is obtained as its hydrochloride

when a solution of *o*-aminodiphenylethylene in hydrochloric acid is diazotised at the ordinary temperature. The base, liberated by the action of ammonia on the salt, crystallises from light petroleum in sulphur-yellow, glistening prisms, m. p. 67—67·5°. The *hydrochloride*, $\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{HCl} \cdot \text{H}_2\text{O}$, forms yellow crystals, m. p. 130° (decomp.), and the *hydrobromide*, pale yellow, glistening crystals, m. p. 202—204°. The *basic hydriodide*, $2\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{HI}$, forms dark orange-coloured needles, m. p. 93—95°; its solutions in water, alcohol, and ether have a pale yellow colour, whereas those in chloroform have a reddish-brown colour. The *normal hydriodide*, $\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{HI}$, forms well-developed, red crystals, which decompose at 150°. The *sulphate*, $\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{H}_2\text{SO}_4$, forms golden-yellow crystals, m. p. 181—182°; the *nitrate*, pale yellow needles, m. p. 156—157°; the *picrate*, $\text{C}_{20}\text{H}_{13}\text{O}_7\text{N}_5$, deep golden-yellow, felted needles from benzene, m. p. 156—158° after sintering at 147—148°, and the *platinichloride*, $2\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$, pale brown crystals which are not molten at 300°. The *normal aurichloride*, $\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{HAuCl}_4$, forms a sparingly soluble, pale yellow powder sintering at 158°; a second *aurichloride*, $2\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{H}_2\text{AuCl}_5$, forms golden-yellow, glistening crystals, m. p. 145—147°. The *argentinitrate*, $\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{AgNO}_3$, crystallises from alcohol in slender, yellow plates, m. p. 260° (decomp.); the *methiodide*, $\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{MeI}$, crystallises from methyl alcohol in brilliant, red, glistening needles, which decompose at 220°, and the *methochloride*, in pale yellow plates, which begin to decompose at 70°.

When oxidised with hot permanganate solution, the phenylcinnoline yields 4-phenylpyridazine-5 : 6-dicarboxylic acid (4-phenylcinnolinic acid), $\text{CO}_2\text{H} \cdot \text{C} \begin{smallmatrix} \text{C}(\text{CO}_2\text{H}) \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{CPh} : \text{CH} \end{smallmatrix} \text{N}$, which crystallises from dilute nitric acid in colourless needles containing $1\text{H}_2\text{O}$, and m. p. 220—221° (decomp.). It forms a *normal silver salt*, $\text{C}_{12}\text{H}_6\text{O}_4\text{N}_2\text{Ag}_2 \cdot \text{H}_2\text{O}$, an *acid silver salt*, $3\text{C}_{12}\text{H}_6\text{O}_4\text{N}_2\text{Ag}_2 \cdot \text{C}_{12}\text{H}_8\text{O}_4\text{N}_2$, and a *barium salt*, $\text{C}_{12}\text{H}_6\text{O}_4\text{N}_2\text{Ba}$. When heated during four hours at 125°, the dibasic acid yields 4-phenylpyridazine-5-carboxylic acid, $\text{CO}_2\text{H} \cdot \text{C} \begin{smallmatrix} \text{CH} - \text{N} \\ \diagup \quad \diagdown \\ \text{CPh} : \text{CH} \end{smallmatrix} \text{N}$, which crystallises from alcohol and melts at 220—221° (decomp.). When either of the acids is distilled under diminished pressure, 4-phenylpyridazine,



is obtained; it separates from light petroleum in colourless crystals, m. p. 86—86·5°.

The *platinichloride*, $2\text{C}_{10}\text{H}_8\text{N}_2\cdot\text{H}_2\text{PtCl}_6\cdot\text{H}_2\text{O}$, forms a yellow, flesh-coloured precipitate, m. p. $295-300^\circ$ (decomp.).

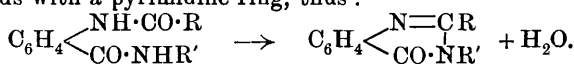
4-*p-Tolylcinnoline*, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{N}=\text{N} \\ \text{C}(\text{C}_7\text{H}_7):\text{CH} \end{smallmatrix}$, obtained from *o*-aminophenyl-*p*-tolylethylene, crystallises from light petroleum in yellow prisms, m. p. $58-59^\circ$. The *nitrate* and *hydrochloride* are sparingly soluble, but the *sulphate* is readily soluble in water.

4-*Phenyl-3-methylcinnoline*, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{N}=\text{N} \\ \text{CPh}:\text{CMe} \end{smallmatrix}$, forms pale, yellowish-brown crystals, m. p. $135-136^\circ$. Its salts are rather more soluble than those of phenylcinnoline. The *platinichloride*,

$2\text{C}_{15}\text{H}_{12}\text{N}_2\cdot\text{H}_2\text{PtCl}_6$, forms yellowish-brown plates, which decompose at about 180° .

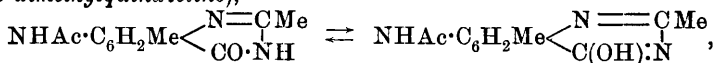
4-*Phenyl-3-methylcinnolinic acid*, $\text{C}_{13}\text{H}_{10}\text{O}_4\text{N}_2\cdot\text{H}_2\text{O}$, forms colourless crystals, m. p. $228-229^\circ$ (decomp.). J. J. S.

Quinazolines. XXIII. 7-Amino-6-methylquinazolones, 7-Nitroquinazolone-6-carboxylic Acids, and 1:3:7:9-Naphthatetrazines. MARSTON T. BOGERT and ALFRED H. KROPFF (*J. Amer. Chem. Soc.*, 1909, 31, 1071-1078).—The authors have previously described (this vol., i, 583) some amino- and nitroamino-derivatives of benzoic, *m*-toluic, and *isophthalic* acids containing an amino-group adjacent to a carboxyl group. The present paper gives an account of some quinazoline condensations of these acids, depending on the intermediate formation of acylantranilamides, which lose water and form compounds with a pyrimidine ring, thus :



The intermediate amides have not been isolated.

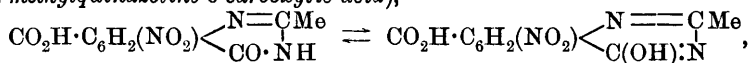
7-*Acetylamino-2:6-dimethyl-4-quinazolone* (7-*acetylamino-4-hydroxy-2:6-dimethylquinazoline*),



m. p. about 330° , obtained by the action of ammonium hydroxide on 2-acetylamino-1-methyl-4:5-acetylanthranil, forms colourless needles, and when boiled with potassium hydroxide is converted into 7-*amino-2:6-dimethyl-4-quinazolone*, m. p. above 300° . 7-*Acetylamino-3-phenyl-2:6-dimethyl-4-quinazolone*, $\text{NHAc}\cdot\text{C}_6\text{H}_2\text{Me}\begin{smallmatrix} \text{N}=\text{CMe} \\ \text{CO}\cdot\text{NPh} \end{smallmatrix}$, m. p. 271°

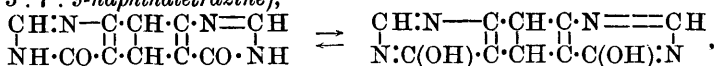
(uncorr.), obtained by heating the acetylanthranil with aniline, crystallises in diamond-shaped plates.

7-*Nitro-2-methyl-4-quinazolone-6-carboxylic acid* (7-*nitro-4-hydroxy-2-methylquinazoline-6-carboxylic acid*),

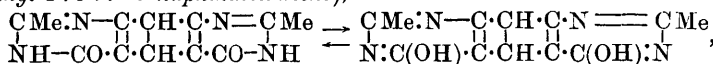


m. p. above 300° , obtained by boiling 4-nitroacetylanthranil-5-carboxylic acid with dilute ammonium hydroxide, forms colourless needles. 7-*Nitro-3-phenyl-2-methyl-4-quinazolone-6-carboxylic acid*, m. p. 315° (uncorr.), prepared by the action of aniline on 4-nitroacetylanthranil-5-carboxylic acid, crystallises in yellow prisms.

4 : 6-Diketotetrahydro-1 : 3 : 7 : 9-naphthatetrazine (4 : 6-dihydroxy-1 : 3 : 7 : 9-naphthatetrazine),

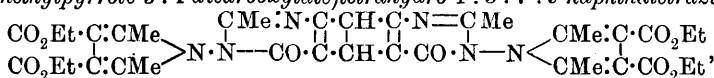


m. p. above 310°, obtained by heating diethyl 4 : 6-diaminoisophthalate with formamide, forms a reddish-yellow powder. 4 : 6-Diketo-2 : 8-dimethyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine (4 : 6-dihydroxy-2 : 8-dimethyl-1 : 3 : 7 : 9-naphthatetrazine),



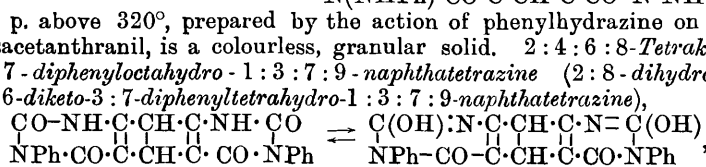
m. p. above 310°, prepared by the action of alcoholic ammonia on ethyl 4 : 6-diacetylaminisophthalate, forms a pale yellow, amorphous powder; it can be obtained in better yield by boiling the bisacetanthranil from 4 : 6-diaminoisophthalic acid with dilute ammonium hydroxide. 4 : 6-Diketo-2 : 3 : 7 : 8-tetramethyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine,

$\begin{array}{c} \text{CMe:N} \text{---} \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{N} \text{=CMe} \\ | \quad | \quad | \quad | \\ \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{CO} \cdot \text{NMe} \end{array}$ m. p. above 350°, obtained by heating the bisacetanthranil with aqueous methylamine, forms long, colourless needles. 4 : 6-Diketo-2 : 8-dimethyl-3 : 7-dipropyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine, m. p. 220° (uncorr.), crystallises in small, lustrous needles. 4 : 6-Diketo-3 : 7-diphenyl-2 : 8-dimethyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine, m. p. 315°, prepared by heating the bisacetanthranil with aniline, forms minute, colourless needles. 4 : 6-Diketo-3 : 7-di-β-naphthyl-2 : 8-dimethyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine, m. p. 304° (uncorr.), crystallises in fluorescent needles. 3 : 7-Diamino-4 : 6-diketo-2 : 8-dimethyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine, obtained by the action of hydrazine hydrate on the bisacetanthranil, forms yellow, nacreous scales; the hydrochloride, m. p. above 360° (decomp.), crystallises in colourless prisms; the diacetyl derivative, m. p. above 360°, forms small, colourless needles; the dibenzylidene derivative, m. p. above 350°, crystallises in granular form. When this diamidonaphthatetrazine is boiled with ethyl diacetyl-uccinate dissolved in glacial acetic acid, 4 : 6-diketo-2 : 8-dimethyl-3 : 7-di(ethyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate)tetrahydro-1 : 3 : 7 : 9-naphthatetrazine,



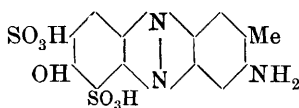
m. p. 268.2° (corr.), is produced, which forms colourless needles or prisms. 3 : 7-Diphenylamino-4 : 6-diketo-2 : 8-dimethyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine,

$\begin{array}{c} \text{CMe} \text{---} \text{N} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{N} \text{=CMe} \\ | \quad | \quad | \quad | \\ \text{N(NHPh)} \cdot \text{CO} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{CO} \cdot \text{N} \cdot \text{NHPh} \end{array}$ m. p. above 320°, prepared by the action of phenylhydrazine on the bisacetanthranil, is a colourless, granular solid. 2 : 4 : 6 : 8-Tetraketo-3 : 7-diphenyloctahydro-1 : 3 : 7 : 9-naphthatetrazine (2 : 8-dihydroxy-4 : 6-diketo-3 : 7-diphenyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine),

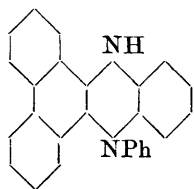


m. p. above 300°, obtained by heating diethyl 4 : 6-diphenyluraminisophthalate with aniline at 225°, is a colourless, amorphous solid. E. G.

[Preparation of Substituted Azines.] CARL JÄGER (D.R.-P. 210702).—Compounds of the type shown by the annexed formula are formed when the sodium hydrogen salt of *p*-aminophenol- α -disulphonic acid (29.1 parts) is treated with *m*-tolylenediamine (12.2 parts) in 1000 parts of water, and sodium dichromate (40 parts) in 200 parts of water stirred in at the ordinary temperature. A dark precipitate separates, the mixture is heated with steam until a blood-red coloration appears, filtered, and the soluble dye salted out. The tolylenediamine can be replaced by other *m*-diamines and the sodium dichromate by manganese dioxide. F. M. G. M.



Remarks on Dihydroazines. OSCAR HINSBERG (*Ber.*, 1909, 43, 3333—3336).—The statement made by Freund and Richard (this vol., i, 417) that *N*-phenyl- α -benzyl dihydrophenanthraphenazine is a yellow compound yielding red salts contradicts to some extent the observation of Hinsberg and Garfunkel (*Abstr.*, 1897, i, 123), who describes the mother substance of the above compound, *as-N*-phenyl dihydrophenanthraphenazine, as an almost colourless compound not forming coloured salts. The author finds that the latter compound forms faint yellow prisms or needles, m. p. 231—232° (m. p. previously given as 230°), and is neither coloured by concentrated hydrochloric acid nor altered by boiling for five minutes with acetic anhydride; if, however, the boiling be prolonged for several hours, a *monoacetyl* derivative, $C_{28}H_{20}ON_2$, crystallising from alcohol in colourless needles, m. p. 196—197°, is obtained. The dihydroazine is hence only relatively stable towards acetic anhydride, and is to be regarded as *s-N*-phenyl dihydrophenanthraphenazine (annexed formula).



These results are in agreement with those of Freund and Richard (*loc. cit.*), the colourless benzyl derivative corresponding with the almost colourless *s-N*-phenyl dihydrophenanthraphenazine.

The conclusion is drawn that acetylation is insufficient to determine whether a dihydroazine belongs to the *s*- or *as*-series.

It may be assumed that also the non-alkylated dihydroazines, or at any rate the complex ones, of the *as*-series and their salts exhibit yellow or red colours, whilst those of the *s*-series are colourless (compare Freund and Richard, *loc. cit.*). T. H. P.

Decomposition of the Leucosulphonic Acids of Rosaniline Hydrochloride and Crystal-Violet in Aqueous Solution. JOSEPH H. KASTLE (*Amer. Chem. J.*, 1909, 42, 293—300).—It has been shown in an earlier paper (*Abstr.*, 1905, ii, 154) that the relative strengths of acids can be determined colorimetrically by means of solutions of certain vegetable colouring matters which have been bleached with sulphur dioxide. Unfortunately, such reagents are unstable, and must be freshly prepared from time to time, and the materials employed are only obtainable at certain seasons. A search has therefore been made for an artificial dye, the sulphurous

acid leuco-derivative of which is decomposed by acids with regeneration of the original colour, but without success.

During the course of this work, it has been found that when solutions of the leuco-sulphonic acids of rosaniline hydrochloride and crystal-violet are heated, they rapidly become coloured, but become colourless again on cooling. A number of experiments are described which lead to the conclusion that this behaviour is not due to the action of the air, but to dissociation, either simple or hydrolytic. It is pointed out that these colour changes form a striking lecture experiment to illustrate reversible actions. E. G.

A New Class of Dyes of Biochemical Importance. Tri-indylmethane Dyes. ALEXANDER ELLINGER and CLAUDE FLAMAND (*Zeitsch. physiol. Chem.*, 1909, 62, 276—286. Compare Ellinger, Abstr., 1906, i, 696).—The dye, obtained by boiling 3-indolealdehyde with dilute sulphuric acid, crystallises from glacial acetic acid in long, red needles, with a green metallic lustre resembling magenta. It is hygroscopic, and when heated at 130—140° has the composition $2C_{25}H_{17}N_3 \cdot 3H_2SO_4$. It sinters at 212°, and at higher temperatures decomposes slowly.

The product obtained when hydrochloric acid is used has the composition $C_{25}H_{17}N_3 \cdot HCl$. These dyes appear to be derived from tri-indylmethane, $CH(C_8H_6N)_3$, and to be analogous to the basic triphenylmethane dyes.

The same dye can be synthesised by heating oxalic or formic acid with indole and sulphuric acid, or, even better, by boiling the product formed from the action of alcoholic potassium hydroxide and chloroform on indole with sulphuric acid.

When the dye base is heated with water at 220°, it yields indole and indolealdehyde.

Dyes can also be obtained by condensing indolealdehyde with various indole derivatives, for example, scatole, indolecarboxylic acid, indoleacetic acid, etc.

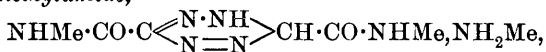
Urorosein is probably a tri-indylmethane dye (Herter, Abstr., 1908, ii, 410). J. J. S.

Alkylamides of 3:4-Dihydro-1:2:4:5-tetrazine-3:6-dicarboxylic Acid and 1:2-Dihydro-1:2:4:5-tetrazine-3:6-dicarboxylic Acid. ERNST MÜLLER (*Ber.*, 1909, 42, 3270—3284. Compare Curtius, Darapsky, and Müller, Abstr., 1908, i, 924).—An investigation on the action of methylamine, ethylamine, heptylamine, dimethylamine, diethylamine, and piperidine on ethyl diazoacetate. It is found that the alkylamines which most closely resemble ammonia, namely, the lower primary alkylamines, react fairly readily with ethyl diazoacetate, yielding alkylamine salts of 3:4-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylalkylamides together with small quantities of the corresponding 1:2-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylalkylamides, whilst, probably because of the slow rate with which the reaction proceeds, only derivatives of 1:2-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylic acid are formed by the action of heptylamine, dimethylamine, and

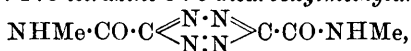
piperidine on ethyl diazoacetate. The only compound obtained from the interaction of diethylamine and ethyl diazoacetate was diethylammonium 1:2-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylate; the water necessary for the hydrolysis of the ester was probably derived from the air.

In their chemical behaviour, the substituted amides resemble most closely the unsubstituted simple amides of 1:2-dihydro- and 3:4-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylic acid (compare Curtius, Darapsky, and Müller, Abstr., 1906, i, 939; 1907, i, 359).

The methylammonium salt of 3:4-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylmethylamide,



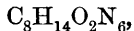
crystallises in rosettes of lemon-yellow needles, m. p. 115° (decomp.). All attempts to obtain the alkylamide by treating the salt with acids were unsuccessful. The salt is converted by acetic acid and potassium nitrite into 1:2:4:5-tetrazine-3:6-dicarboxylmethylamide,



which crystallises in slender, carmine-red leaflets, m. p. 237°, and is reduced by hydrogen sulphide to 1:2-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylmethylamide, $\text{NHMe} \cdot \text{CO} \cdot \text{C} \begin{array}{c} \text{N} - \text{N} \\ \text{NH} \cdot \text{NH} \end{array} > \text{C} \cdot \text{CO} \cdot \text{NHMe}$, which crystallises in slender, reddish-yellow prisms, sinters at 270°, m. p. 295° (decomp.).

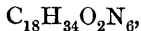
The ethylammonium salt of 3:4-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylethylamide, $\text{C}_{10}\text{H}_{21}\text{O}_2\text{N}_7$, crystallises in stout, lemon-yellow rhombohedra, m. p. 105—106° (decomp.). When hydrolysed by dilute sulphuric acid, it yields ethylamine, glyoxylic acid, nitrogen (1 mol.), and hydrazine (1 mol.); glyoxyethylamide (2 mols.) is formed immediately, and was isolated and estimated as the phenylhydrazone, $\text{C}_{10}\text{H}_{13}\text{ON}_3$, which crystallises in almost colourless, slender, felted needles, m. p. 199—200°. 1:2:4:5-Tetrazine-3:6-dicarboxylethylamide, $\text{C}_8\text{H}_{12}\text{O}_2\text{N}_6$, crystallises in carmine-red leaflets, m. p. 195—196°.

1:2-Dihydro-1:2:4:5-tetrazine-3:6-dicarboxylethylamide,



forms slender, pale yellow needles, which turn brown at 230° and decompose at 287°; it is hydrolysed by concentrated hydrochloric acid into oxalic acid (2 mols.), ethylamine (2 mols.), and hydrazine (2 mols.).

1:2-Dihydro-1:2:4:5-tetrazine-3:6-dicarboxylheptylamide,



crystallises in pale yellow, rectangular, slender leaflets, m. p. 240°.

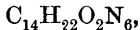
1:2-Dihydro-1:2:4:5-tetrazine-3:6-dicarboxyldimethylamide,



forms large, yellow, hexagonal prisms, m. p. 178—179°.

Diethylammonium 1:2-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylate, $\text{C}_{12}\text{H}_{26}\text{O}_4\text{N}_6$, crystallises in large, orange-yellow, hexagonal prisms, m. p. 179—180°.

1:2-Dihydro-1:2:4:5-tetrazine-3:6-dicarboxylpiperidide,



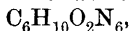
forms small, faintly yellow needles, m. p. 266° (decomp.), and is

oxidised by nitric acid (D 1.33) to 1 : 2 : 4 : 5-tetrazine-3 : 6-dicarboxyl-piperidide, $C_{14}H_{20}O_2N_6$, slender, vermilion leaflets, m. p. 196° (decomp.).
W. H. G.

ψ -Diazoacetamide (3 : 4-Dihydro-1 : 2 : 4 : 5-tetrazine-3 : 6-dicarboxylamide). THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1909, 42, 3284—3292).—The action of diazomethane on ψ -diazoacetamide leads to the formation of a methyl derivative which must be 4-methyl-3 : 4-dihydro-1 : 2 : 4 : 5-tetrazine-3 : 6-dicarboxylamide, $NH_2 \cdot CO \cdot C \begin{smallmatrix} N \cdot NMe \\ N = N \end{smallmatrix} CH \cdot CO \cdot NH_2$, since it yields nitrogen, glyoxylamide, and methylhydrazine when boiled with dilute acids. It is thus shown that the metal of the salts of ψ -diazoacetamide is undoubtedly attached to nitrogen as assumed originally (Abstr., 1906, i, 939), and not to carbon as stated more recently (Abstr., 1908, i, 924).

4-Methyl-3 : 4-dihydro-1 : 2 : 4 : 5-tetrazine-3 : 6-dicarboxylamide, as obtained in the manner described, is a fiery, yellow powder, m. p. 118° (decomp.), which contains as impurity, however, small quantities of 3 : 4-dihydro-1 : 2 : 4 : 5-tetrazine-3(or 6)-carboxylmethylamide-6(or 3)-carboxylamide, since, when boiled with water, it yields a solution which deposits 1 : 2-dihydro-1 : 2 : 4 : 5-tetrazine-3(or 6)-carboxylmethylamide-6(or 3)-carboxylamide, $C_5H_8O_2N_6$, as small, rectangular leaflets, m. p. 234° (decomp.). 4-Methyl-3 : 4-dihydro-1 : 2 : 4 : 5-tetrazine-3 : 6-dicarboxylamide, when treated with cold concentrated hydrochloric acid, yields oxamic acid hydrazide in addition to the normal products of hydrolysis; this compound probably results from the hydrolysis of the methyltetrahydrotetrazinedicarboxylamide produced by the reducing action of the glyoxylic acid, formed primarily, on the parent substance.

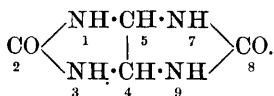
4-Ethyl-3 : 4-dihydro-1 : 2 : 4 : 5-tetrazine-3 : 6-dicarboxylamide,



is a sulphur-yellow powder, m. p. 125° (decomp.).

W. H. G.

Methyl Derivatives of Diphenylacetylenediureine. HEINRICH BILTZ [with CHAIM RIMPEL] (*Annalen*, 1909, 368, 243—261. Compare Abstr., 1908, i, 62).—The system of numbering employed by the author in indicating the positions of substituents in derivatives of acetylenediureine is the following (annexed formula).

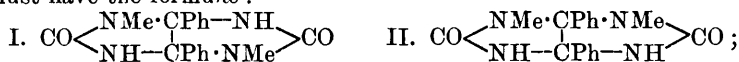


It is deemed advisable, owing to the close relationship of acetylenediureine to uric acid, to give the nitrogen atoms in both compounds the same numbers, hence the number 6 is not employed in the present case.

It is shown that acetylenediureine has the symmetrical constitution represented by the formula just given, since methyl derivatives of 4 : 5-diphenylacetylenediureine containing a different number of methyl groups in the two glyoxalone rings may be prepared either by the interaction of a methylglyoxalone with a carbamide containing fewer methyl groups, or of a methylcarbamide with a glyoxalone containing a smaller number of methyl groups. For example, the 1 : 3-dimethyl-derivative may be prepared from 4 : 5-diphenyl-1 : 3-dimethylglyoxalone

and carbamide or from 4:5-dihydroxy-4:5-diphenyldihydroglyoxalone and *s*-dimethylcarbamide.

Although acetylenediureine yields a tetra-acetyl derivative, only a diacetyl derivative of the 4:5-diphenyl compound can be prepared. In order to account for this, the suggestion was made previously (*loc. cit.*) that the entrance of the acetyl groups produced a displacement of the phenyl groups which prevented the acetylation of the two remaining imino-groups. The behaviour of the methyl derivatives of diphenylacetylenediureine on acetylation gives support to this view. The fact that diphenylmethylacetylenediureine yields a diacetyl derivative shows that the displacement of the phenyl group produced by the methyl group is not sufficient to prevent acetylation of the neighbouring imino-group. It has been found possible to determine the constitutions of the two isomerides resulting from the condensation of 4:5-diphenyl-1-methylglyoxalone with methylcarbamide by investigating their behaviour on acetylation. The two isomerides must have the formulæ:



a compound having the first formula should yield a diacetyl derivative, whilst a substance having the second formula would only yield a mono-acetyl derivative. In agreement with this, it is found that one isomeride yields a diacetyl derivative, whilst the other yields a mono-acetyl derivative.

The methyl derivatives of 4:5-diphenylacetylenediureine are prepared: (1) by the condensation of 4:5-dihydroxy-4:5-diphenyldihydroglyoxalones or their ethers with carbamides in alcohol containing hydrogen chloride; if possible, the methyl groups should be present in the glyoxalone; (2) by treating an alcoholic solution of the diphenylglyoxalone and carbamide with bromine.

All attempts to prepare the tetramethyl derivative of 4:5-diphenylacetylenediureine were unsuccessful, as were also attempts to obtain asymmetrical double ring systems by condensing 4:5-dihydroxy-4:5-diphenyldihydroglyoxalone with *o*-phenylenediamine or tolylene-3:4-diamine.

4:5-Diphenyl-1-methylacetylenediureine, $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_4$, forms colourless, glistening crystals, m. p. 340° (decomp.); the *diacetyl* derivative, $\text{C}_{21}\text{H}_{20}\text{O}_4\text{N}_4$, crystallises in flat prisms, sinters at 230° , m. p. 240° (decomp.).

4:5-Diphenyl-1:3-dimethylacetylenediureine, $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_4$, crystallises in rhombic leaflets, or short prisms with rhombic facets, and remains unchanged at 365° ; the *diacetyl* derivative, $\text{C}_{22}\text{H}_{22}\text{O}_4\text{N}_4$, crystallises in large, rhombic leaflets, m. p. 225° . The isomeric 1:9-dimethyl compound forms small rhombohedra which do not melt at 365° ; its *diacetyl* derivative crystallises in rhombic leaflets, m. p. 230° . The isomeric 1:7-dimethyl compound forms large, glistening, rhombic plates, m. p. 345° (decomp.); its crystalline *acetyl* derivative, $\text{C}_{20}\text{H}_{20}\text{O}_3\text{N}_4$, has m. p. $272\text{--}273^\circ$ (slight decomp.).

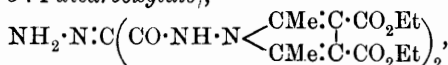
4:5-Diphenyl-1:3:7-trimethylacetylenediureine, $\text{C}_{19}\text{H}_{20}\text{O}_2\text{N}_4$, crystallises in small, rectangular leaflets; the crystalline *acetyl* derivative, $\text{C}_{21}\text{H}_{22}\text{O}_3\text{N}_4$, has m. p. 234° .

W. H. G.

Ethyl Mesoxalylhydrazone-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate). CARL BÜLOW [With OTTO SCHÄRER] (*Ber.*, 1909, 42, 3311—3326. Compare Bülow and Weidlich, *Abstr.*, 1906, i, 981; 1907, i, 1089).—A number of substances of the general formula $\text{NHR}'\cdot\text{N}:\text{C}(\text{CO}\cdot\text{NH}\cdot\text{N} < \begin{smallmatrix} \text{CMe}:\text{C}\cdot\text{CO}_2\text{R} \\ \text{CMe}:\text{C}\cdot\text{CO}_2\text{R} \end{smallmatrix})_2$ have been prepared by coupling the malonyl derivatives of Bülow and Weidlich (*Abstr.*, 1906, i, 981) with aromatic diazonium salts in the presence of sodium acetate. The phenylhydrazone derivative may also be prepared by warming ethyl mesoxalylloxime-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate) with phenylhydrazine. The oximino-compound, just mentioned, is formed when ethyl malonyl-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate) in acetic acid solution is treated with sodium nitrite.

It is found that substances having the general formula given above behave as monobasic acids, possibly because the imino-hydrogen atom of the hydrazone residue, under the influence of an alkali, wanders to one of the carbonyl groups.

Ethyl mesoxalylloxime-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate), $\text{OH}\cdot\text{N}:\text{C}(\text{CO}\cdot\text{NH}\cdot\text{N} < \begin{smallmatrix} \text{CMe}:\text{C}\cdot\text{CO}_2\text{Et} \\ \text{CMe}:\text{C}\cdot\text{CO}_2\text{Et} \end{smallmatrix})_2$, forms white crystals, m. p. 171°, and, when heated with a 60% solution of hydrazine hydrate on a water-bath, yields *ethyl mesoxalylhydrazone-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate)*,



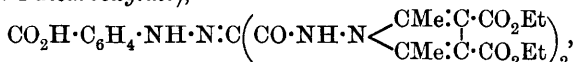
which crystallises in white needles, m. p. 204—205°.

Ethyl mesoxalylphenylhydrazone-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate), $\text{C}_{33}\text{H}_{40}\text{O}_{10}\text{N}_6$, crystallises in yellow needles, m. p. 269°, and, when boiled with aqueous sodium hydroxide and treated subsequently with acid, yields the corresponding tetracarboxylic acid, $\text{C}_{25}\text{H}_{24}\text{O}_{10}\text{N}_6$, a crystalline substance, m. p. 209° (decomp.). The ester is converted (1) by acetic acid and zinc dust into aniline and *ethyl aminomalonyl-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate)*,

$\text{C}_{27}\text{H}_{37}\text{O}_{10}\text{N}_5$, slender, white needles, m. p. 219°; (2) by the nitrogen oxides evolved from nitric acid and arsenious oxide into *ethyl nitrosomesoxalyl-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate)*, $\text{C}_{33}\text{H}_{39}\text{O}_{11}\text{N}_7$, a yellow, crystalline substance, m. p. 246°.

Ethyl mesoxalyl-o-tolylhydrazone-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate), $\text{C}_{34}\text{H}_{42}\text{O}_{10}\text{N}_6$, has m. p. 248°; the corresponding *m-xylhydrazone* compound, $\text{C}_{35}\text{H}_{44}\text{O}_{10}\text{N}_6$, has m. p. 216°; the *p-acetylaminophenylhydrazone* compound, $\text{C}_{35}\text{H}_{43}\text{O}_{11}\text{N}_7$, commences to soften at 186°, becomes again solid at a higher temperature, and then has m. p. 225°; the *α-naphthylhydrazone* compound, $\text{C}_{37}\text{H}_{42}\text{O}_{10}\text{N}_6$, crystallises in slender, brownish-yellow needles, m. p. 272°; the isomeric *β-naphthylhydrazone* compound forms very slender, yellow needles, m. p. 223°; the *p-sulphophenylhydrazone* compound, $\text{C}_{38}\text{H}_{40}\text{O}_{13}\text{N}_6\text{S}$, has m. p. 222—223°; the *p-sulpho-α-naphthylhydrazone* compound, $\text{C}_{37}\text{H}_{42}\text{O}_{13}\text{N}_6\text{S}$, crystallises in small, brown needles.

Ethyl mesoxalyl-o-carboxyphenylhydrazone-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate),

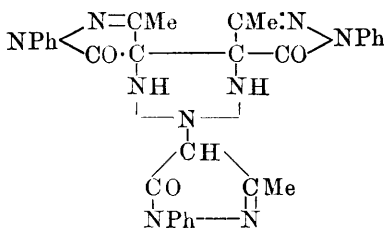


has m. p. 265—266°; the corresponding *meta*-isomeride forms slender, yellow needles, m. p. 234—235°; the *para*-isomeride has m. p. 286°.

W. H. G.

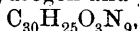
Condensation of Phenylazoimide with Phenylmethylpyrazolone. A. HEIDUSCHKA and O. ROTHACKER (*J. pr. Chem.*, 1909, [ii], 80, 289—302).—The red product, m. p. 184°, obtained by Walther and Rothacker by the interaction of sodium ethoxide, 1-phenyl-3-methyl-5-pyrazolone, and phenylazoimide in alcoholic solution (Abstr., 1906, i, 911), has been further examined. The

annexed probable constitution is based on the analytical data and the following chemical behaviour of the substance.



The molecular weight lies between 556 and 575, and is determined by means of the salts, of which the dark red *sodium*, orange *di-sodium*, dark red *potassium*, orange *di-potassium*, dark red *ammonium*, orange

di-ammonium, yellow *calcium*, and orange-red *barium* salts are described. The substance contains two imino-groups and forms a red *methyl derivative*, m. p. 207°, yellow *dimethyl derivative*, m. p. 273° (decomp.), orange *diacetyl compound*, m. p. 157°, red *benzoyl derivative*, m. p. 162°, and orange-yellow *dibenzoyl derivative*, m. p. 201—202°. The substance is reduced by zinc dust, yielding rubazonic acid, and by stannous chloride and hydrochloric acid, forming the stannichloride of 4-amino-1-phenyl-3-methyl-5-pyrazolone hydrochloride. When oxidised by 20% nitric acid at 50°, the substance loses 2 atoms of hydrogen and yields a *compound*,



m. p. 181°, which forms brown crystals, no longer contains hydrogen replaceable by metals or alkyl groups, and is converted by dilute potassium hydroxide into pyrazole blue and bisphenylmethylpyrazolone almost exactly in the ratio 1 : 2.

A chloroform solution of the red product is converted by bromine into an unstable *dibromo-derivative*, $\text{C}_{30}\text{H}_{25}\text{O}_3\text{N}_9\text{Br}_2$, and by chlorine into 4 : 4-dichloro-1-phenyl-3-methyl-5-pyrazolone. C. S.

Reductions with Ethyl Alcohol. GIACOMO PONZIO (*Gazzetta*, 1909, 39, ii, 321—324).—Acylazoaryl derivatives (this vol., i, 681) are readily reduced to the corresponding acylarylhydrazines by boiling their absolute alcoholic solutions until these become colourless (compare Paternò, this vol., i, 240). This reaction, which is accompanied by the formation of acetaldehyde, is possibly applicable to other azo-compounds, but it seems probable that the simultaneous action of either light or a high pressure would be necessary. When

reduced in this way, benzoylazobenzene yields α -benzoyl- β -phenylhydrazine; *p*-toluylazobenzene, α -*p*-toluoyl- β -phenylhydrazine; anisoylazobenzene, α -anisoyl- β -phenylhydrazine; benzoylazo-*p*-bromobenzene, α -benzoyl- β -*p*-bromophenylhydrazine; *p*-toluylazo-*p*-bromobenzene, α -*p*-toluoyl- β -*p*-bromophenylhydrazine; anisoylazo-*p*-bromobenzene, α -anisoyl- β -*p*-bromophenylhydrazine; benzoylazo-*p*-chlorobenzene, α -benzoyl- β -*p*-chlorophenylhydrazine; and benzoylazo-*o*-*p*-dichlorobenzene, α -benzoyl- β -*o*-*p*-dichlorophenylhydrazine. T. H. P.

[Sulphonation of 2':3-Dichloro-4-aminoazobenzene.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 210598).—2':3-Dichloro-4-aminoazobenzene disulphonic acid is prepared by sulphonating 2':3-dichloro-4-aminoazobenzene (Niementowski, Abstr., 1903, i, 133). The dye is a yellowish-brown powder. F. M. G. M.

Action of Potassium Hydroxide on Aniline. A. BACOVESCU (*Ber.*, 1909, 42, 2938—2940).—Wohl (Abstr., 1900, i, 157) showed that on heating nitrobenzene with potassium hydroxide, potassium-*o*-nitrophenol is formed; subsequently Wohl and Aue (Abstr., 1901, i, 612) isolated azoxybenzene as the chief product of the action of potassium hydroxide on a mixture of aniline and nitrobenzene. It is now shown that by the action of potassium hydroxide in large excess on aniline, azobenzene and the *o*-benzeneazophenol first described by Bamberger (Abstr., 1900, i, 531) are formed. Potassium hydroxide forms benzeneazophenol from azobenzene, and converts hydrazobenzene into azobenzene. E. F. A.

Behaviour of Ethers of *o*-Hydroxyazo-compounds when Reduced with Stannous Chloride and Hydrochloric Acid. PAUL JACOBSON (*Annalen*, 1909, 369, 1—40. Compare Jacobson, Franz, and Zaar, Abstr., 1904, i, 121; Jacobson and Hönigsberger, *ibid.*, 202).—The present communication deals with the reduction in acid solution of azophenol ethers containing the grouping $\text{C}_6\text{H}_4\text{N}(\text{N} \cdot \text{OEt})$ (2) and a methyl group in the position para to the azo-group.

In all the cases investigated it is found that, apart from the bases formed by the fission of the azo-compound, considerable quantities of two bases, namely, a parasemidine and a diphenyl base, are formed. For example, *p*-tolueneazo-*o*-phenetole yields 4-amino-3'-ethoxy-4-methyldiphenylamine and 4':6-diamino-3'-ethoxy-3-methyldiphenyl. Occasionally, very small quantities of an orthosemidine are also formed, but, as found formerly (*loc. cit.*), the presence of a substituent ortho to the azo-group hinders the orthosemidine transformation.

[With L. HUBER.]—*p*-Tolueneazo-*o*-phenetole, $\text{C}_{15}\text{H}_{16}\text{ON}_2$, prepared by condensing *p*-nitrosotoluene with *o*-phenetidine in glacial acetic acid, crystallises in long, red needles and prisms, m. p. 92—93°.

4'-Amino-3'-ethoxy-4-methyldiphenylamine, $\text{C}_{15}\text{H}_{18}\text{ON}_2$, crystallises in small, colourless rods, m. p. 75°; the hydrochloride, $\text{C}_{15}\text{H}_{18}\text{ON}_2\text{HCl}$, forms slender, white needles; the salicylidene derivative, $\text{C}_{22}\text{H}_{22}\text{O}_2\text{N}_2$, crystallises in microscopic, yellow plates with a violet-red shimmer, m. p. 133—134°; the acetyl derivative, $\text{C}_{17}\text{H}_{20}\text{O}_2\text{N}_2$, forms fan-like

aggregates of small, slender, bluish-white needles, m. p. 168—169°. The base is oxidised by chromic acid, yielding 2-ethoxy-*p*-benzoquinone-*p*-tolylimine, $C_6H_4Me \cdot N : C_6H_3(OEt) : O$, which forms large, red crystals, m. p. 137—138°.

4':6-Diamino-3'-ethoxy-3-methyldiphenyl, $C_{15}H_{18}ON_2$, crystallises in tufts of slightly yellow needles, m. p. 88—89°; the di-*p*-nitrobenzylidene derivative, $C_{29}H_{24}O_5N_4$, forms long, yellowish-red needles, m. p. 204—205°; the dibenzoyl derivative, $C_{29}H_{26}O_3N_2$, crystallises in white, microscopic rods, m. p. 174°.

The reduction of *p*-tolueneazo-*o*-phenetole with stannous chloride and hydrochloric acid yields, in addition to the bases just described, small quantities of (1) a substance, $C_{15}H_{17}O_2N$, probably 6-amino-4'-hydroxy-5'-ethoxy-3-methyldiphenyl, which forms small, bluish-white crystals, m. p. 139—140°; (2) 6-amino-2'-ethoxy-3-methyldiphenylamine, $NH_2 \cdot C_6H_3Me \cdot NH \cdot C_6H_4 \cdot OEt$, which forms small, white crystals, m. p. 75—77°, and condenses with benzil, yielding the stilbazonium base, $CPh(OH) \cdot N \cdot C_6H_4 \cdot OEt$
 $CPh : N - C_6H_3Me$, obtained in small, pale yellow, hexagonal plates, m. p. 140—142°.

[With E. JANKOWSKI.]—The reduction of *p*-tolueneazo-*p*-cresetole has already been investigated by Jacobson and Piepenbrink (compare Abstr., 1895, i, 26). The results recorded by these authors have been confirmed and their work extended.

4-Ethoxy-2:5-toluquinone, $C_9H_{10}O_3$, prepared by the oxidation of 4-amino-5-ethoxy-2:4'-dimethyldiphenylamine with chromic acid, crystallises in yellow cubes, m. p. 101°, and when reduced with sulphurous acid yields 2:5-dihydroxy-4-ethoxytoluene, $C_9H_{12}O_3$, colourless plates, m. p. 131°.

4:6'-Diamino-5-ethoxy-2:3'-dimethyldiphenyl could not be obtained in a crystalline form; when diazotised and coupled with phenol it yields the corresponding bisazo-compound,

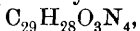
$OH \cdot C_6H_4 \cdot N_2 \cdot C_6H_3Me \cdot C_6H_2Me(OEt) \cdot N_2 \cdot C_6H_4 \cdot OH$,
 a brown, amorphous powder, m. p. 135°.

[With H. L. FULDA.]—*p*-Tolueneazo-4-*m*-xylenol (6-hydroxy-3:5:4'-trimethylazobenzene), $C_{15}H_{16}ON_2$, prepared by coupling *p*-toluene-diazonium chloride with 4-*m*-xylenol, crystallises in bright red needles, m. p. 99°; the ethyl ether, $C_{17}H_{20}ON_2$, forms red, prismatic leaflets, m. p. 51·5—52·5°, and yields on reduction *p*-toluidine, 4-ethoxy-5-*m*-xylidine, 4-amino-3-ethoxy-2:6:4'-trimethyldiphenylamine, small quantities of the corresponding orthosemidine, and 4:6'-diamino-3-ethoxy-2:6:3'-trimethyldiphenyl.

The acetyl derivative of 4-ethoxy-5-*m*-xylidine, $C_{12}H_{17}O_2N$, has m. p. 65—66°; the thiocarbamide, $CS(NH \cdot C_6H_2Me_2 \cdot OEt)_2$, crystallises in long, white prisms, m. p. 141—142°.

4-Amino-3-ethoxy-2:6:4'-trimethyldiphenylamine is a colourless oil; the salicylidene derivative, $C_{24}H_{26}O_2N_2$, crystallises in yellow needles, m. p. 147—148°. The base is oxidised by chromic acid, yielding 4-ethoxy-*m*-2:5-xylquinone, $C_{10}H_{12}O_3$, which crystallises in long, brownish-yellow needles, m. p. 41—42°, and is reduced by sulphurous acid to the corresponding dihydroxy-compound crystallising in long, colourless needles.

4 : 6'-Diamino-3-ethoxy-2 : 6 : 3'-trimethyldiphenyl, $C_{17}H_{22}ON_2$, crystallises in glistening, transparent, colourless rhombohedra, m. p. 117—118°; the *disalicylidene* derivative, $C_{31}H_{30}O_3N_2$, forms oblique-angled plates, m. p. 201—202°; the *diformyl* derivative, $C_{19}H_{22}O_3N_2$, crystallises in small, colourless prisms, m. p. 189°. The base when diazotised and coupled with phenol yields the *bisazo*-compound,



a dark brown powder decomposing at 145°.

[With O. FABIAN.]—4-m-Xyleneazo-p-cresol (6-hydroxy-3 : 2' : 4'-trimethylazobenzene), $C_{15}H_{16}ON_2$, prepared from 4-m-xylylidine and *p*-cresol, crystallises in reddish-brown needles, m. p. 85°, b. p. 230—233°/30 mm. (very slight decomp.); the *ethyl ether*, $C_{17}H_{20}ON_2$, forms red, oblique-angled plates, m. p. 51°, b. p. 238—242°/25 mm., and when reduced yields 4'-amino-5'-ethoxy-2 : 4 : 2'-trimethyldiphenylamine and 4 : 2'-diamino-5-ethoxy-2 : 3' : 5'-trimethyldiphenyl. The former base could not be crystallised; the *acetyl* derivative, $C_{19}H_{24}O_2N_2$, forms tufts of white, hair-like needles, m. p. 114°; the *salicylidene* derivative, $C_{24}H_{26}O_2N_2$, crystallises in long, slender, orange needles, m. p. 116°. The base is oxidised by chromic acid, yielding 4-ethoxy-2 : 5-toluquinone-2(4)-m-xylylimine, $CMe \begin{smallmatrix} \text{CH:CMe} \\ \text{CH-CH} \end{smallmatrix} > C \cdot N : C \begin{smallmatrix} \text{CMe=CH} \\ \text{CH:C(OEt)} \end{smallmatrix} > C : O$, which crystallises in garnet-red prisms, m. p. 118°, and is reduced by zinc dust and acetic acid to 4'-hydroxy-5'-ethoxy-2 : 4 : 2'-trimethyldiphenylamine, $C_{17}H_{21}O_2N$, white, elongated, hexagonal plates, m. p. 103°.

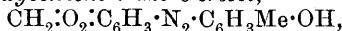
4 : 2'-Diamino-5-ethoxy-2 : 3' : 5'-trimethyldiphenyl, b. p. 240—260°/50 mm., forms a *disalicylidene* derivative, $C_{31}H_{30}O_3N_2$, crystallising in nodules, m. p. 161—162°, and when boiled with glacial acetic acid yields a basic substance crystallising in pyramids, m. p. 167—168°.

W. H. G.

Hydroxyazo-derivatives obtained from 4-Amino-1:2-catechol Methylene Ether [4-Amino-1:2-methylenedioxybenzene]. EFISIO MAMELI (*Gazzetta*, 1909, 39, ii, 314—321).—The author has prepared several azo-phenolic derivatives from 4-amino-1:2-methylenedioxybenzene (compare this vol., i, 711). These compounds give coloured crystals and act as acid colouring matters, dyeing wool, silk, and cotton in acid solutions.

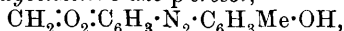
1 : 2-Methylenedioxybenzeneazophenol, $CH_2 : O_2 : C_6H_3 \cdot N_2 \cdot C_6H_4 \cdot OH$, forms yellow crystals, m. p. 180° (decomp.), and yields *p*-aminophenol when reduced by means of phenylhydrazine.

1 : 2-Methylenedioxybenzene-6-azo-o-cresol,



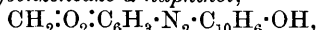
prepared from *o*-cresol, crystallises in yellow scales, m. p. 157°.

1 : 2-Methylenedioxybenzene-5-azo-p-cresol,



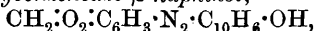
prepared from *p*-cresol, has m. p. 165°.

1 : 2-Methylenedioxybenzeneazo- α -naphthol,



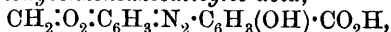
forms dark red crystals, m. p. 170° (decomp.).

1 : 2-Methylenedioxybenzeneazo- β -naphthol,



forms red scales, m. p. 156—158°, and yields an *acetyl* derivative, $C_{19}H_{14}O_4N_2$, m. p. 105—107°.

1 : 2-Methylenedioxybenzeneazosalicyclic acid,



forms yellow crystals, m. p. 218—222°.

T. H. P.

Thiophenols. I. *o*-Azothioanisole and *o*-Thiodianisidine. KURT BRAND (*Ber.*, 1909, 42, 3463—3468).—The sodium derivatives of the nitrophenyl mercaptans necessary for the formation of the thioethers are obtained best by reducing the dinitrodiphenyl disulphides in the presence of sodium hydroxide by sodium hydrosulphide, sodium sulphide, or sodium disulphide. When too much reducing agent is used, the nitro-group is also attacked.

A solution of sodium *o*-nitrophenyl mercaptide, obtained by heating an alcoholic suspension of 1:1'-dinitrophenyl disulphide with aqueous sodium hydroxide (2 mols.) and sodium hydrosulphide ($>\frac{1}{2}$ mol.), or sodium sulphide ($\frac{1}{2}$ mol.), or sodium disulphide ($\frac{1}{3}$ mol.), yields *o*-nitrothioanisole by treatment with aqueous potassium methyl sulphate (2 mols.) or with sodium hydroxide and methyl sulphate. *o*-Nitrothioanisole, $NO_2 \cdot C_6H_4 \cdot SMe$, m. p. 85—87°, crystallises in yellow needles, and is reduced by Elbs's electrolytic method to *o*-azothioanisole, $SMe \cdot C_6H_4 \cdot N:N \cdot C_6H_4 \cdot SMe$, m. p. 156—158°, which forms an intensely blue, crystalline hydrochloride. *o*-Hydrazothioanisole, $C_8H_{10}N_2S_2$, m. p. 104°, is obtained by reducing *o*-azothioanisole, suspended in ethyl acetate and alcohol, by a solution of sodium or ammonium hydrosulphide, or more conveniently by reducing alcoholic *o*-nitrothioanisole by zinc dust and sodium hydroxide. It crystallises in colourless needles, is oxidised in alcoholic solution by air or mercuric oxide to *o*-azothioanisole, and is converted by 30% hydrochloric acid into the *hydrochloride* of *o*-thiodianisidine, $C_{14}H_{16}N_2S_2 \cdot 2HCl$, m. p. 260° (decomp.). The free base, $C_{14}H_{16}N_2S_2$, m. p. 110—112°, liberated by ammonium hydroxide, forms a *diacetyl* derivative, m. p. 245—247°, and a bisdazo-compound which unites with phenols and amines to form substantive cotton dyes.

C. S.

Diazotisation of Feebly Basic, Sparingly Soluble Primary Amines. OTTO N. WITT (*Ber.*, 1909, 42, 2953—2961).—Primary amines of pronounced basic character are very easily diazotised in acid aqueous solution by means of the theoretical quantity of sodium nitrite. When, however, acid groups are introduced into the benzene nucleus, the salts of such amines are more readily dissociated, and it becomes increasingly difficult to diazotise them. It has been found that strong nitric acid ($D=1.48$ and higher) forms an excellent solvent for such amines and also for nitrous acid. Both the latter and also nitrosylsulphate act as very efficient diazotising agents in presence of nitric acid. No side reactions take place, even if the acid is warmed to 60° or 70°. This is due to the very rapid formation of the diazonium nitrate, which itself is totally resistant towards nitric acid. Diazotisation in nitric acid solution is most conveniently effected by adding exactly the amount of sulphurous acid required to reduce sufficient

nitric to nitrous acid. Equally convenient is the use of the commercial potassium metadisulphite, $K_2S_2O_5$, which dissolves in nitric acid, forming nitrous acid and potassium pyrosulphate. The base to be diazotised is finely powdered with the metadisulphite, and the mixture introduced in small portions into the nitric acid.

These diazo-compounds can be preserved in the nitric acid solution for months without decomposition.

When dichloronitroaniline is oxidised with strong nitric acid, *dichloro-p-nitrophenylnitroamine* is formed; this separates in colourless crystals, m. p. 120° . It has acid properties, turns litmus red, and forms crystalline salts with bases. It probably has the constitution of a ψ -acid in the free state. The metallic salts are easily soluble with the exception of the *thorium* salt; insoluble salts are formed with diazonium bases.

E. F. A.

Inhibiting Action of Neutral Salts on the Swelling of Fibrin through Acids and Alkalis. MARTIN H. FISHER and GERTRUDE MOORE (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 197—199. Compare Abstr., 1908, i, 929).—Neutral salts hinder the action of alkalis and acids in producing swelling of fibrin. Quantitative investigation of a number of salts leads to the conclusion that the ions can each be given an inhibition value.

The inhibiting effect brought about by adding comparable amounts of equimolecular salt solutions under identical conditions is proportionate to the sum of the values for the two ions in question in each case. Tables of quantitative determinations are given. Irregular results are to be expected, and are found, when the acid or alkali bringing about the swelling and the neutral salt interact chemically.

G. S. W.

Hydrolysis of Casein and the Detection of the Monoamino-acids Formed. R. ENGELAND (*Ber.*, 1909, 42, 2962—2969).—Most of the monoamino-acids as obtained by the hydrolysis of proteins, being amphoteric indifferent substances, are difficult to isolate. The amino-acids are converted by alkyl halides into betaines, which form characteristic aurichlorides, by means of which they can be identified even when present in small quantity. Use may be made of the varying solubility of their double salts with mercury, platinum and gold chlorides to separate the various amino-acid betaines.

The method is applied to the isolation of the products of hydrolysis of casein.

The methylation must be carried out in the cold; at higher temperatures a number of high molecular and, in part, oxygen-free condensation products are formed, all of which are characterised by the pronounced tendency to crystallise of their sparingly soluble aurichlorides. In view of the well known tendency of the animal and vegetable organisms to bring about methylation, it is possible that similar products may be formed in the living organism. An explanation is also afforded of the wide distribution of betaine in plants as well as of its higher homologues. The diamino-acids and the proteins themselves are less easily methylated.

E. F. A.

The Action of Light on Blood-pigments and Blood-corpuscles, and the Optical Sensitisation of the Action. K. A. HASSELBALCH (*Biochem. Zeitsch.*, 1909, 19, 435—493).—A Kromayer mercury lamp was used as the source of light, and the blood or other liquid was exposed in specially devised vessels which could be shaken so as to continually expose fresh surfaces. The sides of the vessels exposed to light could be either of quartz or glass, which permit the passage of different light rays. The vessels could be evacuated, so that the light action could be studied in a vacuum or analyses made of the gases from time to time. It was found that the original blood-pigment is converted by light into methæmoglobin, which further changes into hæmatin. This action only takes place in the presence of oxygen. Reduced hæmoglobin is not changed by light. The action is due chiefly to rays of wave-length under 310μ , although those of greater length are not entirely inactive. The change by light of hæmoglobin into methæmoglobin follows the course of a unimolecular reaction. Methæmoglobin is converted in a vacuum by light into reduced hæmoglobin. If the mixture is placed in the dark, the oxygen thus set free leads to the formation of oxyhæmoglobin. Hæmatin in the light is changed into hæmochromogen; the reaction can be reversed by keeping the mixture thus obtained in the dark. Carbon monoxide-hæmoglobin is partly changed by light into reduced hæmoglobin; this action is also reversible on darkening. Blood-corpuscles are lysed by light, both in presence of air and in a vacuum, chiefly by rays of smaller wave-length than 310μ . Colour sensitisers increase the reaction rate of light actions only in such reactions accompanied by a scission of oxygen. The sensitiser acts as a light absorbing, readily oxidisable substance.

S. B. S.

The Behaviour of Acetylene to Blood. LOUIS LEWIN, A. MIETHE, and E. STENGER (*Pflüger's Archiv*, 1909, 129, 603—606).—After treatment of blood with acetylene, the pigment is apparently unaltered; chemically and spectroscopically it behaves like normal blood.

W. D. H.

The Pigment of Blood. II. So-called Hæmatopyrrolidinic Acid. OSCAR PILOTY and S. MERZBACHER (*Ber.*, 1909, 42, 3253—3258).—The oil obtained by the oxidation of hæmatopyrrolidinic acid (compare this vol., i, 539) is named provisionally *hæmopyrroline*. It is also formed together with hæmopyrrolecarboxylic acid by fusing the zinc salt of hæmatopyrrolidinic acid with potassium hydroxide at 270 — 320° , and apparently consists of a mixture of three compounds, namely: (1) an *oil*, $C_8H_{15}N$ or $C_8H_{13}N$, probably a hydrogenated hæmopyrrole, the crystalline *picrate*, $C_{14}H_{18}O_7N_4$ or $C_{14}H_{16}O_7N_4$, of which has m. p. 99 — 100° ; (2) an *oil*, $C_7H_{11}N$ (?), probably a lower homologue of hæmopyrrole; (3) an *oil* with a high b. p., having a piperidine-like odour, which is possibly a pyrogenous product and may be regarded as an impurity.

It has been shown previously (*loc. cit.*) that the hæmopyrrole and hæmopyrrolecarboxylic acid complexes are present as such in hæmatopor-

phyrin; since hæmatopyrrolidinic acid also contains the hæmopyrrole-carboxylic acid complex, it follows that hæmatoporphyrin contains two carboxyl groups. It may be assumed, therefore, that the atom of iron in hæmin and hæmatin is combined with these two carboxyl groups and with the four nitrogen groups of the four pyrrole nuclei to form a complex.

W. H. G.

The Pigment of Blood. III. New Cleavage of Hæmatoporphyrin. OSCAR PILOTY and S. MERZBACHER (*Ber.*, 1909, 42, 3258—3261. Compare preceding abstract).—It is shown that hæmopyrrole and hæmopyrrolecarboxylic acid are primary products of the degradation of hæmatoporphyrin, since the latter compound when fused with potassium hydroxide yields substances which contain carbon and hydrogen in the same proportions as hæmopyrrole and hæmopyrrolecarboxylic acid.

Hæmatoporphyrin when fused with potassium hydroxide yields an oil, termed provisionally *hp-pyrrole*, which has b. p. 70—95°/35 mm., and yields on fractionation (1) an oily substance, $C_8H_9N(?)$, probably a lower homologue of hæmopyrrole; (2) an oily substance, $C_8H_{13}N(?)$, the *picrate* of which forms large, prismatic leaflets, m. p. 126°. An *acid* is also formed simultaneously, which crystallises in colourless, odourless leaflets, m. p. about 100°, and is very similar to hæmopyrrole-carboxylic acid.

W. H. G.

The Pentose in Nucleic Acids. II. PHÆBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1909, 42, 3247—3251. Compare this vol., i, 541, 620).—The pentose derived from inosic acid, guanylic acid, and yeast nucleic acid is undoubtedly *d*-ribose, and for the following reasons: (1) It has the same m. p. and approximately the same optical rotatory power, but of the opposite sign, as *l*-ribose (compare A. van Ekenstein and Blanksma, this vol., i, 457); (2) when oxidised it yields *d*-ribotrihydroxyglutaric acid, which is obtained as its lactone (compare Fischer and Piloty, *Abstr.*, 1892, 437), and (3) the *p*-bromophenylosazone is the antipode of arabinose-*p*-bromophenylosazone.

d-Ribose-*p*-bromophenylosazone, $C_{17}H_{18}O_3N_4Br_2$, forms small, glistening, pale yellow, hexagonal plates, sinters at 175°, m. p. 180—185° (corr.), α_D in a 2-dm. tube ($c=0.1004$ gram in 5 c.c. of alcohol-pyridine, 2:3) = -0.56° (10 mins. after dissolution), -0.36° (final value); ($c=0.0499$ gram in 5 c.c. of alcohol) = -0.12° (10 mins. after dissolution), -0.08° (final value). The *additive* compound with 1 mol. of pyridine(?) forms long, slender, matted needles, sinters at 75°, and shrinks together at 80—85°.

l-Arabinose-*p*-bromophenylosazone (compare Neuberg, *Abstr.*, 1900, i, 139) forms crystals having the same appearance and m. p. as its antipode; the final values of α_D were $+0.40^\circ$ ($c=0.1$ gram in 5 c.c. of alcohol-pyridine) and $+0.09^\circ$ ($c=0.0501$ gram in 5 c.c. of alcohol).

W. H. G.

The Pentose from the Pancreas. BRUNO REWALD (*Ber.*, 1909, 42, 3134—3136).—The author's object is to settle the identity of the pentose which is extracted in the form of a protein compound when

pancreatic glands are boiled with water. The pentose is set free on hydrolysing this protein with acid, and was considered by Neuberg to be *l*-xylose. Recently, Levene has regarded it as a new pentose, carnose, or *d*-ribose (this vol., i, 447, 620). The author finds that the *p*-bromophenylosazone of the pentose, prepared from the hydrolysed pancreatic extract, is identical with *p*-bromophenyl-*l*-xylosazone. A mixture of the two substances possessed the same m. p., 204°.

R. V. S.

The Occurrence of Azelaic Acid among the Oxidation Products of Keratin. TH. LISSIZIN (*Zeitsch. physiol. Chem.*, 1909, 62, 226—228).—Small quantities of azelaic acid are formed when keratin is oxidised with potassium permanganate. From 240 grams of keratin, 0.0468 gram of the acid was obtained. The amount is about the same when horn which has been extracted with ether is used instead of keratin.

J. J. S.

Comparative Investigations on the Composition and Cleavage Products of Different Kinds of Silk. V. Monoamino-acids from Niët ngō tsám Silk from China. EMIL ABDERHALDEN and G. ALESSANDRO BROSSA. VI. Monoamino-acids from Indian Tussore Silk. EMIL ABDERHALDEN and WLADIMIR SPACK. VII. Monoamino-acids from the Gelatin (leim) of Canton Silk. EMIL ABDERHALDEN and WORMS (*Zeitsch. physiol. Chem.*, 1909, 62, 129—130, 131—132, 142—144. Compare this vol., i, 757).—The following table gives the percentages of monoamino-acids derived from the three sources above specified :

	Niët ngō tsám silk.	Indian Tussore silk.	Silk gelatin of Canton silk.
Glycine	24.0	9.5	1.2
Alanine	18.5	24.0	9.2
Leucine	1.2	1.5	5.0
Serine	1.5	2.0	5.8
Aspartic acid	2.0	2.5	2.5
Glutamic acid	3.0	1.0	2.0
Phenylalanine	1.0	0.6	0.6
Tyrosine	7.8	9.2	2.3
Proline	1.2	1.0	2.5

W. D. H.

The Products Obtained by the Partial Hydrolysis of Proteins. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1909, 62, 315—321. Compare this vol., i, 273).—By what is described as a lucky accident, it was found possible to prepare glycyl-8-tyrosine directly from the products of partial hydrolysis of silk. The hydrolysis had been carried out with 75% sulphuric acid at room temperature. Similarly, two dipeptides, one of them leucyl-glycine and the other probably glycyl-leucine, were obtained from elastin. Full details of the preparation, separation, and identification of the dipeptides are given.

W. D. H.

Hydrolysis of Wild Silk. UMETARO SUZUKI, K. YOSHIMURA, and R. INOUE (*J. Coll. Agric. Imp. Univ. Tōkyō*, 1909, 1, 59—75).—De-

terminations of nitrogen dissolved by hot hydrochloric acid, insoluble nitrogen, and ash in wild silks gave the following results :

		Dry matter.	Per cent. in dry matter.		
			Soluble N.	Insoluble N.	Ash.
1.	Antheraea Pernyi	86·84	16·39	2·48	2·92
2.	„ Yamamai ..	88·71	17·26	0·47	4·73
3.	Bombyx mori	87·10	18·86	0·12	0·63
4.	Caligula japonica	88·29	15·77	0·96	3·85

The following amounts of the various cleavage products were found (% in dry matter) :

	1.	2.	4.		1.	2.	4.
Glycine	5·7	6·3	7·7	Aspartic acid.....	1·0	1·0	0·2
d-Alanine	4·8	7·2	15·3	L-Tyrosine	1·4	2·0	5·5
L-Leucine	1·2	1·3	7·95	Histidine	2·7	1·6	1·0
Phenylalanine	—	+	+	Arginine	3·1	3·8	1·74
Proline	+	+	* 4·0	Lysine	?	7·4	2·43
Glutamic acid	+	0·6	?	Ammonia	0·6	0·8	0·8

* Active and racemic respectively.

N. H. J. M.

The Non-existence of Protagon as a Definite Chemical Compound. OTTO ROSENHEIM and M. CHRISTINE TEBB (*Quart. J. exp. Physiol.*, 1909, 2, 317—333).—A continuation of the controversy with Cramer. Fresh experimental and analytical evidence is adduced which confirms the authors' previous contention that "protagon" is not a definite chemical compound, but a mixture of various lipoids.

W. D. H.

Electrolytic Dissociation and Physiological Activity of Pepsin and Trypsin. JACQUES LOEB (*Biochem. Zeitsch.*, 1909, 19, 534—537).—The accelerating action of acids in the case of pepsin and of alkalis in the case of trypsin can be explained on the assumption that the former is a weak base and the latter a weak acid, and the addition of the acid or alkali causes the formation of salts. The salts of weak acids and bases are more strongly dissociated than the acids and bases themselves. If the enzyme action, therefore, is due to the enzyme ion, its acting mass will be greater in the presence of enzyme salts. These remarks also apply if the enzyme be of amphoteric character, as in this case the addition of acid or alkali will cause dissociation into either electronegative or electropositive ions as the case may be.

S. B. S.

Action of Trypsin on 3:5-Di-iodo-L-tyrosine. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1909, 62, 432—442. Compare this vol., i, 123).—A faintly alkaline solution of 3:5-di-iodotyrosine can be left for several weeks at 35—37° without any appreciable amount of iodine being removed, but in the presence of trypsin appreciable amounts of iodine are eliminated as hydrogen iodide. The amount varies with the specimen of pancreatin used, and in some cases is as high as 45% of the

total iodine, and the general behaviour is similar to that of iodo-thyreoglobulin.

The solutions of di-iodotyrosine which have undergone considerable decomposition do not give Millon's reaction, and it is suggested that the decomposition consists in the replacement of iodine by hydroxyl, and that the resulting α -amino- β -3:4:5-trihydroxyphenylpropionic acid is immediately oxidised.

Gorgonia corals also give up their iodine as hydriodic acid when treated with pancreatin in faintly alkaline solution (compare Drechsel, Abstr., 1896, ii, 378).
J. J. S.

Intracellular Enzymes of Lower Fungi, especially those of *Penicillium camemberti*. ARTHUR WAYLAND DOX (*J. Biol. Chem.*, 1909, 6, 461—467).—The enzymes in *Penicillium camemberti* were those specially investigated, as a contribution to the knowledge of ripening in soft cheeses. The proteolytic enzyme closely resembles erepsin; it does not act on native proteins, except on casein, but it rapidly decomposes proteoses. Nuclease, amidases (liberating ammonia from amides), an enzyme which resolves hippuric acid into benzoic acid and glycine, emulsin, amylase, inulase, raffinase, sucrase, lactase, and maltase were also found, but the presence of lipase is doubtful.
W. D. H.

Studies on Enzymes. II. Measurement and Meaning of the Concentration of the Hydrogen Ions in Enzymatic Processes. SÖREN P. L. SÖRENSEN (*Biochem. Zeitsch.*, 1909, 21, 131—304. Compare Abstr., 1908, i, 115).—A distinction has to be made between degree of acidity and the concentration of hydrogen ions, only the latter having a rôle in enzymatic decompositions. Methods for measuring the concentration of hydrogen ions, in which the concentration changes during the measurement (as in the usual acidimetric and alkalimetric titration methods), are useless, and the "catalytic" methods generally fail. Two methods are recommended, the accurate electro-method and the less exact, but very simple, colorimetric method.

The optimal concentration of hydrogen ions in invertin cleavage remains almost the same, independently of the kind and amount of the invertin and of the acid. Under the conditions employed, the optimal concentration was $p_H = 4.4$ to 4.6 .

With invertin the optimal point of the concentration of hydrogen ions moves slightly, as the duration of the experiment increases towards the alkaline side. In catalase cleavage at 0° the optimal concentration is very near the neutral point, but seems to tend towards the acid side when the time is increased.

At a temperature of 37° , the optimal concentration in pepsin cleavage distinctly depends on the time.
N. H. J. M.

Effect of Shaking on Ptyalin. MARIE M. HARLOW and PERCY G. STILES (*J. Biol. Chem.*, 1909, 6, 359—362).—Mere shaking in a bottle does not affect the activity of ptyalin, but reduction in digestive power occurs when the surface is increased by the introduction of glass

beads or glass wool. This is believed to be due to adsorption upon the glass. If ptyalin is shaken in the presence of starch, no loss of digestive power occurs; it is therefore suggested that the enzyme is protected by its substrate. A few experiments with taka-diastase gave similar results.

W. D. H.

Retarding Influence of Certain Compounds on Hydrolysis of Glucosides by Emulsin. Mlle. A. FICHTENHOLZ (*J. Pharm. Chim.*, 1909, [vi], 30, 199—204).—Attention has already been drawn to the extreme slowness with which emulsin hydrolyses arbutin (Abstr., 1908, ii, 995); this appears to be due to the retarding influence of the quinol produced during the decomposition. The addition of quinol, however, effected only a slight retardation of the hydrolysis of other glucosides, such as salicin, gentiopicrin, and amygdalin, which do not produce this substance themselves under the action of the ferment. Gallic and tannic acids exert a retarding influence on the hydrolysis of glucosides by emulsin, but the extent to which this is exhibited depends mainly on the nature of the glucoside.

W. O. W.

Influence of Salts on the Dialysis of Peroxydase. I. JAN BIELECKI (*Biochem. Zeitsch.*, 1909, 21, 103—107).—The addition of nitrates (of potassium, ammonia, and calcium) to a solution of peroxydase leads to its passing through a dialyser, in amounts roughly proportionate to the amount of salt added. Whether the nitrate acts as a kind of inorganic co-enzyme, or whether more complex questions still are involved, is left open.

W. D. H.

General Process of Oxidation by Oxidising Ferments. ÉMILE BOURQUELOT (*J. Pharm. Chim.*, 1909, [vi], 30, 101—105).—The author reviews recent work carried out by his pupils in connexion with oxidising ferments. He does not agree with the view that tyrosinase is the active substance in *Russula* extract which transforms morphine into ψ -morphine, inasmuch as gum arabic, which has no action on tyrosine, is capable of oxidising morphine. There is no evidence against the existence of two oxidising ferments, laccase and tyrosinase, and possibly a third, "morphinase," may exist (compare Bougault, Abstr., 1902, i, 638; Bertrand, this vol., i, 601).

W. O. W.

Specific Action of Oxydases. JULES WOLFF (*Compt. rend.*, 1909, 149, 467—469. Compare this vol., i, 279).—A record of observations, some of which have been published previously, which support Bourquelet's views on the existence of oxidising ferments other than laccase and tyrosinase (preceding abstract). Extract of *Russula* brings about oxidation of orcinol, and the action is accelerated by the addition of sodium hydrogen phosphate to the solution; an extract containing laccase, however, is inactive except in presence of an alkali. The specific action of the *Russula* extract depends, therefore, either on the presence of a new specific diastase, *orcinase*, or on the influence of other factors, such as the alkalinity of the medium, in conjunction with the ferments already recognised.

W. O. W.

Oxidations of Biological Importance. II. The Preparation of Pure *Medicago* Laccase and its Chemical Constitution. III. HANS EULER and IVAN BOLIN (*Zeitsch. physiol. Chem.*, 1909, 61, 1—11, 72—91. Compare Abstr., 1908, ii, 1021).—II. The chemical nature of oxydases is uncertain, although numerous views on the question have been expressed. The present research relates to laccase prepared from *Medicago sativa*; it is found to be a mixture of the calcium salts of mono-, di-, and tri-basic hydroxy-acids, among which citric, malic, mesoxalic, and probably a good deal of glycollic acids were identified.

The Rhus laccase of Bertrand is different from the *Medicago* laccase, and is differently influenced by amount of acidity and certain reagents.

III. The activity of peroxydase can be estimated by the guaiacum reaction, and the influence of acidity and various reagents on the activity of a peroxydase from *Cochlearia armoracia* was determined. Exposure to 100° for less than a minute reduces its activity by one-half.

W. D. H.

The Alcoholic Ferment of Yeast-juice. IV. The Fermentation of Dextrose, Mannose, and Lævulose by Yeast-juice. ARTHUR HARDEN and WILLIAM J. YOUNG (*Proc. Roy. Soc.*, 1909, B, 81, 336—347).—The influence of the addition of sodium phosphate on the rate of fermentation of dextrose, mannose, and lævulose by yeast-juice was investigated, and it was found that mannose behaves both in the presence and absence of phosphates in the same way as dextrose; lævulose, on the other hand, is fermented much more rapidly in the presence of phosphates, and the optimum concentration of these salts is higher. Lævulose has the property of inducing fermentation in solutions of dextrose and mannose which contain such an excess of phosphate that the fermentation is only proceeding very slowly. No similar property is possessed by dextrose or mannose.

S. B. S.

Attempts to Explain Cell-free Fermentation by means of Experiments with the Ultra-filter. A. VON LEBEDEFF (*Biochem. Zeitsch.*, 1909, 20, 114—125).—The author has already shown that the rates of disappearance of sugar and formation of carbon dioxide during fermentation are not parallel (*ibid.*, 1908, 10, 456), and that sugar partly disappears when co-enzyme-free inactive expressed yeast-juice is employed. Further experiments have been made in which the co-enzyme has been separated by means of the Bechhold ultra-filter. The experiments showed that in the residue from the filtration (filtrans), sugar disappeared without appearance of the corresponding amount of carbon dioxide; the reducing power of the filtrate, on the other hand, remained unchanged even after eight days. A certain amount of phosphoric acid could be set free by hydrolysis, and in the filtrans the amount of sugar which could be set free by hydrolysis decreased with time, whereas in the case of the non-filtered juice it increased. These facts indicate that some form of sugar ester is formed as an intermediate product. The hot-water extract of yeast-juice was therefore subjected to ultra-filtration, and to the filtrate acetone was added. From the precipitate, which yielded phosphoric acid on hydrolysis, a precipitate with phenylhydrazine was obtained (m. p. 148—149°). Other derivatives were

also prepared, of which the preliminary investigation led to the surmise that this filtrate contains a phosphoric acid ester of dextrose, which is regarded as an intermediate product in sugar fermentation.

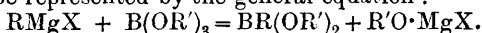
S. B. S.

α -Siliconaphthoic Acid. EUGEN KHOTINSKY (*Ber.*, 1909, 42, 3088—3089. Compare Abstr., 1908, i, 1032).— α -Siliconaphthoic acid has m. p. 138° after sintering at 133° . The m. p. previously given (239°) is incorrect (compare Melzer, Abstr., 1908, i, 967); ethyl ortho- α -siliconaphthoate has b. p. $174\text{—}177^\circ/15\text{—}18$ mm.

J. J. S.

Action of Organo-magnesium Compounds on Boric Esters. EUGEN KHOTINSKY and M. MELAMED (*Ber.*, 1909, 42, 3090—3096).—Organo-magnesium compounds react with alkyl borates in much the same manner as with the ortho-esters of silicic acid (Abstr., 1908, i, 1032), only more readily.

The boric esters are best prepared by the action of alcohol on boric anhydride under pressure. The reaction with the magnesium compounds may be represented by the general equation:



The resulting esters of alkylated boric acids are readily hydrolysed: methyl and ethyl esters by cold water, the *iso*amyl and *isobutyl* esters by warm water. The best yields of arylboric acids are obtained when *isobutyl* borate reacts with aryl magnesium halides, but the best yields of aliphylboric acids are obtained when methyl borate is used. These aliphylboric acids are unstable and excessively volatile. The methyl derivative, $BMe(OH)_2$, is so unstable that so far it has not been isolated in a pure state.

It has been noticed that methyl borate has a methylating action on magnesium phenyl bromide, the products consisting of toluene and phenylboric acid (compare Michaelis and Becker, Abstr., 1880, 396). *iso-Butyl phenylborate*, $BPh(O \cdot C_4H_9)_2$, is a colourless liquid, b. p. $180\text{—}187^\circ/30\text{—}35$ mm.

m-Tolylboric acid, $C_6H_4Me \cdot B(OH)_2$, has m. p. $137\text{—}140^\circ$, and the *isobutyl* ester, has b. p. $195\text{—}207^\circ/66$ mm. The acid reacts with a concentrated mercuric chloride solution, yielding *m*-tolyl mercuric chloride, $C_6H_4Me \cdot Hg \cdot Cl$.

iso-Butyl benzylborate, $CH_2Ph \cdot B(O \cdot C_4H_9)_2$, has b. p. $189\text{—}196^\circ/36$ mm., and *benzylboric acid*, $CH_2Ph \cdot B(OH)_2$, m. p. 161° .

Ethylboric acid (Frankland, *Annalen*, 1862, 124, 142) sublimes readily at 40° , and has a sweet taste. *Propylboric acid*,



has m. p. $74\text{—}75^\circ$; *isobutylboric acid*, $CHMe_2 \cdot CH_2 \cdot B(OH)_2$, m. p. 104° , and *isoamylboric acid*, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot B(OH)_2$, m. p. 101° . Ammonium and sodium salts have been prepared from some of the acids; the ammonium salts are unstable, and readily evolve ammonia.

J. J. S.

Organic Chemistry.

Action of Metallic Magnesium on Acetylene. J. NOVÁK (*Ber.*, 1909, 42, 4209—4213).—When magnesium powder is heated in a stream of pure acetylene, reaction begins to take place at a temperature of about 450°, carbon being deposited, and a mixture of magnesium acetylide and allylide formed. The product formed reacts violently with water, a mixture of acetylene and allylene being evolved. These two gases were identified by making various derivatives.

T. S. P.

Aliphatic Compounds of Polyvalent Iodine. III. Derivatives of Ethylene with Tri- and Quinqui-valent Iodine. JOHANNES THIELE and HERMANN HAAKH (*Annalen*, 1909, 369, 131—147. Compare *Abstr.*, 1905, i, 735; this vol., i, 879).—Iodochlorides and the corresponding iodoso-derivatives may be readily obtained from $\alpha\beta$ -di-iodoethylene and α -chloro- β -iodoethylene, the compounds derived from the latter being far more stable than those prepared from the former. Iodosochloroethylene when boiled with water yields chloroiodoxyethylene, the first iodoxy-compound in the aliphatic series to be prepared.

Attempts to prepare bischlorovinylidonium hydroxide by the action of silver oxide or alkali oxides on a mixture of iodoso- and iodoxy-chloroethylene were unsuccessful. Willgerodt and his co-workers (*Abstr.*, 1895, i, 635; 1900, i, 338, 432; 1902, i, 17, 18; 1904, i, 483, 657) have shown that aliphatic-aromatic iodonium salts may be prepared by the action of aromatic iodochlorides on acetylene silver chloride; for example, phenyl iodochloride is said to react with acetylene silver chloride, yielding phenyldichloroethylidonium chloride. It is found, however, that chloroethylene iodochloride reacts with acetylene silver chloride, yielding dichlorovinylchlorovinylidonium chloride, and not dichloroethylchlorovinylidonium chloride, as would be expected if the reaction follow the course depicted by Willgerodt. The work of this author was repeated, therefore, with the result that the compounds described by him as dichloroethylidonium compounds are found to be dichlorovinyl compounds.

Experiments which were performed with the object of preparing iodochlorides from acetyl iodide and benzoyl iodide led only to the discovery of a better method of preparing the first-named substance. Benzoyl iodide cannot be prepared in the manner described by Liebig and Wöhler; it is probable that this compound has not yet been prepared.

Iodoethylene iodochloride, $\text{CHI}:\text{CH}\cdot\text{ICl}_2$, prepared by passing chlorine into a solution of di-iodoethylene in chloroform cooled in a freezing mixture, crystallises in lemon-yellow needles and decomposes at about 37°; it is very unstable, and cannot be kept; when treated with a

cold 20% aqueous solution of sodium carbonate, it yields β -iodo- α -iodosoethylene, $\text{CHI}:\text{CH}\cdot\text{IO}$, a very unstable, slightly yellow, amorphous substance, which explodes slightly at about 62° .

Chloroethylene iodochloride, $\text{CHCl}:\text{CH}\cdot\text{ICl}_2$, crystallises in lemon-yellow needles, m. p. $75-77^\circ$, and is converted by a 20% aqueous solution of sodium carbonate into β -chloro- α -iodosoethylene, $\text{CHCl}:\text{CH}\cdot\text{IO}$, an unstable, amorphous, pale yellow powder, which explodes at about 63° , and forms an *acetate*, $\text{CHCl}:\text{CH}\cdot\text{I}(\text{OAc})_2$, colourless leaflets, m. p. 96° , and *chromate*, an unstable, yellow powder. β -Chloro- α -iodoxyethylene, $\text{CHCl}:\text{CH}\cdot\text{IO}_2$, prepared by treating chloroethylene iodochloride with water at $72-75^\circ$, forms white crystals, which explode with great violence at 135° , also when struck or rubbed on a porous plate; it is decomposed by aqueous sodium hydroxide and by water at 100° , yielding acetylene.

Dichlorovinylchlorovinylidonium chloride, $\text{CHCl}:\text{CH}\cdot\text{ICl}\cdot\text{CCl}:\text{CHCl}$, crystallises in short, white needles, and decomposes at 207° ; the following salts are obtained from the chloride by double decomposition: *aurichloride*, $\text{C}_4\text{H}_3\text{Cl}_3\text{I}\cdot\text{AuCl}_4$, golden-yellow needles, m. p. 111° (decomp.); *platinichloride*, $(\text{C}_4\text{H}_3\text{Cl}_3\text{I})_2\text{PtCl}_6$, brownish-red granules, m. p. $93-94^\circ$ (decomp.); *bromide*, white powder, volatile at about 200° (decomp.); *iodide*, white powder, which rapidly turns yellow, m. p. 97° (decomp.).

Phenyldichlorovinylidonium bromide, $\text{C}_6\text{H}_5\text{Cl}_2\text{I}\cdot\text{Br}$, is a white powder, volatile at 162° (decomp.). W. H. G.

Aliphatic Compounds of Polyvalent Iodine. IV. Decomposition of Aliphatic and Aliphatic-Aromatic Iodonium Compounds. JOHANNES THIELE and ANNA UMNOFF (*Annalen*, 1909, 369, 147—149).—Phenyldichlorovinylidonium bromide, when heated at 180° , decomposes into iodobenzene and $\alpha\beta$ -dichloro- α -bromoethylene, and, when acted on by cold dilute aqueous sodium hydroxide, yields chloroacetylene, iodobenzene, and hypochlorous acid.

Dichlorovinylchlorovinylidonium bromide decomposes in an analogous manner when treated similarly. W. H. G.

Aliphatic Compounds of Polyvalent Iodine. V. Simple Alkyl Iodochlorides. JOHANNES THIELE and WILLI PETER (*Annalen*, 1909, 369, 149—156).—An account of part of the work described in this paper has already appeared (compare Abstr., 1905, i, 735).

The first representative of a new class of compounds, namely, *methyl iodobromide*, $\text{CH}_3\cdot\text{IBr}_2$, has been prepared by the action of bromine on methyl iodide in light petroleum at about -70° ; it crystallises in glistening, orange-yellow leaflets, and decomposes at about -45° . *Phenyl iodobromide* appears to be formed by acting on iodobenzene with bromine in light petroleum.

Alkyl iodides also combine with iodine at very low temperatures, yielding brown, crystalline *polyiodides*, probably tri-iodides, RI_3 .

Ethyl iodochloride is a faintly yellow substance, which decomposes at -36° . Methylene iodide dichloride, $\text{CH}_2\text{I}\cdot\text{ICl}_2$, is a yellow powder, and decomposes at -11.5° . W. H. G.

Reactions of Hypohalites with Organic Compounds. Reactions with Derivatives of Methane. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1909, 31, 1220—1233).—Although numerous reactions between hypohalites and organic compounds have been recorded, there has not hitherto been any attempt made to study the whole subject systematically. The author has therefore undertaken an investigation with the object of elucidating the mechanism of the reaction between hypohalites and organic compounds generally. The present paper gives an account of experiments made with compounds containing one atom of carbon.

It is shown that these reactions cannot be explained on the basis of ionisation or of methylene dissociation, but that they can be satisfactorily accounted for by the author's theory of molecular coalescence (*Abstr.*, 1908, i, 721).

Methane is not affected by sodium hypobromite at the ordinary temperature. Methyl iodide reacts with sodium hypobromite with formation of sodium iodide, iodate, periodate, formate, and carbonate, and the sodium formate, if left for some days with excess of the hypobromite, is completely oxidised to the carbonate according to the equations: $\text{CH}_3\text{I} + 2\text{NaOBr} + 2\text{NaOH} \rightarrow \text{H}\cdot\text{CO}_2\text{Na} + \text{NaI} + 2\text{NaBr} + \text{H}_2\text{O}$ and $\text{H}\cdot\text{CO}_2\text{Na} + \text{NaOBr} + \text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{NaBr} + \text{H}_2\text{O}$. The sodium iodide is oxidised by the hypobromite to the iodate and periodate. The formation of the formate and carbonate is explained thus



The following reactions show that the hypohalites afford a general method of formation of tetrahalogenmethanes. Chloroform reacts with sodium hypochlorite with production of sodium chloride formate, and carbonate, and carbon tetrachloride. A similar reaction takes place with sodium hypobromite, with formation of trichlorobromomethane and small quantities of dichlorodibromomethane and tetrabromomethane. With sodium hypoiodite, trichloriodomethane and dichlorodi-iodomethane are produced.

Bromoform, when treated with sodium hypochlorite, yields chlorotribromomethane, tetrabromomethane, and possibly dichlorodibromomethane, whilst with sodium hypobromite, it gives tetrabromomethane. When iodine is added gradually to a mixture of bromoform and sodium hydroxide solution, *tribromoiodomethane* is obtained as a golden-yellow, crystalline precipitate, which darkens and decomposes at 35°; if a large quantity of iodine is used, iodoform and tetraiodomethane are also produced.

Iodoform reacts with sodium hypochlorite to form a mixture of brick-red and white crystals, which could not be purified. With sodium hypobromite, it yields *bromotri-iodomethane*, m. p. 113°, as a brick-red, amorphous solid.

When sodium hypobromite is added to a dilute aqueous solution of methyl alcohol, tetrabromomethane is immediately precipitated; this reaction can be employed for the detection of wood-spirit in methylated spirit and other mixtures. If an excess of dilute methyl alcohol is added gradually to the hypobromite solution, bromoform and tetrabromomethane are produced. On adding the hypobromite to ex-

cess of dilute methyl alcohol and distilling the mixture, methylal is obtained in the distillate, showing that formaldehyde is formed as an intermediate product of the reaction between methyl alcohol and the hypobromite. When a solution of methyl alcohol containing potassium iodide is treated with sodium hypobromite, iodoform, tetraiodomethane, and formic acid are produced.

Formaldehyde and trioxymethylene are converted by sodium hypobromite into sodium formate or carbonate, depending on the quantity of the hypobromite added. Formic acid is converted by the reagent into sodium carbonate.

Carbon disulphide reacts with sodium hypobromite to form sodium sulphide, sulphate, formate, and carbonate.

Potassium cyanide is oxidised by sodium hypobromite with formation of cyanate, formate, and carbonate. When potassium cyanate is treated with the reagent, nitrogen is slowly evolved, and formate and carbonate are produced. Potassium thiocyanate gives sulphate and cyanate. Sodium ferrocyanide is converted into the ferricyanide. When sodium ferricyanide is boiled with sodium hypobromite, a deep brownish-red precipitate is obtained, consisting of a mixture of a basic ferric formate and ferric oxide.

When methylamine is treated with the hypobromite, nitrogen is slowly evolved and tetrabromomethane is produced, methyl-bromoamine or -dibromoamine being formed as an intermediate product. Schestakoff (Abstr., 1905, i, 332) has shown that when sodium hypochlorite reacts with carbamide, hydrazine is formed as an intermediate compound. It is pointed out that the formation of this substance can be easily explained as follows: $(\text{NH}_2)_2\text{C}:\text{O}:\text{Br}\cdot\text{ONa} \rightarrow (\text{NH}_2)_2\text{C}(\text{OBr})\cdot\text{ONa} \rightarrow \text{N}_2\text{H}_4 + \text{CO}_2 + \text{NaBr}$. Ammonia, like carbamide, gives a quantitative yield of nitrogen. Guanidine and semicarbazide yield about two-thirds of their nitrogen, whilst urethane furnishes only a very small quantity of the gas. It is evident from these reactions that the evolution of nitrogen is not determined merely by the presence of an amino-group, but that it depends very largely on the other groups in the compound. The dissimilarity of the reactions with these amino-compounds can be best explained by assuming the formation of different aggregates, such as $\text{NH}_3\text{Br}(\text{ONa})$, $\text{OH}\cdot\text{NH}_2\text{Br}(\text{ONa})$, and $\text{NH}_2\text{MeBr}(\text{ONa})$, which vary in stability or in the way in which they decompose.

E. G.

Specific Gravities of Alcoholic Solutions. I. Mixtures of Methyl Alcohol with Water. ANTONY G. DOROSCHEWSKY and M. S. ROSCHDESTVENSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 977—996).—After reviewing previous work on the specific gravities of methyl alcohol and its aqueous mixtures, the authors give the results of their determinations at 15°/15° for a series of twenty-five mixtures varying in concentration from 0% to 100%. From these results they calculated the values of D_{15}^{15} for each integral percentage of alcohol from 0 to 100 in two different ways: (1) by graphic interpolation, and (2) by means of the contraction occurring on mixing. The mean difference between the two sets of numbers thus obtained is 0.00002. For absolute methyl alcohol, D_{15}^{15} has the value 0.79647 (compare

Young and Fortey, *Trans.*, 1902, **81**, 735 ; Klason and Norlin, *Abstr.*, 1906, **i**, 921).
T. H. P.

Electrolytic Oxidation of Ethyl Alcohol to Acetic Acid. PAUL ASKENASY, R. LEISER, and N. GRÜNSTEIN (*Zeitsch Elektrochem.*, 1909, **15**, 846—860).—The experiments are made with the object of testing the economic possibility of the process. Using platinum gauze electrodes 3 mm. apart, and a solution containing about 190 grams of alcohol and 27 to 30 grams of sulphuric acid in 750 c.c., it is found that a current density of about 0.2 ampere per sq. cm. can be maintained with 4.5 volts. At first considerable quantities of ethyl acetate are formed, but as the alcohol is oxidised by electrolysis, this diminishes. Aldehyde also escapes, and is condensed in a small subsidiary cell and there oxidised. The yield appears to be rather better at 30° or 40° than it is at lower temperatures. In the best circumstances the current efficiency is about 78%, and the yield on the alcohol about 80%. Other experiments made with a cheap 8% alcohol obtained by the direct fermentation of the expressed juice of sugar beets gave even better results ; a little chromium sulphate was added to the solution to act as an oxygen carrier.
T. E.

Ether-like Compounds. I. Ether Alcohols of the Type $R \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$. M. H. PALOMAA (*Ber.*, 1909, **42**, 3873—3878).—To prepare ethylene glycol monomethyl ether, $OMe \cdot CH_2 \cdot CH_2 \cdot OH$, sodium is dissolved in ethylene glycol under special conditions, the sodium glycol oxide brought into reaction with methyl iodide, and the product purified by fractional distillation. It has b. p. 124.9°/767.5 mm., is a colourless liquid with an odour resembling impure methyl alcohol, and is miscible with water ; D_{15}^{15} 0.96928. The *acetate*, $OMe \cdot CH_2 \cdot CH_2 \cdot OAc$, has b. p. 144.5—145° ; the *propionate*, $OMe \cdot CH_2 \cdot CH_2 \cdot O \cdot COEt$, has b. p. 159.56°/741.9 mm., D_{15}^{15} 0.9867. The *butyrate* has b. p. 177.5°/767.8 mm. The *benzoate*, $OMe \cdot CH_2 \cdot CH_2 \cdot OBz$, has b. p. 254—256°/760 mm., D_{15}^{15} 1.1067.

Ethylene glycol monoethyl ether, $OEt \cdot CH_2 \cdot CH_2 \cdot OH$, prepared similarly to the methyl derivative, has b. p. 134.8°/748 mm., D_{15}^{15} 0.93535, agreeing with the constants given by Demole (*Ber.*, 1876, **9**, 745). *Ethylene glycol monopropyl ether*, $OPr \cdot CH_2 \cdot CH_2 \cdot OH$, has b. p. 150.2°/753 mm., D_{15}^{15} 0.91432. *Ethylene glycol monoallyl ether*, $CH_2 \cdot CH \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$, has b. p. 159°/755 mm., D_{15}^{15} 0.96095.

The acetic, propionic, butyric, *isobutyric*, and benzoic acid esters of the last three glycol ethers are colourless liquids, easily obtained by the pyridine method, and distil without decomposition with the exception of the esters of the monoallyl ether.
E. F. A.

Purification of Glycerol Dinitrate. CONRAD CLAESSEN (*D.R.-P.* 210990).—When glycerol dinitrate is exposed for some hours in an atmosphere containing 70—80% of moisture (or treated with damp infusorial earth), frozen, and triturated with a glass rod, a crystalline *hydrate*, $3C_3H_5(OH)(ONO_2)_2 \cdot H_2O$, colourless prisms, m. p. 25°, is formed ;

when heated at 40° it loses its water of crystallisation, regenerating liquid glycerol dinitrate.

F. M. G. M.

Lipoids. VII. Kephalin. SIGMUND FRÄNKEL and ERNST NEUBAUER (*Biochem. Zeitsch.*, 1909, 21, 321—336).—The kephalin was prepared by extracting human brains, dried rapidly at 100°, first with cold and then with hot alcohol. The residue was extracted with light petroleum, and alcohol was then added to this solution after concentration. The precipitate thus formed was extracted with hot alcohol, and then redissolved in hot petroleum, from which a galactoside separated on cooling; this was separated by centrifuging, and the kephalin was then precipitated from the solution by alcohol. From the crude kephalin, purer preparations were made (I) by suspending the crude substance in water, with which it forms a mucilagenous solution, and precipitating therefrom with hydrochloric acid and hardening the precipitate with acetone; (II) by repeated solution of this precipitate in light petroleum and precipitation therefrom with alcohol; (III) by precipitation of the mucilagenous aqueous solution with sodium sulphate. The kephalin forms with water a colloidal solution, from which it can be precipitated by various salts, the precipitating power of several of which has been quantitatively investigated by the author. The purest preparation contained 62.05% C, 9.85% H, 1.69% N, 3.45% P, and 1.86% CH₃ (determined by the method of Herzg and Mayer). The ratio of P:N:CH₃ according to these numbers is 1:1.07:0.98. The melting point of this preparation was 175°; it was laevorotatory and unsaturated (iodine number = 280).

S. B. S.

Lipoids. VIII. The Scission Products of Kephalin. SIGMUND FRÄNKEL and LUDWIG DIMITZ (*Biochem. Zeitsch.*, 1909, 21, 337—347).—The hydrolysis was carried out with alcoholic hydrochloric acid. As products of hydrolysis were obtained: acids, which probably consisted of a mixture of palmitic and stearic acids; and a glycerophosphoric acid, which was dextrorotatory, and differs in this respect from the glycerophosphoric acid from egg-lecithin, which is laevorotatory.

S. B. S.

Electrolysis of Carboxy-acids. FELIX KAUFLEDER and C. HERZOG (*Ber.*, 1909, 42, 3858—3873).—Three different theories have been put forward to account for the formation of ethane in the electrolysis of solutions of sodium or potassium acetate, namely: (1) the discharged acetanion breaks up into carbon dioxide and methyl, two methyls then uniting to form ethane (Abstr., 1891, 1192); (2) two discharged acetanions combine to form acetyl peroxide, which then breaks up into ethane and carbon dioxide (Abstr., 1897, i, 317); (3) two discharged acetanions form acetic anhydride and oxygen, and then further changes take place, resulting in the formation of ethane and carbon dioxide. The authors produce evidence in favour of the first theory.

A solution of potassium acetate, containing either free iodine or potassium iodide, was electrolysed in a divided cell, and the anode gases could be passed over moist red phosphorus in order to absorb

any iodine carried over, and then through an alcoholic solution of dimethylaniline, which, if the methyl radicle is liberated, would be converted into phenyltrimethylammonium iodide. This compound was actually obtained by the authors. It is further shown that the methyl iodide did not result from an iodoacetic acid which might be formed as an intermediate product of the electrolysis of the above solution. Prolonged electrolysis of a solution of potassium acetate containing iodine did not give rise to iodoacetic acid.

The second theory was disproved by submitting acetyl peroxide to the action of iodine; methyl iodide was not formed. Foerster and Piguet (Abstr., 1904, i, 965) were in favour of this theory, because they found that there was a considerable anodic resistance to the passage of the current, but by experiments on the electrolysis of sulphuric acid solutions the authors show that this is a characteristic of platinum electrodes (anode or cathode), and not of an acetate electrolyte.

The third theory is untenable, because, according to it, the oxidation or introduction of halogen would be expected to take place to a much greater extent than is actually the case.

The electrolysis of a solution of sodium chloroacetate gave rise to the anodic formation of chlorine, carbon monoxide, carbon dioxide, and hydrogen chloride; as subsidiary products were also formed methylene chloride and chloromethyl chloroacetate. The mechanism of the reaction is probably as follows: the discharged chloroacetanion decomposes, for the most part, into carbon monoxide, chlorine, and formaldehyde. The hydrogen chloride is then produced by the action of chlorine on the formaldehyde or the carbon monoxide. Carbon dioxide also results from the ordinary decomposition of the discharged chloroacetanion; this would leave the residue CH_2Cl , which either combines with chlorine to form methylene chloride, or with the residue $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{O}$ to form chloromethyl chloroacetate. This latter compound separates as a heavy oil during the electrolysis. Formaldehyde was also identified. No trace of ethylene dichloride was found.

Electrolysis of a solution of sodium bromoacetate gave rise to the anodic formation of bromine, carbon monoxide, carbon dioxide, and oxygen as primary products. Methyl bromide was also isolated, and also small quantities of an oil, which was probably bromomethyl bromoacetate.

In the electrolysis of sodium iodoacetate, the only non-gaseous products which could be isolated were iodine and methylene iodide.

From sodium dichloroacetate, dichloromethyl dichloroacetate was obtained, which distilled at $93\text{--}95^\circ/33\text{ mm.}$; $D_4^{20} 1.588$. In the electrolysis of salts of the aromatic acids, the discharged anion regenerates the acid. In order to see if the difference in behaviour from that of the aliphatic acids is due to the stronger acid character of the phenyl group, or to a special chemical influence of this group, the potassium salt of *p*-dimethylaminobenzoic acid was electrolysed; the acid was regenerated. The acid is also regenerated from the salts of phenylacetic and acetylmandelic acids. Walker (Trans., 1896, 69, 1279) obtained hydrobenzoin by the electrolysis of mandelic acid,

but, since he worked without a diaphragm, it was probably formed by the interaction of the anodic and cathodic products.

Acetylmandelic (α -acetoxyphenylacetic) acid was prepared from acetic anhydride and mandelic acid. It crystallises with $\frac{1}{2}$ H₂O, and has m. p. 52°, or when anhydrous, m. p. 76°. T. S. P.

Salts of an Acetatoferri-base and of Two Acetatochromi-ferri-Bases. III. RUDOLF F. WEINLAND and E. GUSSMANN (*Ber.*, 1909, 42, 3881—3894. Compare Abstr., 1908, i, 847; this vol., i, 757).—Acetatoferri-salts have now been prepared of similar composition to the acetatochromo-salts previously described. Solutions of chromic acid and ferric chloride in acetic acid also yield mixtures of salts of bases containing both chromium and iron. All the salts of these bases with any given acid are isomorphous, and some of the salts previously described are certainly isomorphous mixtures. The dichroism observed in certain cases is a sign of the presence of isomorphous mixtures.

Of the triferri-base, the following salts have been prepared: dichromate-acetate, $\left[\text{Fe}_3 \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \text{Cr}_2\text{O}_7$, formerly described as containing only 1 H₂O. The *mono-acetate*, $\left[\text{Fe}_3 \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \text{OAc} \cdot \text{H}_2\text{O}$, obtained by dissolving ferric hydroxide, freshly precipitated in the cold, in 95% acetic acid, and evaporating over sulphuric acid, forms dark orange, rhombic leaflets, slowly soluble in cold water, rapidly in hot, sparingly soluble in glacial acetic acid. The *diacetate*, $\left[\text{Fe}_3 \begin{smallmatrix} (\text{OAc})_6 \\ \text{OH} \end{smallmatrix} \right] (\text{OAc})_2$, prepared by heating the mono-acetate with excess of acetic acid to boiling for twelve hours, forms minute, orange tablets. The *platinichloride*, $\left[\text{Fe}_3 \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \frac{1}{2} \text{PtCl}_6 \cdot 5\text{H}_2\text{O}$, prepared by adding platinic chloride to a solution of the mono-acetate, forms minute bundles of prisms, soluble in water. The *stannichloride*, $\left[\text{Fe}_3 \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \frac{1}{2} \text{SnCl}_6 \cdot 5\text{H}_2\text{O}$, prepared from the acetate and sodium chlorostannate, is similar in character, whilst the *nitrate*, $\left[\text{Fe}_3 \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \text{NO}_3 \cdot 4\text{H}_2\text{O}$, from the acetate and lithium nitrate, forms minute, orange tablets.

Salts of the dichromiferri-base are prepared by mixing the two hydroxides in the required proportions, dissolving in acetic acid, and precipitating. The *platinichloride*, $\left[\text{Cr}_2\text{Fe} \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \frac{1}{2} \text{PtCl}_6 \cdot 5\text{H}_2\text{O}$, forms minute, reddish-violet prisms, and the *stannichloride* resembles it closely. The *chloride*, $\left[\text{Cr}_2\text{Fe} \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \text{Cl} \cdot 6\text{H}_2\text{O}$, obtained by the aid of lithium chloride, crystallises from water containing lithium chloride in rhombic, violet prisms. The *chromate*, $\left[\text{Cr}_2\text{Fe} \begin{smallmatrix} (\text{OAc})_6 \\ \text{OH} \end{smallmatrix} \right] \text{CrO}_4 \cdot 4\text{H}_2\text{O}$, forms large, black plates.

The *mono-acetate* of the chromidiferri-base, $\left[\text{CrFe}_2 \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \text{OAc} \cdot \text{H}_2\text{O}$,

forms sparingly soluble, microscopic, brownish-red leaflets. The *platinichloride*, $\left[\text{CrFe}_2 \begin{pmatrix} \text{OAc} \\ \text{OH} \end{pmatrix}_6 \right] \frac{1}{2} \text{PtCl}_6 \cdot 5\text{H}_2\text{O}$, is brownish-red, and the *chloride*, $\left[\text{CrFe}_2 \begin{pmatrix} \text{OAc} \\ \text{OH} \end{pmatrix}_6 \right] \text{Cl} \cdot 8\text{H}_2\text{O}$, forms black prisms.

The aqueous solutions of all these salts have an acid reaction. In the presence of ferric chloride, ferrichlorides are formed. Ammonia does not precipitate iron or chromium from the solutions unless heated.

The characteristic colours of these salts (deep violet for the Cr_2Fe and reddish-brown for the CrFe_2 salts) indicate that they are not isomorphous mixtures of salts of the green Cr_3 and red Fe_3 bases.

C. H. D.

Ethyl Acetate. JOSEF HABERMANN and H. BREZINA (*J. pr. Chem.*, 1909, [ii], 80, 349—354).—A mixture of 400 grams of 96 volume % alcohol, 240 grams of glacial acetic acid, and 160 grams of anhydrous copper sulphate is kept at the ordinary temperature for twenty-four hours, and is then heated for twelve to fourteen hours on the water-bath, in both cases with frequent shaking. The liquid is decanted from the copper sulphate, heated again for ten hours with another 50 grams of anhydrous copper sulphate, and then distilled after the removal of the metallic salt. The distillate is fractionally distilled, and the main fraction, b. p. $70-72^\circ$, is repeatedly washed with saturated brine, dried by ignited magnesium sulphate, and again distilled. The distillate has b. p. $70-72^\circ$, and a vapour density corresponding with that of an equimolecular compound of ethyl alcohol and ethyl acetate. By prolonged shaking with calcium chloride, the ethyl alcohol seems to be removed, for the liquid now has b. p. 77° and a vapour density corresponding with that of ethyl acetate.

A small quantity of the same compound, b. p. $70-72^\circ$, can be isolated from commercial ethyl acetate by systematic fractionation.

C. S.

Production of Alkyl Chloroacetates from Dihalogenated Vinyl Ethers. GEORGES IMBERT and CONSORTIUM FÜR ELEKTRO-CHEMISCHE INDUSTRIE (D.R.-P. 212592. Compare this vol., i, 453, 694).—The reaction between dihalogenated vinyl ethers and alcohol takes place at the ordinary temperature in the absence of moisture and in the presence of a catalyst, such as aluminium chloride. Methyl chloroacetate is prepared from dichlorovinyl ether and methyl alcohol, and ethyl bromoacetate from dibromovinyl ether and alcohol.

F. M. G. M.

Some Organic Compounds of Glucinum. CHARLES L. PARSONS and GEORGE J. SARGENT (*J. Amer. Chem. Soc.*, 1909, 31, 1203—1206).—It has been shown by Parsons (Abstr., 1905, ii, 34; 1906, i, 479; 1908, ii, 105) that a definite compound cannot be obtained by saturating an acid with glucinum hydroxide or carbonate. The so-called basic salts obtained in this way are not definite compounds, but consist of solid solutions of the normal salts in the hydroxide.

Glassmann (Abstr., 1908, i, 120) and Tanatar and Kurovski (Abstr., 1908, i, 166) have described a number of glucinum compounds with organic acids. A study has now been made of all the salts which these authors prepared by saturating the acid with glucinum hydroxide or carbonate, and it is shown that the supposed compounds are merely indefinite mixtures or solid solutions.

A crystalline *trichloroacetate*, $\text{Gl}(\text{C}_2\text{O}_2\text{Cl}_3)_2 \cdot 2\text{H}_2\text{O}$, can be obtained by dissolving glucinum carbonate in excess of trichloroacetic acid.

Normal glucinum salts of acids having a much lower ionisation constant than that of oxalic acid have not been made, and it is improbable that a sufficiently high concentration of hydrogen ions can be obtained to enable them to separate as definite compounds from aqueous solutions. E. G.

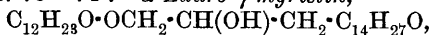
Aliphatic Nitro-compounds. VI. Free Nitroacetic Acid. WILHELM STEINKOPF (*Ber.*, 1909, 42, 3925—3929. Compare this vol., i, 216, 559).—It is possible to prepare the sodium or potassium salts of nitroacetic acid in one operation from nitromethane by the action of sodium or potassium hydroxide. Nitromethane is allowed to drop into the alkali, and the mixture ultimately boiled for ten minutes. On cooling, the nitroacetate crystallises.

Nitroacetic acid, $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, is obtained by acting on a finely divided suspension of potassium nitroacetate in dry ether with dry hydrogen chloride gas, removal of the salt by filtration, and evaporation of the ether. Nitroacetic acid may be crystallised from chloroform or benzene without decomposition in long needles, m. p. 87—89° (slight decomp.). Larger quantities explode when melted. The acid is rapidly decomposed by water into carbon dioxide and nitromethane, but it can be in part recovered from aqueous solution if this be rapidly extracted with ether. It forms colourless, crystalline salts with primary amines. *Aniline nitroacetate* yields silvery, glistening plates; *phenylhydrazine nitroacetate* has m. p. 58° (decomp.). Attempts to prepare nitroacetyl chloride were not successful. E. F. A.

Synthesis of the Triple Mixed Glycerides. ADOLF GRÜN and A. VON SKOPNIK (*Ber.*, 1909, 42, 3750—3759).—An account of the synthesis of glycerides containing three different acid groups, namely, those derived from lauric, myristic, and stearic acids.

α -Chlorohydrin and lauryl chloride yield *γ -lauro- α -chlorohydrin*, $\text{CH}_2\text{Cl} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_{12}\text{H}_{23}\text{O}$, a pale yellow, mobile oil. *γ -Lauro- $\alpha\beta$ -dichlorohydrin*, obtained by boiling the laurochlorohydrin, dissolved in carbon tetrachloride, with phosphorus pentachloride in a current of hydrogen, is a bright yellow, fairly mobile liquid. The dichlorohydrin produced on saponifying it with alcoholic potash could not be identified, but the constitution of the substance follows from its conversion by the action of silver nitrite (compare Abstr., 1907, i, 464) into *α -monolaurin*, $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_{12}\text{H}_{23}\text{O}$, which forms shining laminae of m. p. 52°. When the substance has solidified after fusion, it has m. p. 40—41°. It does not give a phenylurethane with phenylcarbimide, thus differing from β -monolaurin. *β -Monolaurin*, from *β -lauro- $\alpha\gamma$ -dichlorohydrin*, has m. p. 58.5°. *β -Monolaurin phenyl-*

carbamate (from β -monolaurin and phenylcarbimide) forms white crystals of m. p. 73—74°. *a*-Lauro- γ -myristin,



is prepared by heating together at 140° γ -lauro- α -chlorohydrin and potassium myristate. It forms very small, white crystals, m. p. 40—42°, or, after having been once melted, 34—35°. *a*-Lauro- γ -myristo- β -stearin, $\text{C}_{12}\text{H}_{23}\text{O} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{O} \cdot \text{C}_{18}\text{H}_{35}\text{O}) \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_{14}\text{H}_{27}\text{O}$, is formed by heating the preceding compound with the calculated amount of stearyl chloride for one hour on the water-bath. It forms small, white, very soft crystals, m. p. 37—38°, or, after having been melted, 35°. *a*-Stearo- γ -chlorohydrin (from stearyl chloride and α -chlorohydrin) forms white, granular crystals, m. p. 48—49°, or, after having been fused, 39—40°. γ -Lauro- α -stearin, prepared by heating the preceding compound with potassium laurate for ten hours at 120° in an atmosphere of hydrogen, forms dense, granular, white crystals, m. p. 52—53°, or, after solidification, 45°. γ -Lauro- β -myristo- α -stearin is prepared in the same way as the lauro-myristostearin above described; it forms dull white, soft, crystalline grains, m. p. 48—49° (after solidifying, 44—45°). The m. p. sinks, on keeping, to 46°. γ -Myristo- α -stearin is obtained in white, granular crystals by heating together stearo-chlorohydrin and potassium myristate; it has m. p. 52—53° (softening at 47°), or, after fusion, at 44°. β -Lauro- γ -myristo- α -stearin is prepared by acting on the above diglyceride with lauryl chloride; the crystals are white and yellow, and are not well-defined; they have m. p. 42°, or, after fusion, 32°. These three isomeric triglycerides show great similarity in physical properties, but the differences in m. p. show them to be distinct substances. The melting points of mixtures of them are not very sharp, but lie in all cases between those of the components, as was also the case with the "doubly mixed" triglycerides.

The synthetic methods described in the paper are to be extended to the production of optically active glycerides. R. V. S.

Preparation of Chlorohydroxy-acids and their Glycerides. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE and GEORGES IMBERT (D.R.-P. 212001).—Oleic, linoleic, and erucic acids are converted into the corresponding chlorohydroxy-saturated acids by treatment with chlorine in the presence of excess of either sodium carbonate or sodium hydrogen carbonate. F. M. G. M.

Some Transformations of Ricinoleic Acid. ADOLF GRÜN (*Ber.*, 1909, 42, 3759—3763).—The action of sulphuric acid on ricinoleic acid as described by Chonowsky (this vol., i, 760) differs considerably from the results obtained by others, including the author. His fraction of b. p. 73—74° is probably a mixture of the isomerides of b. p. 60.5° and 90°. The author maintains his former statements, and has recently repeated the preparation of the dihydroxystearic acids on a larger scale, with the result that he has isolated from the fourth fraction a substance in the form of small, white needles, m. p. 126°, which from its properties is the fourth isomeric *dihydroxystearic acid*. Chonowsky's substance, m. p. 115—116°, is also probably a mixture. Other discrepancies may be due to the formation of internal anhydrides,

which is characteristic of hydroxy-acids of high molecular weight. For instance, the author finds that ricinoleic acid when treated with acetic anhydride yields, not acetylricinoleic acid, but *acetylricinoleylricinoleic acid*, $\text{OAc} \cdot \text{C}_{17}\text{H}_{32} \cdot \text{CO} \cdot \text{O} \cdot \text{C}_{17}\text{H}_{32} \cdot \text{CO}_2\text{H}$.
R. V. S.

ϵ -Nitro- γ -ketohexoxic Acid and its Transformation Products. JOHANNES THIELE and HERMANN LANDERS (*Annalen*, 1909, 369, 300—310).— ϵ -Nitro- γ -ketohexoxic acid, $\text{NO}_2 \cdot [\text{CH}_2]_2 \cdot \text{CO} \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H}$, prepared by boiling furfurylidenenitroethane with fuming hydrochloric acid, crystallises in glistening, white needles, m. p. 91—92°; the *methyl* ester is an oil, which decomposes when heated; the *semicarbazone*, $\text{C}_7\text{H}_{12}\text{O}_5\text{N}_4$, forms small, white needles, m. p. 167° (decomp.). The acid is oxidised by an aqueous solution of potassium permanganate or by strong nitric acid, yielding oxalic acid and succinic acid; when heated with fuming hydrochloric acid in a sealed tube at 150°, it yields

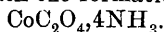
3-chloroisooxazole-5-propionic acid, $\begin{array}{c} \text{N} \text{---} \text{O} \\ | \quad \diagup \\ \text{Cl} \cdot \text{CH} \text{---} \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$, which

crystallises in glistening, white leaflets, m. p. 84—85°, and forms a *methyl* ester, $\text{C}_7\text{H}_8\text{O}_3\text{NCl}$, crystallising in white needles, m. p. 40°. 3-Bromoisooxazole-5-propionic acid, $\text{C}_6\text{H}_6\text{O}_3\text{NBr}$, prepared by heating ϵ -nitro- γ -ketohexoxic acid with a solution of hydrogen bromide in glacial acetic acid at 100°, crystallises in colourless leaflets, m. p. 103°; the *methyl* ester, $\text{C}_7\text{H}_8\text{O}_3\text{NBr}$, forms colourless needles, m. p. 70—72°. The acid just described or the corresponding chloro-compound, when reduced with sodium amalgam in an alkaline aqueous solution, yields ω -cyanolaevulic acid, $\text{CN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, small, colourless crystals, m. p. 86—88°.

3-Methoxyisooxazole-5-propionic acid, $\text{C}_7\text{H}_9\text{O}_4\text{N}$, is formed when the corresponding halogen compound is boiled with a concentrated solution of potassium hydroxide in methyl alcohol; it crystallises in slender needles, m. p. 100°; the *methyl* ester, $\text{C}_8\text{H}_{11}\text{O}_4\text{N}$, has m. p. 56—57°. The acid is converted by hot concentrated nitric acid into a *nitro*-derivative, $\text{C}_7\text{H}_8\text{O}_6\text{N}_2$, which forms large, white crystals, m. p. 136—138°.

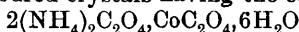
isoOxazole-5-propionic acid, $\text{C}_6\text{H}_7\text{O}_3\text{N}$, is prepared by treating the nitroketohexoxic acid with tin and hydrochloric acid; it crystallises in white needles, m. p. 95—96°, and is converted by a methyl-alcoholic solution of potassium hydroxide into ω -cyanolaevulic acid. W. H. G.

Cobalto-oxalate-ammonia and Ammonium Cobalto-oxalate. FRITZ EPHRAIM (*Ber.*, 1909, 42, 3850—3856).—When cobalt oxalate, $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, is dissolved in concentrated ammonia and the solution precipitated with alcohol, the compound $\text{CoC}_2\text{O}_4 \cdot 2\text{NH}_3 \cdot 3\text{H}_2\text{O}$ is produced if care is taken to prevent oxidation. When quite dry it is reddish-violet in colour. The dry substance has an odour of ammonia, and on exposure to the air one molecule of ammonia is gradually replaced by water, with the formation of the compound $\text{CoC}_2\text{O}_4 \cdot \text{NH}_3 \cdot 3\text{H}_2\text{O}$. On the other hand, when exposed to an atmosphere of dry ammonia, the compound $\text{CoC}_2\text{O}_4 \cdot 3\text{NH}_3 \cdot \text{H}_2\text{O}$ is produced. Anhydrous cobalt oxalate combines with ammonia, with the formation of the compound



Precipitated cobalt oxalate which has been dried at 80° contains $2\text{H}_2\text{O}$; when the precipitation and drying take place at atmospheric temperature, the salt contains $4\text{H}_2\text{O}$.

Cobalt oxalate dissolves in a boiling mixture of one part of ammonium oxalate with five times its volume of water. If the cobalt oxalate is added only so long as it dissolves readily and the solution then filtered, rose-coloured crystals having the composition



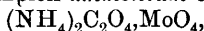
are obtained on cooling. They are decomposed to some extent by water; the concentrated aqueous solution is deep violet in colour.

If an excess of cobalt oxalate is added to the solution of ammonium oxalate and the whole heated for some time in a reflux apparatus, a deep violet-coloured solution is obtained, which, on cooling, gives brown crystals having the composition $(\text{NH}_4)_2\text{C}_2\text{O}_4, \text{CoC}_2\text{O}_4, 6\text{H}_2\text{O}$. They are readily decomposed by water. T. S. P.

Complex Oxalates of Cobalt and Nickel. STELLA DEAKIN, MARGARET SCOTT, and BERTRAM D. STEELE (*Zeitsch. physikal. Chem.*, 1909, 69, 123—135).—The nature of the complex oxalates present in solutions containing potassium oxalate and the oxalates of cobalt and nickel respectively has been established by solubility measurements at 25° and 49° . The respective oxalates of cobalt and nickel were shaken with solutions of potassium oxalate until equilibrium was established and the solutions analysed. The results accord best with the view that the solutions contain mainly the complexes $(\text{K}_2\text{C}_2\text{O}_4)_2, (\text{CoC}_2\text{O}_4)_3$ and $(\text{K}_2\text{C}_2\text{O}_4)_2, (\text{NiC}_2\text{O}_4)_3$, but the solutions are in equilibrium with solid double salts of the respective formulæ $\text{K}_2\text{C}_2\text{O}_4, \text{CoC}_2\text{O}_4$ and $\text{K}_2\text{C}_2\text{O}_4, \text{NiC}_2\text{O}_4$. The magnitude of the equilibrium constant increases with temperature in the case of cobalt and diminishes with temperature in the case of nickel. The interpretation of the results was complicated by the formation of solid solutions of potassium oxalate with both the other oxalates, and also by the occurrence of two equilibria in the nickel solutions, doubtless depending on the presence of two hydrates or other modifications of nickel oxalate.

From the results of electrical conductivity measurements, it is probable that the complex nickel salt is more highly ionised than potassium oxalate, but the velocity of the complex ion is much less than that of the oxalate ion. G. S.

Complex Acids of Molybdenum. ARRIGO MAZZUCHELLI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 259—264).—Ammonium molybdo-oxalate, in presence of hydrogen peroxide, increases considerably in solubility, giving a bright yellow liquid, which deposits shining crystals of the complex ammonium compound,

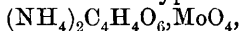


analogous in composition to the barium salt (Abstr., 1907, i, 748). The corresponding potassium salt, $\text{K}_2\text{C}_2\text{O}_4, \text{MoO}_4$, forms lemon-yellow scales.

Unlike these salts, the acid molybdo-oxalates, $\text{RHC}_2\text{O}_4, \text{MoO}_3$, appear to alter in composition when hydrogen peroxide is added, the excess of oxalic acid being eliminated. Thus, the potassium salt, with 15% hydrogen peroxide solution, partly dissolves and then deposits yellow

crystals, $K_2C_2O_4 \cdot 2MoO_4 \cdot 3H_2O$. Also, the ammonium hydrogen salt dissolves readily in hydrogen peroxide solution, which deposits an orange-coloured powder, $(NH_4)_2C_2O_4 \cdot 2MoO_4 \cdot 3H_2O$, sparingly soluble in water, but hydrolysed by it with liberation of the active oxygen and oxalic acid; the sodium salt similarly gives $Na_2C_2O_4 \cdot 2MoO_4$.

From molybdotartrates, solid hyper-salts could not be isolated, owing to their great solubility and ready decomposability. A solution of $(NH_4)_2C_4H_4O_6 \cdot MoO_3$ with an equivalent quantity of hydrogen peroxide becomes yellow, its molecular rotation, calculated on the tartaric acid (compare Rosenheim and Itzig, *Abstr.*, 1900, i, 272), changing from $+528^\circ$ to $+203^\circ$; as the latter value is not altered by addition of a triple proportion of hydrogen peroxide, the change in rotation is due to the formation of a hyper-salt, evidently



and not to decomposition of the original compound into ammonium permolybdate and tartrate. The rotations of solutions of tartaric acid containing increasing proportions of yellow molybdic acid and hydrogen peroxide increase from $+183^\circ$ to $+428^\circ$ for $4MoO_4$ per $C_4H_4O_6$, after which further addition of molybdic acid causes no further increase in rotation. Similarly, the rotation of sodium molybdomalate changes from $+134^\circ$ to the constant value, -140° , on addition of hydrogen peroxide; in this case, the catalytic decomposition of the hydrogen peroxide is far more rapid than with the tartrate, and, ultimately, the rotation assumes a value, $+150^\circ$, nearly equal to the original value.

Cryoscopic measurements with ammonium molybdo-oxalate show that the number of molecules remains practically unchanged by addition of hydrogen peroxide, not only in the proportion of 1 mol. to 1 mol. (corresponding with the solid hyper-salt obtained), but almost up to the proportion of 2 mols. H_2O_2 to 1 mol. of molybdo-oxalate. That a partial scission into ammonium oxalate and permolybdate is here caused by the excess of hydrogen peroxide is confirmed by the cryoscopic results obtained with ammonium hydrogen molybdo-oxalate.

The cryoscopic data for molybdo-iodic acid do not show, with certainty, the existence of a hyper-acid, but indicate that the molybdo-iodic acid undergoes polymerisation.

A higher degree of polymerisation is found for yellow molybdic acid than was obtained by Rosenheim and Bertheim (*Abstr.*, 1903, ii, 374), and cryoscopic measurements of solutions of molybdic acid containing hydrogen peroxide indicate that the per-acid, $MoO_3 \cdot H_2O_2$, also undergoes polymerisation, thus explaining the possibility of adding $4MoO_4$ to the tartrate (*vide supra*). With the molybdic acid obtainable from methyl molybdate, Me_2MoO_4 , which acid Rosenheim and Davidsohn (*Abstr.*, 1904, ii, 128) assert consists of a simple molecule, results are obtained similar to those given by yellow molybdic acid.

The number of molecules in solutions containing either the molybdic acid obtained from methyl molybdate or the yellow acid, together with various proportions of sulphuric acid, indicate that a compound between SO_3 and MoO_3 persists in these solutions. T. H. P.

Aliphatic Compounds of Polyvalent Iodine. I. Iodo-chlorides and Iodoso-compounds from Chloriodofumaric Acid. JOHANNES THIELE and WILLI PETER (*Annalen*, 1909, 369, 119—128).—An account of this work has already appeared (compare Abstr., 1905, i, 735). The following compounds have not been described hitherto.

Methyl iodofumarate, $C_6H_7O_4I$, crystallises in yellow prisms, m. p. 52—52.5°. Neither this substance nor the acid itself yields an iodochloride when the solution in chloroform is treated with chlorine at 0°.

Iodomaleic acid, $C_4H_3O_4I$, is obtained by heating iodofumaric acid with phosphoryl chloride on a water-bath; it crystallises in almost colourless prisms, m. p. 153—154°.

Chloriodosuccinic acid, $CO_2H \cdot CHI \cdot CHCl \cdot CO_2H$, formed by the action of chlorine iodide on maleic acid in ethereal solution, crystallises in colourless spangles, m. p. 164—166°. Although chloriodosoacrylic acid is stable at the ordinary temperature, it is not possible to prepare in the same way an iodosochloride of chloriodosuccinic acid, showing that the stability of the former compound is due to the union of iodine with an ethenoid carbon atom.

The compound described previously (*loc. cit.*) as an acetyl derivative of chlorofumaric acid iodosochloride is now shown to be the iodosochloride of chloroacrylic acid.

W. H. G.

Aliphatic Compounds of Polyvalent Iodine. II. Derivatives of Di-iodofumaric Acid with Polyvalent Iodine. WILLI PETER (*Annalen*, 1909, 369, 128—130. Compare preceding abstract).—Di-iodofumaric acid in aqueous solution is converted by chlorine

into the *iodosochloride* of iodofumaric acid, $O \begin{smallmatrix} \text{CO-Cl} \\ \diagup \\ \text{ICl} \cdot \text{C} \cdot \text{CO}_2\text{H} \end{smallmatrix}$, which crystallises in small, greenish-yellow needles, decomposes at 117°, and when treated with hot water loses carbon dioxide, yielding *iodiodosoacrylic acid*, $O \begin{smallmatrix} \text{CO} \text{---} \text{CI} \\ \diagup \\ \text{I(OH)} \cdot \text{C} \cdot \text{H} \end{smallmatrix}$, small, colourless crystals, m. p. 169—170°.

The latter substance is reduced by sulphurous acid, yielding $\alpha\beta$ -di-iodoacrylic acid.

It is remarkable that only one of the iodine atoms of di-iodofumaric acid combines with chlorine (compare this vol., i, 865).

W. H. G.

Preparation of Iron Hydrogen Phosphotartrates and Phosphocitrates. CARL SORGER (D.R.-P. 211529 and 211530).—*Ferrous hydrogen phosphotartrate* is prepared by stirring tartaric acid into a suspension of ferrous phosphate in water until a solution is obtained. After several days the colourless, crystalline precipitate is collected, and dried at a low temperature in the dark.

Ferric hydrogen phosphotartrate slowly separates as a greenish-yellow powder when a solution of ferric tartrate is treated with phosphoric acid. These compounds, which are tasteless, odourless, and sparingly soluble in water or dilute acids, but readily so in ammonium hydroxide and alkalis, are of therapeutic value.

Ferrous hydrogen phosphocitrate, a greyish-white powder, is prepared by adding citric acid to a suspension of ferrous phosphate.

Ferric hydrogen phosphocitrate is formed (1) when citric acid is added to ferric phosphate (2) by treating a solution of ferric citrate with phosphoric acid. These salts are more readily soluble in water and dilute acids than the corresponding phosphotartrates. F. M. G. M.

Preparation of Alkyl Methylenecitrates. FARBENFABRIKEN VORM F. BAYER & Co. (D.R.-P. 212554).—*Diethyl methylenecitrate* is prepared by heating together methylenecitric acid, alcohol, and sulphuric acid; it crystallises as tasteless, odourless tablets, m. p. 55°.

Amyl methylenecitrate is prepared by heating the acid chloride with amyl alcohol in benzene solution in the presence of pyridine. It has similar properties, and crystallises in scales, m. p. 52—55°.

F. M. G. M.

Nitroacetaldehydediethylacetal. MILIVOJ S. LOSANITSCH (*Ber.*, 1909, 42, 4044—4049. Compare Meister, *Abstr.*, 1907, i, 886).— β -Nitroacetaldehydediethylacetal, $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$, can be prepared by heating β -iodoacetaldehydediethylacetal (Hesse, *Abstr.*, 1897, i, 457) with silver nitrite during three days. It has b. p. 89—91°/14 mm., forms a clear, colourless liquid heavier than water, and has a faint odour. It gives V. Meyer's nitroso-reaction feebly, yields sodium derivatives, and can be reduced by sodium and boiling alcohol to the amino-acetal (Wohl), b. p. 78—80°/15 mm.

When mixed with concentrated hydrochloric acid, and subsequently treated with phenylhydrazine acetate, the nitro-compound yields glyoxalosazone.

J. J. S.

Preparation of Disulphoacetaldehydesulphoxylates. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 212070).—*Sodium disulphoacetaldehydesulphoxylate*, $(\text{SO}_3\text{Na})_2\text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{O} \cdot \text{SONa}$, is prepared by treating sodium acetaldehydedisulphonate, $\text{CH}(\text{SO}_3\text{Na})_2 \cdot \text{CHO}$, with zinc dust and a current of sulphur dioxide; the solution of the sodium salt is evaporated at a low temperature in a vacuum and treated with alcohol. The salts of this acid are odourless and of therapeutic value. The corresponding formaldehyde compound was not obtained in a pure state.

F. M. G. M.

Ketens. XII. Preparation of Keten. HERMANN STAUDINGER and J. KUBINSKY (*Ber.*, 1909, 42, 4213—4215).—It was shown by Staudinger and Klever (*Abstr.*, 1908, i, 246) that keten may be prepared by treating bromoacetyl bromide in ether or ethyl acetate with zinc, but that no keten is obtained in this way from chloroacetyl chloride. The authors have now carried out further experiments with (1) bromoacetyl bromide, which yielded from 7 to 13% of keten; (2) bromoacetyl chloride, which gave 3—4% of keten; (3) chloroacetyl bromide, and (4) chloroacetyl chloride, neither of which yielded keten, the conditions being the same in each case. If, therefore, for the preparation of a new keten the α -brominated acid bromide is not available, it is better to employ the α -brominated acid chloride rather

than the α -chlorinated acid bromide, since it is the chlorine atom of the CH_2Cl group which is so strongly combined that it is not attacked. The fact that diphenylchloroacetyl chloride readily enters into reaction under conditions where chloroacetyl chloride is not attacked is explained by the loosening of the chlorine atom by the two phenyl groups; the same reason applies to the relatively great reactivity of diphenyl- and triphenyl-chloromethane compared with chloromethane itself.

Bromoacetyl bromide is attacked readily by magnesium, giving a large yield of keten, but at the end of the reaction such large quantities of hydrogen bromide are formed that no keten can be isolated; the action of silver is slight, whilst with potassium, sodium, calcium, iron, aluminium, and cadmium, no action is observed.

T. H. P.

Sugar Scissions. VI. The Electrolytic Reduction of Dextrose. WALTHER LÖB (*Biochem. Zeitsch.*, 1909, 21, 102—105).—It has already been shown (Abstr., 1909, i, 767) that dextrose can give rise to pentose and formaldehyde when submitted to electrolysis at the lead anode. The same products can also be detected when the sugar solution is electrolysed at a lead cathode.

S. B. S.

Action of Fehling's Solution on Galactose. ERNEST ANDERSON (*Amer. Chem. J.*, 1909, 42, 401—431).—Nef (Abstr., 1908, i, 7) has shown that when dextrose, *d*-mannose, and *l*-ævulose are oxidised with Fehling's solution, the products consist of carbonic, formic, oxalic, glycollic, *d*- and *l*-glyceric, *l*-threonic, *d*-erythronic, and isomeric hexonic acids. A study has now been made of the oxidation of galactose, and it has been found that, whilst the members of the dextrose series yield a large amount of *d*-gluconic acid, smaller quantities of *d*-mannonic acid, and probably some α -hydroxymethyl-*d*-arabonic acid, *d*-galactose gives much *d*-galactonic acid, relatively smaller amounts of *d*-talonic acid, and probably small quantities of α -hydroxymethyl-*d*-lyxonic acid. The mechanism of the oxidation is discussed.

The oxidation of 118 grams of *d*-galactose yielded 2.49 grams of carbon dioxide, 15.69 grams of formic acid, and 102.1 grams of non-volatile acids. From the last-mentioned were isolated 13 grams of *d*-galactonic acid, 5.33 grams of *d*-talonic acid, 0.5 gram of oxalic acid, 2.58 grams of *l*-threonic lactone, traces of *d*-erythronic lactone, about 11 grams of *dl*-glyceric acid, and 11.75 grams of glycollic acid. It is estimated that the 102 grams of non-volatile acids actually contained 20—30 grams of glycollic acid, 20—30 grams of glyceric acid, 4—8 grams of trihydroxybutyrolactones, and 20—30 grams of hexonic acids.

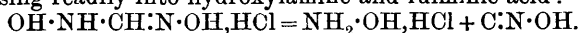
E. G.

Lactic Acid in Alcoholic Sucrose Fermentation. EDUARD BUCHNER and JAKOB MEISENHEIMER (*Landw. Jahrb.*, 1909, 38, v, 265—288. Compare Abstr., 1904, ii, 199; 1905, ii, 274; 1906, i, 919, ii, 790).—A detailed account of experiments leading to the conclusion that lactic acid is not formed as a by-product during the cell-free alcoholic fermentation of sucrose.

F. M. G. M.

Action of Calcium Hydroxide on Lactose. HEINRICH KILIANI (*Ber.*, 1909, 42, 3903—3904).—By the action of calcium hydroxide on lactose a mixture of the three saccharinic acids is obtained. An alteration in the method of procedure enables these substances to be relatively easily prepared. A solution of one part of milk sugar in nine parts of water with 0.2 part of calcium hydroxide is shaken in a closed flask for two days and then heated for ten hours in a boiling water-bath. The dark red filtrate is separated from a precipitate, mostly consisting of calcium carbonate, and concentrated, whereby calcium *isosaccharinate* separates. The mother liquors are freed from calcium, evaporated to a syrup, extracted with ether, and the residue converted into a barium salt, which is induced to crystallise in the usual manner; it consists of meta- and para-saccharinate. Since the constitution of the saccharins has been determined, it is advisable to use their correct names: *isosaccharinic acid* is $\alpha\gamma\delta$ -triol- α -methyl-pentoic acid, *metasaccharinic acid* is $\alpha\gamma\delta\epsilon$ -tetrolhexoic acid, *para-saccharinic acid* is $\alpha\beta\gamma$ -triol- α -ethanolbutyric acid, whilst Peligot's saccharinic acid is tetrol- α -methylpentoic acid. E. F. A.

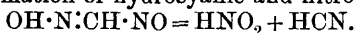
Methylnitrosolic Acid and Allied Compounds. HEINRICH WIELAND and HERMANN HESS (*Ber.*, 1909, 42, 4175—4191).—It was shown by Nef (*Abstr.*, 1895, i, 9) that when an alcoholic solution of formamino-oxime is heated with hydroxylamine hydrochloride, ammonium chloride is deposited and a new compound, hydroxyisouretin, formed. The authors find that the latter is, in reality, formhydroxylamino-oxime, $\text{OH}\cdot\text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$, which could not be isolated even in the form of hydrochloride, the latter decomposing readily into hydroxylamine and fulminic acid:



The base gives with ferric chloride the dark blue coloration characteristic of the hydroxylamino-oximes, reduces silver nitrate immediately, and yields a red coloration with sodium hydroxide.

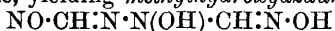
Potassium methylnitrosolate, $\text{OK}\cdot\text{N}\cdot\text{CH}\cdot\text{NO}$, prepared by the action of alcoholic potassium hydroxide on formhydroxylamino-oxime, forms shining, indigo-blue prisms, exploding at 194° , or when subjected to shock. The aqueous solution exhibits no selective absorption, the spectrum being continuous from the red to between the yellow and green. The *silver* salt was analysed, and the *copper*, *lead*, *nickel*, *mercuric*, and *mercurous* salts prepared. Free *methylnitrosolic acid*, the formation of which from formhydroxylamino-oxime is represented by the scheme: $2\text{OH}\cdot\text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{OH} \rightarrow \text{OH}\cdot\text{N}\cdot\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{CH}\cdot\text{N}\cdot\text{OH} \rightarrow \text{NH}_2\cdot\text{CH}\cdot\text{N}\cdot\text{OH} + \text{OH}\cdot\text{N}\cdot\text{CH}\cdot\text{NO}$, separates in the bimolecular form: $\text{OH}\cdot\text{N}\cdot\text{CH}\cdot[\text{NO}]_2\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ (?), exploding at 76° . Secondary nitroso-compounds containing the group $\cdot\text{CH}\cdot\text{NO}$, as a rule, readily undergo enolisation, giving the oxime, $\cdot\text{C}\cdot\text{N}\cdot\text{OH}$, but the bimolecular form of methylnitrosolic acid never yields the dioxime of carbon dioxide, $\text{OH}\cdot\text{N}\cdot\text{C}\cdot\text{N}\cdot\text{OH}$, but always the primary salts of the monobasic methylnitrosolic acid, owing probably to the disinclination of the carbon atom to combine with two groups by two double linkings. The salts of methylnitrosolic acid, under the prolonged action of alkali,

decompose with formation of hydrocyanic and nitrous acids :

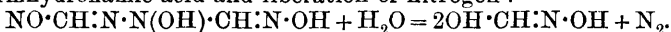


The free acid decomposes extremely readily, mostly into hyponitrous acid and fulminic acid : $2\text{OH}\cdot\text{N}:\text{CH}\cdot\text{NO} = \text{OH}\cdot\text{N}:\text{N}\cdot\text{OH} + (\text{C}:\text{N}\cdot\text{OH})_2$ (compare Abstr., 1907, i, 196 ; this vol., i, 215).

When the action of alkali hydroxide on formhydroxylamino-oxime takes place at low temperatures, no salt of nitrosolic acid is obtained, since, as this acid is formed, it condenses with the excess of formhydroxylamino-oxime, yielding *methylhydroxyazaurolic acid*,



(compare Abstr., 1907, i, 494), in the form of straw-yellow needles exploding at 103°. This acid explodes with a flash when treated with a concentrated mineral acid ; with acidified potassium iodide solution it gives a precipitate of iodine, and with ferric chloride a dark orange-red coloration gradually appears ; it gives Liebermann's reaction with phenol and sulphuric acid, and its scarlet *silver* salt is decomposed by nitric acid, yielding silver cyanide. The *copper* and *potassium* salts, $\text{C}_2\text{H}_2\text{O}_3\text{N}_4\text{K}_2$, were prepared, and also the *benzoyl* derivative, m. p. 141° (decomp.). Its reactions resemble closely those of hydroxyethylazaurolic acid, but it does not undergo transformation into hydroxy-leucazone with loss of nitrous oxide. When gently heated with water, it decomposes partly into nitrogen, carbon dioxide, and hydrogen cyanide, and partly into nitrogen, water, and isocyanic acid (or carbon dioxide and ammonia) : $\text{C}_2\text{H}_4\text{O}_3\text{N}_4 = \text{N}_2 + 2\text{HCON} + \text{H}_2\text{O}$; in the latter case a residue remains consisting apparently of a new acid and its ammonium salt, which were not investigated. By the action of concentrated hydrochloric acid in the cold, it is decomposed with formation of formhydroxamic acid and liberation of nitrogen :



The reduction of methylhydroxyazaurolic acid to methylazaurolic acid does not proceed so readily as with other hydroxyazaurolic acids. But methylazaurolic acid can be obtained by reducing the hydroxy-acid by hydrogen sulphide to hydrazoformoxime and oxidising the latter by means of bromine vapour.

Hydrazoformoxime, $\text{OH}\cdot\text{N}:\text{CH}\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}:\text{N}\cdot\text{OH}$, also prepared by the action of hydrazine hydrochloride on formamino-oxime, forms thin, colourless prisms, decomp. at 138—140°. With ferric chloride, it gives a green coloration, changing to brown, and its *picrate* forms golden-yellow needles, m. p. 226°.

Methylazaurolic acid, $\text{NO}\cdot\text{CH}:\text{N}\cdot\text{NH}\cdot\text{CH}:\text{N}\cdot\text{OH}$, forms long, dark yellow prisms, m. p. 138° (detonat.). The *sodium*, *barium*, *silver*, and *copper* salts, which are all explosive, were prepared. The acid is less readily decomposed than the corresponding hydroxy-acid, and, on boiling with water, it yields gaseous products and 80—90% of an orange-red, amorphous acid. When treated in the cold with concentrated hydrochloric acid, it undergoes isomeric change, yielding

isoazaurolin (isonitrosodihydro-oxotriazine), $\text{CH}\begin{matrix} \text{N} \text{---} \text{O} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{NH} \end{matrix} \text{C}:\text{N}\cdot\text{OH}$,

which forms colourless needles, becoming orange-yellow at about 85° and exploding at 112—113°. This base undergoes oxidation in the air to a red azo-compound, but it is not attacked by concentrated

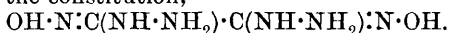
hydrochloric acid even at 140° . Its *hydrochloride*, $C_2H_4O_2N_4 \cdot HCl$, decomposes at $148-150^{\circ}$.

Formoximehydrazocarbonamide, $OH \cdot N : CH \cdot NH \cdot NH \cdot CO \cdot NH_2$, prepared by the action of semicarbazide on formamino-oxime, forms colourless needles, decomposing at 154° . It reduces ammoniacal silver solutions instantaneously, and, with ferric chloride, gives a dark blue coloration, rapidly changing to green.

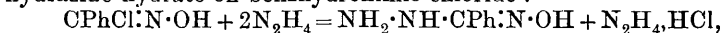
Formoximeazocarbonamide, $OH \cdot N : CH \cdot N : N \cdot CO \cdot NH_2$, prepared by oxidising formoximehydrazocarbonamide by means of bromine vapour, was obtained in impure, orange-red, stellate aggregates of broad needles, decomposing at $123-126^{\circ}$ or 138° . It gives Liebermann's reaction with phenol and sulphuric acid, and, when it is heated with ferric chloride, hydrogen cyanide is evolved, and an intense, greenish-brown coloration formed. When heated in alkali solution, it decomposes according to the equation: $OH \cdot N : CH \cdot N : N \cdot CO \cdot NH_2 = HCN + N_2 + CO_2 + NH_3$. The *silver* salt and the soluble *barium* and *lead* salts were prepared.

Phenylhydrazoformaldoxime, obtained by Bamberger and Frei (Abstr., 1902, i, 404) by the action of hydrogen sulphide on α -nitroformaldehydephenylhydrazone, is also formed by the action of phenylhydrazine on formamino-oxime. T. H. P.

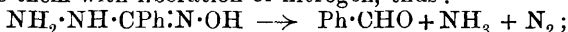
Hydrazide-oximes. HEINRICH WIELAND (*Ber.*, 1909, 42, 4199—4206).—The action of the hydrazine hydrate on dibromofuroxan yields the hydrazine analogue of oxamidedioxime (compare this vol., i, 892) having the constitution,



To the compounds of this type the author gives the name *hydrazide-oximes*. The reactions of benzhydrazide-oxime, prepared by the action of hydrazine hydrate on benzhydroximic chloride:



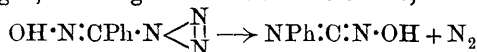
have been investigated. The hydrazide-oximes possess an amphoteric character and, like the amino-oximes, dissolve in both mineral acids and alkalis. Towards acids they are moderately stable, but alkalis readily decompose them with liberation of nitrogen, thus:



the benzaldehyde then condenses with unchanged hydrazide-oxime, giving, as final product, the stable benzylidenebenzhydrazide-oxime, $CHPh : N \cdot NH \cdot CPh : N \cdot OH$, which, in contact with acids, readily

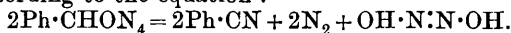
undergoes transformation into diphenyltriazole, $CPh \begin{smallmatrix} \nwarrow NH \cdot N \\ \nearrow N \end{smallmatrix} CPh$ (compare Pinner, Abstr., 1897, i, 637).

Assuming that the hydrazine residue of the hydrazide-oximes reacts with nitrous acid in the same way as does that of the acid hydrazides, benzhydrazide-oxime should yield benzhydroximic azoimide, which, by loss of nitrogen, should give the carbimide oxime,



(compare Forster, Trans., 1909, 95, 184). But this is not actually the case, the reaction between benzhydrazide-oxime and nitrous acid

yielding the 1-hydroxy-5-phenyltetrazole obtained by Forster by the interaction of benzhydroximic chloride and sodium azoimide (*loc. cit.*). The decomposition of 1-hydroxy-5-phenyltetrazole by dilute alkali proceeds according to the equation :

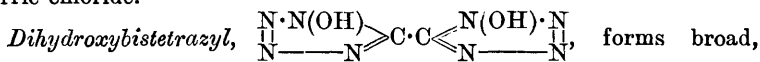


A similar decomposition is exhibited by the dihydroxybistetrazyl obtained by the action of nitrous acid on oxaldihydrazide-oxime.

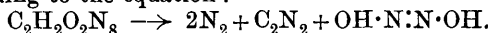
Benzhydrazide-oxime, $\text{OH}\cdot\text{N}:\text{CPh}\cdot\text{NH}\cdot\text{NH}_2$, forms snow-white needles, decomp. at 110° , and is stable in a desiccator or in the air, but decomposes rapidly in a closed vessel. It reduces Fehling's solution and ammoniacal silver solutions instantaneously, and with ferric chloride gives an intense, cherry-red coloration. Its *hydrochloride* forms stellate aggregates of needles.

Benzylidenebenzhydrazide-oxime, $\text{OH}\cdot\text{N}:\text{CPh}\cdot\text{NH}\cdot\text{N}:\text{CHPh}$, forms fan-shaped aggregates of white, silky needles, m. p. 120° (decomp.), and with ferric chloride gives a blue coloration, rapidly changing to green.

Oxaldihydrazide-oxime, $\text{OH}\cdot\text{N}:\text{C}(\text{NH}\cdot\text{NH}_2)\cdot\text{C}(\text{NH}\cdot\text{NH}_2):\text{N}\cdot\text{OH}$, formed by the interaction of dibromofuroxan and hydrazine hydrate, is extremely soluble in water and decomposes very readily, so that it could be obtained only as its *hydrazine* salt, $\text{C}_2\text{H}_8\text{O}_2\text{N}_6\cdot\text{N}_2\text{H}_4$, in colourless leaflets, which explode violently in a melting-point tube at 108° . The salt is stable in an open vessel in the dark, but is decomposed readily by hydrochloric acid, giving nitrogen and hydrocyanic and oxalic acids. With ferric chloride it yields a dark blue coloration, which is not affected by acids. With benzaldehyde it forms benzalazine and colourless *benzylideneoxaldihydrazide-oxime*, which was not obtained pure and which gives a brownish-green coloration with ferric chloride.

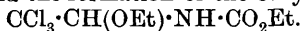


colourless needles, exploding violently when subjected to friction or a blow, or when heated to 176° in a melting-point tube. It gives a brownish-red coloration with ferric chloride, and is decomposed by alkalis according to the equation :



T. H. P.

Chloralurethane. OTTO DIELS and CARL SEIB (*Ber.*, 1909, 42, 4062—4072. Compare Bischoff, *Ber.*, 1874, 7, 631; Moscheles, *Abstr.*, 1891, 1003).—According to Hantzsch (*Abstr.*, 1894, i, 363), anhydrochloralurethane reacts with sodium ethoxide, yielding hydrogen chloride and dichloroethyleneurethane, $\text{CCl}_3\cdot\text{CH}\cdot\text{N}\cdot\text{CO}_2\text{Et} = \text{HCl} + \text{CCl}_2\cdot\text{C}:\text{N}\cdot\text{CO}_2\text{Et}$, but, according to the authors, the reaction consists in the addition of ethyl alcohol to the double linking in the anhydro-compound and the formation of the ethyl ether,

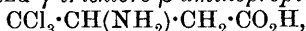


Methyl alcohol unites itself in a similar manner, and additive compounds with urethane or ethyl malonate can also be obtained, namely, chloraldiurethane and $\text{CCl}_3\cdot\text{CH}(\text{NH}\cdot\text{CO}_2\text{Et})\cdot\text{CH}(\text{CO}_2\text{Et})_2$ respectively.

Chloralurethane ethyl ether, $\text{CCl}_3 \cdot \text{CH}(\text{OEt}) \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, has an odour of cloves, distils at $134^\circ/13$ mm., and solidifies to crystalline rosettes, m. p. 37° . With concentrated sulphuric acid it yields chloral. The corresponding *methyl ether*, $\text{C}_6\text{H}_{10}\text{O}_3\text{NCl}_3$, has b. p. $137^\circ/22$ mm., and m. p. 64° .

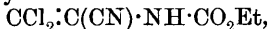
Chloraldiurethane, $\text{CCl}_3 \cdot \text{CH}(\text{NH} \cdot \text{CO}_2\text{Et})_2$, obtained by the action of sodium urethane on an ethereal solution of anhydrochloralurethane and treatment of the product with dilute hydrochloric acid, crystallises from acetone in well-developed needles, m. p. 172° . The same product is formed by the prolonged action of chlorine on urethane in the presence of a little iodine, or by the action of a few drops of concentrated sulphuric acid on a mixture of chloral (5 parts) and urethane (6 parts).

The compound, $\text{CCl}_3 \cdot \text{CH}(\text{NH} \cdot \text{CO}_2\text{Et}) \cdot \text{CH}(\text{CO}_2\text{Et})_2$, distils at $198\text{--}199^\circ/12$ mm., and γ -trichloro- β -aminopropionic acid,



obtained by hydrolysing at $95\text{--}100^\circ$ the above compound with a glacial acetic acid solution of hydrogen bromide (saturated at 0°), crystallises from ethyl acetate in colourless prisms, m. p. 189° (decomp.).

The *acetyl* derivative of chloralurethane, $\text{CCl}_3 \cdot \text{CH}(\text{OAc}) \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, prepared by the action of acetyl chloride on the urethane, is a viscid, strongly refractive liquid, b. p. $165^\circ/15$ mm. It solidifies slowly, and has m. p. $47\text{--}49^\circ$. Hydrolysing agents convert it into anhydrochloralurethane, and boiling for some time with a saturated aqueous solution of potassium cyanide converts it into the *nitrile*,



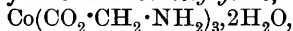
which crystallises from dilute alcohol in colourless, felted needles, m. p. $113\text{--}114^\circ$.

When hydrolysed in sealed tubes with an acetic acid solution of hydrogen bromide at 0° , the nitrile yields ethyl bromide and β -dichloro- α -aminoacrylic acid?, $\text{CCl}_2 \cdot \text{C}(\text{NH}_2) \cdot \text{CO}_2\text{H}$, m. p. 113° after sintering at 80° .

J. J. S.

Stereoisomerism of Internally Complex Salts. HEINRICH LEY and H. WINKLER (*Ber.*, 1909, 42, 3894—3902).—Cobaltiglycine, $\text{Co}(\text{CO}_2 \cdot \text{CH}_2 \cdot \text{NH}_2)_3$, a typical internal complex salt, is found to exist in two modifications, which must be stereoisomeric, as the chemical behaviour of both is almost the same, and a difference of molecular weight does not exist. Two configurations are possible for the cobaltic compound, namely, a *bis-cis* and a *trans-cis* configuration, using Werner's octahedral scheme. It is not yet possible to determine the modification to which each configuration corresponds.

Air oxidises a mixture of glycine with a cobaltous salt, but mixtures of different cobaltic salts are obtained. A solution of glycine in water is boiled for five hours with an excess of cobaltic hydroxide. The filtered red solution, when concentrated on the water-bath, deposits dark violet crystals of α -cobaltiglycine,



which separates from hot water in large, rhombic, pleochroic crystals.

The solution in sulphuric acid has two absorption bands, at $1/\lambda$ 2000 and 2800 respectively.

β -Cobaltglycine, $\text{Co}(\text{CO}_2 \cdot \text{CH}_2 \cdot \text{NH}_2)_3 \cdot \text{H}_2\text{O}$, is obtained as an insoluble residue in the above preparation, and, after washing with hot water, forms minute, pale red needles. The position of the absorption bands in sulphuric acid solution is only slightly different from the α -form. The difference of water of crystallisation does not account for the difference of properties, as the colours are little altered by dehydration. The β -modification reacts readily with potassium nitrite to form a complex salt, the α -form only with great difficulty.

Other properties of the salts are under investigation. C. H. D.

Synthesis of Polypeptides. XXXI. Derivatives of Leucine, Alanine, and *N*-Phenylglycine. EMIL FISCHER and WILHELM GLUUD (*Annalen*, 1909, 369, 247—275. Compare this vol., i, 367).—With the object of gaining some knowledge of the properties of methylated polypeptides, the two dipeptides, *N*-methyl-leucylglycine and *N*-dimethyl-leucylglycine, have been prepared by the action of methylamine and dimethylamine on inactive α -bromoisohexoylglycine. The first named is very similar to leucylglycine, both in its physical and chemical properties; thus, when heated, it passes into an anhydride. The dimethyl compound, from the nature of its constitution, cannot behave in the same way; when heated, it decomposes in a very complex manner. α -Bromoisohexoylglycine, when heated with trimethylamine at 100° , yields α -hydroxyisohexoylglycine; the same compound is formed when an aqueous solution of pyridine is used instead of trimethylamine.

α -Bromoisohexoyl-*N*-phenylglycine, when treated with ammonia, behaves like α -bromoisohexoylproline, in that it yields α -hydroxyisohexoyl-*N*-phenylglycinamide instead of a dipeptide (compare Fischer and Reif, *Abstr.*, 1908, i, 1007); α -bromopropionyl-*N*-phenylglycine undergoes a similar change when acted on by ammonia, whilst chloroacetyl- and bromoacetyl-*N*-phenylglycine do not yield hydroxyacetyl-*N*-phenylglycinamide as anticipated, but a substance which is probably a diketopiperazine-like anhydride of iminodiacetyl-*N*-phenylglycine,

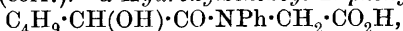
$\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{N} \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix} \text{NPh}$. Glycyl - *N* - phenylglycine is formed together with the latter substance by the action of ammonium hydroxide on chloroacetyl-*N*-phenylglycine at the ordinary temperature (compare Leuchs and Manasse, *Abstr.*, 1907, i, 770).

dl - *N* - Methyl-leucylglycine, $\text{C}_4\text{H}_9 \cdot \text{CH}(\text{NHMe}) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, crystallises in short, compact prisms and small, almost rectangular plates, m. p. 225° (decomp., corr.); the anhydride, $\text{C}_9\text{H}_{16}\text{O}_2\text{N}_2$, crystallises in small, colourless, rhombic plates, m. p. 114° (corr.).

dl-*N*-Dimethyl-leucylglycine, $\text{C}_4\text{H}_9 \cdot \text{CH}(\text{NMe}_2) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, crystallises with $1\frac{1}{2}\text{H}_2\text{O}$ in slender prisms and small, rectangular plates, m. p. 97° (corr.); the anhydrous substance has m. p. 160° , and decomposes at 220° with the elimination of water and dimethylamine; the copper salt, $\text{C}_{10}\text{H}_{20}\text{O}_4\text{N}_2\text{Cu}$, crystallises with H_2O in small, hexagonal, and rhombic plates.

α -Bromoisohexoyl-*N*-phenylglycine, $\text{C}_4\text{H}_9 \cdot \text{CHBr} \cdot \text{CO} \cdot \text{NPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$,

is most readily obtained through the methyl ester by the interaction of *N*-phenylglycine methyl ester and α -bromoisohexoyl bromide in chloroform at about -10° ; it crystallises with $1\text{H}_2\text{O}$ in colourless, nearly rectangular plates, m. p. 66° (corr.). *α -Hydroxyisohexoyl-N-phenylglycinamide*, $\text{C}_4\text{H}_9\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, forms tufts of colourless plates, which lose 10—12% of their weight (benzene?) when kept in a vacuum desiccator; the substance, dried at 100° , has m. p. $128\text{—}129^\circ$ (corr.). *α -Hydroxyisohexoyl-N-phenylglycine*,



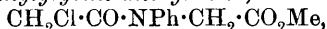
prepared by heating the substance just described with a 5-*N*-hydrochloric acid solution or by acting on the corresponding bromo-compound with sodium hydroxide, crystallises in microscopic, hexagonal, or rhombic plates, m. p. $129\text{—}130^\circ$ (corr.), at which temperature it yields the anhydride, $\text{C}_{14}\text{H}_{17}\text{O}_3\text{N}$, microscopic plates and prisms, m. p. $75\text{—}76^\circ$.

α -Bromopropionyl-N-phenylglycine methyl ester, $\text{C}_{12}\text{H}_{14}\text{O}_3\text{NBr}$, prepared from α -bromopropionyl bromide and *N*-phenylglycine methyl ester, crystallises in large, rectangular plates, m. p. $78\text{—}79^\circ$ (corr.); *α -bromopropionyl-N-phenylglycine*, $\text{CHMeBr}\cdot\text{CO}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, crystallises with $1\text{H}_2\text{O}$ in stellate aggregates of slender, colourless needles, m. p. $79\text{—}80^\circ$ (corr.). *Lactyl-N-phenylglycinamide*,



prepared by the action of a methyl-alcoholic solution of ammonia on the substance just described, forms stellate aggregates of colourless, slender prisms, m. p. 125° (corr.); it is also produced together with ammonium lactyl-N-phenylglycine, $\text{OH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{NH}_4$, crystallising in tufts of microscopic, colourless plates and prisms, m. p. 159° (decomp., corr.), when aqueous ammonia is employed.

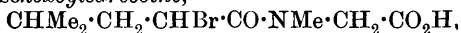
Chloroacetyl-N-phenylglycine methyl ester,



prepared from chloroacetyl chloride and *N*-phenylglycine methyl ester, crystallises in pointed prisms, m. p. $59\text{—}60^\circ$ (corr.); the corresponding bromo-compound, $\text{C}_{11}\text{H}_{12}\text{O}_3\text{NBr}$, crystallises in thin leaflets, m. p. 71° (corr.).

Iminodiacetyl-N-phenylglycine anhydride, $\text{C}_{20}\text{H}_{19}\text{O}_5\text{N}_3$, crystallises with $\frac{1}{2}\text{H}_2\text{O}$ (?) in long, pointed needles and compact prisms; the anhydrous substance has m. p. 226° (decomp., corr.); the copper salt, $\text{C}_{49}\text{H}_{36}\text{O}_{10}\text{N}_6\text{Cu}$, crystallises with H_2O in microscopic, bluish-green needles and short prisms; the anhydrous salt is hygroscopic and decomposes just above 200° .

dl- α -Bromoisohexoylsarcosine,



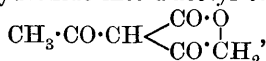
prepared by the action of *dl- α -bromoisohexoyl* bromide on sarcosine in the presence of sodium hydroxide, crystallises in colourless needles and prisms, m. p. about 90° .

α -Hydroxyisohexoylglycine, $\text{C}_4\text{H}_9\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, has m. p. 109° (corr.); the copper salt, $\text{C}_{16}\text{H}_{28}\text{O}_8\text{N}_2\text{Cu}\cdot 2\text{H}_2\text{O}$, forms stellate aggregates of microscopic, pale blue needles.

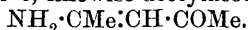
W. H. G.

Acylation of Ethyl β -Aminocrotonate and Analogous Compounds. ERICH BENARY (*Ber.*, 1909, 42, 3912—3925).—The action of chloroacetyl chloride on β -ketonic acid esters proceeds only

with difficulty, and does not lead to uniform products, owing to the acid nature of the ester. The β -amino-ketonic acid esters enter more readily into the reaction. Ethyl β -aminocrotonate reacts with chloroacetyl chloride in molecular proportions to form a crystalline chloroacetyl product, which is obtained in quantity when the operation is performed in presence of pyridine. The chloroacetyl group is attached to carbon, $\text{NH}_2 \cdot \text{CMe} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$, since, on heating, ethyl chloride and a neutral compound, $\text{C}_6\text{H}_7\text{O}_3\text{N}$, are formed, which later is converted by sodium hydroxide into α -acetyl tetronic acid,



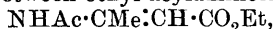
ammonia being eliminated. Ethyl β -anilincrotonate similarly forms a *C*-chloroacetyl derivative, likewise acetylacetanamine,



Acetic anhydride in presence of pyridine acts on ethyl β -aminocrotonate to give an acetyl derivative isomeric with that obtained by Collie (Abstr., 1885, 373), to which he assigned the formula of an *N*-derivative, $\text{COMe} \cdot \text{NH} \cdot \text{CMe} : \text{CH} \cdot \text{CO}_2\text{Et}$. This new isomeride is formed in presence of an excess of the base, but is easily converted into the older form. The isomerism is chemical and not physical. In a similar manner two isomeric benzoyl derivatives are formed, that prepared in presence of pyridine easily passing over into the other. Both isomerides yield benzamide when hydrolysed with acids, and accordingly both are *N*-benzoyl derivatives. The isomeric acetyl compounds must also both be regarded as *N*-derivatives, but no *N*-chloroacetyl compound could be obtained.

Ethyl β -methylaminocrotonate yielded only one acetyl and one benzoyl derivative. Both these are *C*-derivatives; the latter forms benzoylacetone and acetophenone when hydrolysed, gives ethyl diphenylmethylpyrazolecarboxylate with phenylhydrazine and *ethyl 3-phenyl-5-methylisooxazole-4-carboxylate*, $\text{N} \begin{array}{l} \diagup \text{O} - \text{CMe} \\ \diagdown \text{CPh} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array}$ with hydroxylamine. The acetyl derivative under like conditions gives rise to ethyl 1-phenyl-3:5-dimethylpyrazole-4-carboxylate and ethyl 3:5-dimethylisooxazole-4-carboxylate.

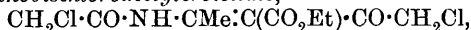
The isomerism of the two *N*-acetyl derivatives may be due either to structural isomerism between ethyl acylaminocrotonate,



and ethyl acyliminobutyrate, $\text{NAc} : \text{CMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, or to *cis*- and *trans*-configuration of the ethylene carbon atom in the first of these formulæ.

Ethyl β -amino- α -chloroacetylcrotonate crystallises in colourless, long needles, m. p. 127—128°, when quickly heated. The fused mass solidifies to α -acetyltetronamide.

Ethyl β -aminobischloroacetylcrotonate,

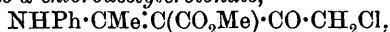


crystallises in colourless needles, m. p. 78°. It is readily decomposed by alkalis, yielding the monoacetyl compound.

α -Acetyltetronamide, $\text{NH}_2 \cdot \text{CMe} : \text{C} \begin{array}{l} \diagup \text{CO} \cdot \text{O} \\ \diagdown \text{CO} \cdot \text{CH}_2 \end{array}$, crystallises in needles,

which become brown at 200° , m. p. $230-231^{\circ}$ (decomp.). *α*-Acetyl-tetronic acid, prepared by hydrolysis of the amide, separates in colourless needles, m. p. $79.5-80.5^{\circ}$; the light blue copper salt has decomp. $275-280^{\circ}$. The anilide forms soft, colourless needles, m. p. $188-189^{\circ}$.

Methyl β-anilino-α-chloroacetylcrotonate,

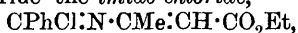


crystallises in radially-grouped needles, m. p. $59-60^{\circ}$.

α-Chloroacetylacetylacetoneamine, $\text{NH}_2 \cdot \text{CMe} \cdot \text{C}(\text{Ac}) \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$, crystallises in thick rods, m. p. 71° .

Ethyl β-amino-α-acetylcrotonate, prepared by acetylation with pyridine and acetyl chloride, forms small, prismatic granules, m. p. $109-110^{\circ}$. When heated with acetic anhydride or dissolved in acetyl chloride, it is converted into the β-isomeride, m. p. 63° (Collie, *loc. cit.*).

Ethyl β-amino-α-benzoylcrotonate, prepared by the action of benzoyl chloride and pyridine on the base, crystallises in four-sided plates, m. p. $95-96^{\circ}$. It passes into the β-isomeride when heated above 200° or when dissolved in acetyl chloride. When warmed with phosphorus pentachloride the imide chloride,



is obtained, crystallising in colourless needles, m. p. $98-99^{\circ}$.

Ethyl β-amino-β-benzoylcrotonate forms short, hard, irregular crystals, m. p. $46-48^{\circ}$; it is obtained also by the condensation of benzamide with ethyl acetoacetate in presence of aluminium chloride. It yields the same imide chloride as the α-isomeride. Both isomerides yield benzamide when boiled with sulphuric acid.

Ethyl β-methylamino-α-acetylcrotonate, $\text{NHMe} \cdot \text{CMe} \cdot \text{C}(\text{Ac}) \cdot \text{CO}_2\text{Me}$, forms four-sided prisms, m. p. $54-55^{\circ}$.

Ethyl β-methylamino-α-benzoylcrotonate forms platelets, m. p. $69-70^{\circ}$, and reacts with hydroxylamine, forming *ethyl 3-phenyl-5-methylisoxazole-4-carboxylate*, which crystallises in needles, m. p. $49-50^{\circ}$; the corresponding acid has m. p. $188-189^{\circ}$, and decomp. 260° .

E. F. A.

Electrolytic Reduction of Aldehyde Ammonias in Sulphuric Acid Solution. PETER KNUDSEN (*Ber.*, 1909, 42, 3994-4003. Compare D.R.-P. 175071; Loeb, *Abstr.*, 1899, i, 122; Brand, this vol., i, 784).—The electrolytic reduction of aldehyde ammonias takes place in presence of sulphuric acid and under such conditions that the compound is largely decomposed. When hexamethylenetetramine is electrolysed, using a lead cathode, the product is a mixture of mono-, di-, and tri-methylamine. A yield of some 50% of the mixed amines can be obtained, but the relative proportions depend on the conditions of the experiment. With small current densities (that is, twenty-four hours for 0.25 mol.) about equal quantities of the three amines are obtained, but with larger densities the proportion of methylamine is increased. The addition of formaldehyde to the electrolyte and the use of high current densities favour the formation of dimethylamine, whereas low current densities in the presence of formaldehyde favour the production of the tertiary amine. When ammonium sulphate is present, the yield of bases is decreased, more especially the yields of

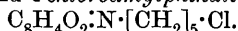
secondary and tertiary amines. The electrolytic reduction of a mixture of ammonium sulphate and formaldehyde leads to the formation of amines; the yield, however, is only small. A mixture of methylamine and formaldehyde yields di- and tri-methylamine. In all the above experiments methyl alcohol is formed, and the yield varies with the conditions.

Aldehyde ammonia gives rise to ethylamine and diethylamine, but not to the formation of tertiary base. Hydrobenzamide yields benzylamine, and benzylidenemethylamine, benzylmethylamine.

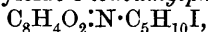
The hydrolysing action of sulphuric acid on hexamethylenetetramine has been studied: at 18° the hydrolysis is nearly complete after one hour, but at 12° some three hours are required, and even then the reaction is not complete. J. J. S.

ζ-Amino-ketones. SIEGMUND GABRIEL (*Ber.*, 1909, 42, 4050—4058. Compare Abstr., 1908, 181, 274, 464, 648, 649; this vol., i, 491, 492, 493).—It has not been found possible to synthesise methyl ζ-amino-hexyl ketone from ethyl acetoacetate and ε-iodobenzoylamylamine (von Braun and Steindorff, Abstr., 1905, i, 206), but it can be prepared from ethyl malonate and ζ-phthaliminoheptoyl chloride or from ethyl acetoacetate and ε-iodoamylphthalimide.

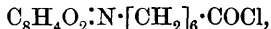
αε-Dichloropentane and potassium phthalimide react at 180°, yielding a small amount of pentamethylenedipthalimide (von Braun, Abstr., 1904, i, 1019) and ε-chloroamylphthalimide,



The latter has m. p. 30—31°, and when boiled with an alcoholic solution of sodium iodide yields ε-iodoamylphthalimide,



which crystallises in compact, pointed prisms, m. p. 75—76°. The iodo-compound reacts with ethyl malonate and sodium ethoxide, yielding ethyl ε-phthalimino-amylmalonate, which gives the corresponding acid, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot[\text{CH}_2]_5\cdot\text{CH}(\text{CO}_2\text{H})_2$, when hydrolysed with hydriodic acid. The acid crystallises in rectangular plates, m. p. 153° (decomp.), and when heated at 170° yields ζ-phthaliminoheptonic acid, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot[\text{CH}_2]_6\cdot\text{CO}_2\text{H}$, which crystallises in flat, pointed needles, m. p. 115—115.5°. The corresponding chloride,



forms a crystalline mass of low m. p., and reacts with ethyl sodio-malonate in the presence of benzene, yielding a product from which methyl ζ-phthaliminoheptyl ketone, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot[\text{CH}_2]_6\cdot\text{COMe}$, can be isolated after hydrolysis with hydriodic acid. The ketone crystallises in colourless plates or needles, m. p. 51°.

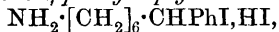
A better yield of the ketone is obtained by hydrolysing with hydriodic acid, ethyl phthaliminoamylacetoacetate, obtained by condensing ε-iodoamylphthalimide with potassium ethoxide and ethyl acetoacetate.

Methyl ζ-aminoheptyl ketone, $\text{NH}_2\cdot[\text{CH}_2]_6\cdot\text{COMe}$, is formed when the crude ethyl phthalimino-amylacetoacetate is hydrolysed with sulphuric acid. It is an oil with a strong amine odour. The *platinichloride*, $2\text{C}_8\text{H}_{17}\text{ON}, \text{H}_2\text{PtCl}_6$, is crystalline, and has m. p. 167—171° (decomp.). The *aurichloride* is not so soluble as the *platinichloride*.

chloride and forms golden-yellow needles, m. p. 80°. The base combines with phenylthiocarbimide, yielding *phenyl- ζ -acetohexylthiocarbamide*, $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot [\text{CH}_2]_6 \cdot \text{COMe}$, m. p. 77°.

Phenyl- ζ -phthaliminohexyl ketone (ζ -*Phthaliminohexophenone*),
 $\text{C}_8\text{H}_4\text{O}_2 \cdot \text{N} \cdot [\text{CH}_2]_6 \cdot \text{COPh}$,

obtained from phthaliminoheptyl chloride, benzene, and aluminium chloride, crystallises in glistening, flat needles, m. p. 96—97°, and, when hydrolysed with sodium hydroxide solution and then with 20% hydrochloric acid, yields *phenyl ζ -aminohexyl ketone* as an oil which rapidly absorbs carbon dioxide. The *hydrochloride*, $\text{C}_{13}\text{H}_{19}\text{ON} \cdot \text{HCl}$, crystallises in oblong plates, m. p. 120°; the *aurichloride* has m. p. 106°, and the *platinichloride*, m. p. 213° (decomp.). When reduced with sodium and alcohol, the amino-ketone yields *η -hydroxy- η -phenylheptylamine*, $\text{NH}_2 \cdot [\text{CH}_2]_6 \cdot \text{CHPh} \cdot \text{OH}$, the *platinichloride* of which has m. p. 206° (decomp.). Concentrated hydriodic acid transforms the base into *η -iodo- η -phenylheptylamine hydriodide*,



in the form of needles, m. p. 109°. The corresponding *picrate*, $\text{C}_{13}\text{H}_{20}\text{NI} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3 \cdot 2\text{H}_2\text{O}$, crystallises in yellow needles, m. p. 84—85°.

The ζ -aminohexophenone thus behaves quite differently from ϵ -aminohexophenone when reduced.

J. J. S.

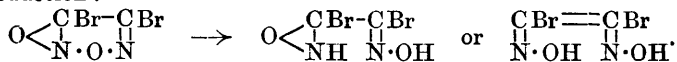
Acid Properties of Halogenated Amides. Hofmann's Migration. CHARLES MAUGUIN (*Compt. rend.*, 1909, 149, 790—793).—On adding the calculated amount of bromoacetamide to a solution of sodium in absolute alcohol at -15° , the *sodium* derivative, $\text{COMe} \cdot \text{NNaBr}$, is formed, and may be precipitated as a white powder by the addition of cooled, anhydrous ether. The *sodium*, *potassium*, and *barium* salts may also be prepared in aqueous solution, but are contaminated with alkali bromide. With silver nitrate the aqueous solutions give an insoluble, white *silver* derivative, which is violently explosive when dry.

The *sodium* derivatives of bromopropionamide and bromoisobutyramide have also been prepared at low temperatures. On attaining the ordinary temperature they undergo explosive decomposition, the metallic bromide with an alkyl cyanate being produced (compare Hofmann, *Abstr.*, 1882, 951). When allowed to decompose in presence of alcohol, substituted urethanes are formed. W. O. W.

Fulminic Acid. IV. Action of Halogens on Mercury Fulminate. HEINRICH WIELAND (*Ber.*, 1909, 42, 4192—4199. Compare this vol., i, 215, 369).—In the light of recent work on the so-called glyoxime peroxides (compare Wieland, Semper, and Gmelin, this vol., i, 609), the “dibromonitroacetonitrile” obtained by Kekulé (*Annalen*, 1858, 105, 279) by the action of bromine on mercury fulminate must be identical with dibromofuroxan, $\text{O} \begin{smallmatrix} \text{CBr} & \text{CBr} \\ \diagdown & \diagup \\ \text{N} & \cdot & \text{N} \end{smallmatrix}$.

The fact that the interaction of dibromofuroxan and aniline yields oxanilidedioxime, instead of dianilinofuroxan (compare Holleman, *Abstr.*, 1893, i, 494), is explained by the formation of aniline-black in large proportions as a secondary product. By bromine-substitution of

the furoxan ring, the latter has assumed considerable oxidising power, so that, in the first phases of most of its reactions, the ring is opened by reduction :



When it is treated with nitrogen-bases, substitution then occurs, the products being amidoximes of oxalic acid. In consequence of the oxidising action, part of the base is oxidised in the case of aniline to aniline-black, and in those of hydrazine and ammonia to nitrogen. Only in the reaction with diethylamine does dibromofuroxan yield a compound in which the furoxan ring is unbroken.

Thus, with ammonia, dibromofuroxan yields nitrogen and oxamide-dioxide.

Tetra-ethyloxamidedioxime, $\text{OH} \cdot \text{N} : \text{C}(\text{NEt}_2) \cdot \text{C}(\text{NEt}_2) : \text{N} \cdot \text{OH}$, prepared by the action of diethylamine on dibromofuroxan, forms large, colourless plates, m. p. 71° .

Tetra-ethyldiaminofuroxan, $\text{O} \begin{array}{c} \diagup \text{C}(\text{NEt}_2) \diagdown \\ \diagdown \text{N} - \text{O} - \text{N} \diagup \end{array} \cdot \text{C} \cdot \text{NEt}_2$, also obtained by the interaction of diethylamine and dibromofuroxan, is a non-basic oil, with an odour resembling those of camphor and pyridine; it could not be obtained pure, as it decomposes at 115° .

In the interaction of chlorine and mercury fulminate, the oxidising action of the halogen results in the liberation of hydrogen chloride, and the principal result is the formation of a polymeride of fulminic acid. A small quantity of *dichlorofuroxan*, $\text{O} \begin{array}{c} \diagup \text{CCl} \diagdown \\ \diagdown \text{N} \cdot \text{O} \cdot \text{N} \diagup \end{array} \cdot \text{CCl}$, was separated in an impure state from the products, which also contain cyanogen chloride, but trichloronitromethane is obtained in appreciable quantity only when excess of chloroform is allowed to act, without cooling, on the fulminate (compare Holleman, Abstr., 1892, 25).

In the action of bromine on mercury (or silver) fulminate, the first product is probably an additive product, $(\text{CBr}_2 \cdot \text{N} \cdot \text{O})_2 \text{Hg}$, which loses mercuric bromide, giving the unstable bromoformonitrile oxide,

$\text{O} \begin{array}{c} \diagup \text{CBr} \diagdown \\ \diagdown \text{N} \diagup \end{array}$, 2 mols. of this compound then polymerising to dibromofuroxan.

A similar explanation holds for the action of chlorine on mercury fulminate, except that, in this case, the marked oxidising action of the halogen causes the predominance of the complete destruction of the fulminate molecule with formation of carbon dioxide. T. H. P.

Formation of "Nitrolime" (Calcium Cyanamide). II. FRITZ FOERSTER and HANS JACOBY. (*Zeitsch. Elektrochem.*, 1909, 15, 820. Compare Abstr., 1907, i, 397).—It is found, in agreement with earlier experiments, that when mixtures of calcium carbide and calcium fluoride are heated in an atmosphere of nitrogen for two hours at 800° to 900° , the greatest amount of nitrogen is taken up by the mixtures containing between 2% and 5% of the fluoride. If the time of reaction is increased to eight or ten hours, however, this difference disappears, all the mixtures taking up the same quantity of nitrogen. At 840°

the limit is reached at about 11%, and at 860° at 15%, of nitrogen in the product (complete conversion would correspond with 25.5%). The rate of absorption of nitrogen is proportional to its pressure (for pressures near 1 atmosphere). The rise of temperature which occurs when a considerable quantity of calcium carbide reacts with nitrogen is measured by heating 200 grams of carbide in a well-closed graphite crucible to the temperature at which reaction just begins, and then removing the blowpipes used for heating. With ordinary calcium carbide alone, the reaction begins at 1000°, and the temperature then rises to 1180°. With a mixture containing 5% of calcium chloride the reaction begins at 640°, and the temperature rises to 1010°. With 5% of calcium fluoride the reaction begins at 840°, and the temperature rises to 980°. In no case does the initial rapid reaction complete the conversion of the carbide; further heating is always necessary. The reaction in the case of the calcium fluoride mixtures is, however, much more under control than in the other cases, and by careful regulation of the heat, the whole conversion may be completed without exceeding a temperature of 960°.

The details of a number of experiments with charges of 80 to 90 kilograms, which were made by F. Carlson, are given; these confirm the conclusions drawn from the smaller experiments.

The technical method of preparing calcium cyanamide by heating an electrical resistance in the axis of a cylindrical mass of calcium carbide exposed to nitrogen is described. An experiment shows that the reaction develops enough heat to propagate itself to a short distance from the heated portion.

Careful estimations of the cyanide present show that the addition of calcium chloride or calcium fluoride does not increase the quantity of it (0.017 to 0.025% of hydrogen cyanide is found). In presence of excess of an alkali chloride, however, very considerable quantities are produced.

T. E.

Reaction between Hydrogen Sulphide and Cyanaminodithiocarbonates. ARTHUR HANTZSCH (*Ber.*, 1909, 42, 4215—4216).—The salt obtained by the action of hydrogen sulphide and potassium cyanaminodithiocarbonate, which the author and Wolvekamp (*Abstr.*, 1904, i, 718) regarded as a salt of thiocarbamidodithiocarbonic acid, $C(SH)_2 \cdot N \cdot CS \cdot NH_2$, has now been shown by Rosenheim, Levy, and Grünbaum (this vol., i, 776) to be a salt of trithioallophanic acid. As thiocarbamidodithiocarbonic acid is isomeric with trithioallophanic acid, $SH \cdot CS \cdot NH \cdot CS \cdot NH_2$, these authors are, however, inaccurate in stating that the latter acid is a reduction product.

T. H. P.

History of Guanino-acids. EMIL FISCHER (*Zeitsch. physiol. Chem.*, 1909, 63, 235—236. Compare Gansser, this vol., i, 702, and H. Ramsay, *ibid.*, i, 88).—The author objects to the name ethyl chloroformate for ethyl chlorocarbonate or the name ethyl guaninoformate for ethyl methylcarbamate. There is a considerable difference in properties between the carbamic esters and glycine esters. Glycine ester and not urethane is to be regarded as the first member of the series of esters of amino-acids.

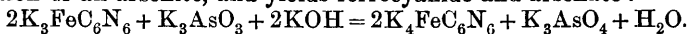
J. J. S.

Preparation of Cyanides. NIKODEM CARO (D.R.-P. 212706).—The alkali and alkaline earth cyanides are prepared by heating the carbonate of the metal with carbon in the presence of an alkaline fluoride (instead of a chloride) at 900—1100°. The employment of a fluoride enables the reaction to proceed below the melting point of the mixture; a porous mass is formed which facilitates the absorption of nitrogen. Moreover, since the fluorides are sparingly soluble only, the required product is dissolved by water; the residue is dried, and employed in subsequent operations. F. M. G. M.

Action of Alkaline Reducing Agents on Cyano-derivatives. AUGUST GUTMANN (*Ber.*, 1909, 42, 3623—3631. Compare this vol., i, 144).—The behaviour of the cyanogen halides towards alkaline reducing agents (sodium arsenite, sulphide, sulphite, and plumbite) has been studied. All three halogen derivatives react with an alkaline solution of sodium arsenite, yielding sodium arsenate, cyanide, and halide. With cyanogen iodide, the reaction proceeds according to the equation: $\text{CNI} + \text{Na}_3\text{AsO}_3 + \text{Na}_2\text{O} = \text{Na}_3\text{AsO}_4 + \text{NaCN} + \text{NaI}$, and the method may be used for estimating cyanogen iodide. An aqueous solution of potassium sulphide reacts with cyanogen iodide according to the equation: $\text{CNI} + \text{K}_2\text{S} = \text{KCNS} + \text{KI}$. When alcoholic solutions are used, a deep yellow coloration is formed together with a precipitate of potassium cyanide, but both coloration and precipitate disappear on the addition of water. It is suggested that the yellow coloration is due to the formation of potassium disulphide, K_2S_2 , or of potassium sulphide, KSI . Sodium plumbite reacts according to the equation: $\text{CNI} + \text{Na}_2\text{PbO}_2 = \text{NaCN} + \text{PbO}_2 + \text{NaI}$. Cyanogen chloride and sodium sulphite yield sodium sulphate, cyanide, and chloride. As the rule, the reactions with the bromide and chloride are analogous to those with the iodide.

The behaviour of the halogen compounds towards these reducing agents leads the author to suggest the following structural formula: $\text{C} \begin{smallmatrix} \nearrow \text{N} \\ \searrow \text{Cl} \end{smallmatrix}$.

Sodium arsenite and sulphite are not oxidised by cyanogen, but sodium sulphide and cyanogen yield cyanide and thiocyanate: $\text{C}_2\text{N}_2 + \text{Na}_2\text{S} = \text{NaCN} + \text{NaCNS}$. Potassium ferricyanide oxidises an alkaline solution of an arsenite, and yields ferrocyanide and arsenate:



Mercuric fulminate and sodium arsenite yield mercury, sodium arsenate, and cyanide.

It appears that compounds of the hydrogen peroxide type, for example, organic disulphides, sulfoxides, and disulphoxides, do not react with the above alkaline reducing agents, whereas compounds which are not of the hydrogen peroxide type, for example, sodium thiosulphate or its ester salts, readily yield an atom of oxygen or sulphur to these reducing agents. J. J. S.

Action of Hydrobromic Acid on Allyl Cyanide. BRULÉ (*Bull. Soc. chim.*, 1909, [iv], 5, 1019—1022).—Lespieau has shown (*Abstr.*, 1905, i, 9) that allyl cyanide when treated with hydrobromic

acid yields β -bromobutyramide. It was, therefore, of interest to ascertain whether Schindler's crotonitrile (Abstr., 1892, i, 32) would also yield β -bromobutyramide with hydrobromic acid, and this proves to be the case. Similarly, crotonic acid combines with hydrogen bromide to furnish β -bromobutyric acid, and not the α -isomeride as stated by Hemilian (Abstr., 1874, 682).

Lespieau also found (Abstr., 1903, i, 684) that the principal product of the action of bromine on allyl cyanide is $\beta\gamma$ -dibromobutyronitrile, with some monobromo-unsaturated compounds, whereas in the same reaction, Palmer (Abstr., 1889, 686) and Lippmann (Abstr., 1892, i, 27) had obtained $\alpha\beta$ -dibromobutyronitrile as the principal product. The author now finds that all three products may be obtained by the action of bromine on allyl cyanide, and that the relative proportion of each formed depends on the age of the allyl cyanide used and the amount of bromine present, the $\alpha\beta$ -isomeride being produced in largest quantity when old cyanide is used, or in presence of excess of bromine, or under experimental conditions leading to the formation of much hydrogen bromide. The mono-bromo-unsaturated products formed probably include a product of the formula $\text{CHMe}:\text{CBr}:\text{CN}$ or $\text{CH}_2:\text{CH}:\text{CHBr}:\text{CN}$, since the portion boiling about 50° gives $\alpha\beta$ -dibromobutyric derivatives with hydrobromic acid.

When $\beta\gamma$ -dibromobutyramide is treated with zinc dust in alcohol, *vinylacetamide* is formed. This has m. p. $72-73^\circ$, and crystallises in colourless leaflets. Contrary to the experience of Beilstein and Wiegand (Ber., 1884, 17, 2008), the author finds that crotonamide can be prepared by distilling ammonium crotonate.

T. A. H.

Oxidation of Naphthene and Benzene Hydrocarbons by the Action of Air in Presence of Alkali. K. W. CHARITSCHKOFF (*Chem. Zeit.*, 1909, 33, 1165).—Petroleum hydrocarbons (naphthenes) on oxidation by means of air with alkali as a "contact" substance, as used by Schall, give naphthenic acid, and, in addition, viscous, reddish-brown acids, which are soluble in ether or carbon disulphide, but insoluble in light petroleum. They reduce Fehling's solution and ammoniacal silver nitrate, but the presence of a $\cdot\text{CHO}$ group could not be proved. The acids furnish viscous esters, and on exposure to air, especially in contact with alkalis, darken and resinify to asphalt-like products, whence it is proposed to call them "asphaltogenic" or polynaphthenic acids. They contain 4 atoms of oxygen per mol., two of which are in hydroxyl groups, and to these the pseudo-acid properties of the substances are due. A hydrocarbon, $\text{C}_{10}\text{H}_{20}$, b. p. $169-171^\circ$, isolated by careful fractionation of petroleum, gave on oxidation by this method at 150° a syrupy acid, $\text{C}_{20}\text{H}_{25}\text{O}_4$, and a similar product was obtained from synthetic menthane. From another decanaphthene, b. p. $164-168^\circ$, isolated from petroleum, an acid, $\text{C}_{24}\text{H}_{34}\text{O}_4$, was prepared.

Cymene gave cumic acid, whilst ψ -cumene gave three isomeric monobasic acids. Of the three xylenes, only the para-isomeride was attacked, yielding a monobasic acid. Benzenoid hydrocarbons therefore yield only simple monobasic acids by this method, whilst the naphthenes yield the complex acids described above.

T. A. H.

Systems formed by Aluminium Chloride and Bromide with Aromatic Hydrocarbons. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1089—1110).—The author discusses the investigations of Gustavson and others (*Abstr.*, 1903, i, 470, 804; 1908, i, 328) on the formation of compounds of aluminium chloride with hydrocarbons which act as ferments in synthetical reactions, and gives the results of his own investigations of the equilibria of systems composed of benzene or toluene and aluminium chloride or bromide.

A solution of aluminium chloride in benzene saturated at (1) 80° contains 0.72% AlCl_3 , and at (2) 17° contains 0.12% AlCl_3 . With toluene the saturated solution contains 0.92% AlCl_3 at 73°, and 0.26% AlCl_3 at 17°. At higher temperatures, in sealed tubes, the solubilities are increased, but the solutions turn brown and the hydrocarbon enters into Friedel and Crafts' reaction.

Investigation of the system benzene-aluminium chloride by the method already described (see this vol., i, 900) yields a freezing-point diagram consisting of two curves meeting at the eutectic point, 1.8°, which corresponds with the composition $\text{AlBr}_3 \cdot 9 \cdot 1 \text{C}_6\text{H}_6$. The crystalline phases of the two curves consist of benzene and aluminium bromide respectively, the diagram indicating that no compound is formed between the two constituents.

With the system toluene-aluminium bromide, the freezing-point diagram is similar to that obtained in the previous case, and indicates that no molecular compound is formed by the two constituents. Here the eutectic point was not observed, owing to the very low temperature at which toluene melts.

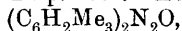
The system *p*-xylene-aluminium bromide gives similar results, the eutectic point, 10.2°, here corresponding with the composition $\text{AlBr}_3 \cdot 7.47 \text{p-C}_6\text{H}_4\text{Me}_2$.

Investigation at different temperatures of the compounds $\text{AlBr}_3 \cdot 3 \text{C}_6\text{H}_6$ and $\text{AlBr}_3 \cdot 3 \text{C}_6\text{H}_5\text{Me}$, formed in presence of hydrogen bromide (compare Gustavson, *Abstr.*, 1903, i, 470, 804), shows that the compositions of the two layers formed alter with change of temperature, indicating the formation of two immiscible solutions. It is possible, also, that the "ferments," if they exist as definite chemical compounds, dissolve with formation of two immiscible solutions. T. H. P.

Constituents of Coal Tar. II—V. GUSTAV SCHULTZ (*Ber.*, 1909, 42, 3602—3619. Compare this vol., i, 639).—II. *ψ-Cumene*. [With E. HERZFELD].—The sulphonic acid obtained by Jacobsen's method (*Annalen*, 1877, 184, 199) is not pure, and it is necessary to recrystallise repeatedly before *ψ*-cumenesulphonic acid is obtained as well-developed, rhombic prisms resembling cubes. The hydrocarbon is obtained by heating the acid to 110°, and then passing over steam heated to 250°. In this manner, 150 grams of pure *ψ*-cumene were isolated from 1080 c.c. of crude oil, b. p. 165—170°. It has b. p. 166°/712 mm. and D^{18} 0.877, and when oxidised with chromic anhydride yields trimellitic acid. When chlorinated in the dark, the hydrocarbon yields Haller's monochloro-derivative (*Abstr.*, 1885,

523), and ultimately *trichloro-ψ-cumene*, $C_6Cl_3Me_3$, which crystallises from alcohol in glistening needles, m. p. 197°.

When nitrated by a method similar to that used in the case of ethylbenzene, but keeping the temperature at 20° and stirring for some time, a good yield of the 5-nitro-derivative is obtained (*Zeitsch. Chem.*, 1867, 12), and, when this is oxidised, *nitrotrimeillic acid*, $NO_2 \cdot C_6H_2(CO_2H)_3$, is formed. The acid crystallises from hot water in long, glistening needles, m. p. 175°. *Azoxy-ψ-cumene*,



obtained by reducing the nitro-compound with sodium methoxide, crystallises from alcohol in pale yellow needles, m. p. 66°. When the nitro-ψ-cumene is further nitrated, 3:5-dinitro-ψ-cumene, $C_9H_{10}O_4N_2$, yellow needles, m. p. 171—172°, is formed, and ultimately 3:5:6-trinitro-ψ-cumene (Fittig and Laubinger, *Annalen*, 1869, 151, 261). It has not been found possible to nitrate ψ-cumene in the side-chains.

III. *n-Decane*. [With E. HARTOGH] (compare Jacobsen, *loc. cit.*; Krafft, *Abstr.*, 1882, 1271; 1883, 1076; Mabery, 1897, i, 450).—The fraction 150—180°, after repeated treatment with sulphuric acid and then with nitric acid, gave an oil (*n*-decane) with b. p. 172° when distilled over sodium, and $D^{15}_D 0.7387$. The monochloro-derivative had b. p. 122°/50 mm. and $D^{20}_D 0.8868$, and the dichloro-derivative, b. p. 157—159°/50 mm. and $D^{19}_D 1.0098$. When boiled with barium hydroxide solution, the monochloro-derivative gave decyl alcohol, b. p. 120°/15 mm., m. p. 6.5°, and $D^{17.5}_D 0.8321$. When oxidised with permanganate, the alcohol gave *n*-hexoic acid, m. p. 30°.

IV. *New Constituents of Solvent Naphtha*. [With A. PERL].—When solvent naphtha is fractionated, an oil is obtained intermediate between xylene and the trimethylbenzenes. From this oil the following fractions have been obtained: I, 153—157°; II, 157—160°; III, 160—162°. Fraction I was nitrated, reduced, and the resulting amino-compound benzoylated. From the crude benzoyl derivative, *p*-benzoylamino-*n*-propylbenzene, m. p. 115°, and benzoylamino-*p*-methyl-ethylbenzene, m. p. 165°, were isolated, together with two other benzoyl derivatives, m. p. 124° and 151°. Fractions II and III were fractionally sulphonated, the sulphonic acids transformed into the sulphonamides, and the non-sulphonated oils fractionated. Fraction II gave mesitylenesulphonamide and *o*-methylethylbenzenesulphonamide, together with an amide, m. p. 113—116°, and, as oils, *n*-decane and *p*-methylethylbenzene. Fraction III gave ψ-cumenesulphonamide, m. p. 181°, *m*-methylethylbenzenesulphonamide, m. p. 128°, *o*-methylethylbenzenesulphonamide (oil), *p*-methylethylbenzenesulphonamide, m. p. 70°, and an amide, m. p. 169°, together with *n*-decane. *p*-Ethylbenzene is much more difficult to sulphonate than its isomerides.

V. *n-Propylbenzene*. [With J. FÜHRER].—Crude cumene contains appreciable amounts of *n*-propylbenzene, and Jacobsen's (*loc. cit.*) sulphonic acid contains *n*-propylbenzenesulphonic acid in addition to ψ-cumenesulphonic acid. To obtain the *n*-propylbenzene, the sulphonic acids are crystallised; after most of the ψ-cumenesulphonic acid has separated, the sulphuric acid is removed, and the acids converted into their barium salts. The readily soluble barium salt is transformed into the sodium salt, and then into the amide. This is crystallised

and the portion m. p. 112—116° heated with concentrated hydrochloric acid at 175°. The resulting oil is fractionated, and the portion with b. p. 159—161° is practically pure *n*-propylbenzene. The pure *sulphonamide* crystallises in plates, m. p. 112°. J. J. S.

Durene. RICHARD WILLSTATTER and HEINRICH KUBLI (*Ber.*, 1909, 42, 4151—4163).—All attempts to prepare a nuclear mononitrodurene have failed. Francis' method with benzoyl nitrate (*Trans.*, 1906, 39, 1) yields *ω*-nitrodurene, $C_6H_2Me_3 \cdot CH_3 \cdot NO_2$, m. p. 52.5°, b. p. 143—144°/10 mm., which separates from methyl alcohol in long, colourless prisms, has a not unpleasant sweet odour, and is slightly volatile with steam. Its solution in concentrated potassium hydroxide yields by dilution, cooling, and acidification by sulphuric acid an iso-compound, m. p. 102—110°, which reverts readily into the more stable form. By nitration, the nitrodurene yields *ω*:3:6-trinitrodurene, m. p. 139°. *ω*-Aminodurene, m. p. 52°, obtained by reducing the nitro-compound by tin and hydrochloric acid, forms a *carbamate*, $C_{21}H_{30}O_2N_2$, m. p. 128—129°; *hydrochloride*, $C_{10}H_{15}N \cdot HCl$, m. p. 275—276°, and an *acetyl* derivative, m. p. 143.5° (corr.). 6-Bromo-3-nitrodurene, m. p. 178—179°, obtained by the action of 98% nitric acid on bromodurene in the presence of chloroform and concentrated sulphuric acid, crystallises in pale yellow prisms. 2- or (3-)Bromo-*ω*-nitrodurene, obtained together with the preceding compound from bromodurene by Francis' method, has m. p. 89—90.5°, and is also produced by brominating *ω*-nitrodurene in chloroform containing a trace of iodine.

Dinitrodureoyl bromide, $C_6Me_3(NO_2)_2 \cdot COBr$, m. p. 121.5°, is obtained by the action of cold fuming nitric acid on bromodurene or 6-bromo-3-nitrodurene, and yields dinitrodurylic acid by treatment with alcoholic potassium hydroxide. In a similar way the *bromide* of dinitrodimethylbenzenedicarboxylic acid, $C_6Me_3(NO_2)_2(COBr)_2$, m. p. 122°, is obtained. 3-Nitrodurene is produced by the interaction of iododurene and silver nitrite, but in such small amount that it cannot be isolated; its presence is proved by its reduction to 3-aminodurene. 3-Aminodurene, b. p. 261—262° (corr.), m. p. 75°, is obtained by reducing 6-bromo-3-nitrodurene by zinc dust in glacial acetic acid and concentrated hydriodic acid; the *hydrochloride* decomposes at 260°, and the *nitrate* at 200—205°; the *acetyl* derivative has m. p. 207°. It is easily oxidised to duroquinone.

Nitration by Francis' method does not yield *ω*-nitrated compounds in the case of *m*-xylene or mesitylene; with pentamethylbenzene, a mixture of about equal parts of *nitropentamethylbenzene*, m. p. 154°, and *ω*-nitropentamethylbenzene, m. p. 63°, is obtained, which is separated by means of methyl alcohol.

Hexamethylbenzene yields, by Francis' method, the *ether* of pentamethylbenzyl alcohol, $O(CH_2 \cdot C_6Me_5)_2$, m. p. 168°, and with an excess of benzoyl nitrate (2 mols.), *ω*:*ω'*-dinitrohexamethylbenzene,



m. p. 139°.

C. S.

Hexahydrophenylacetylene [*cyclo*Hexylacetylene] and **Hexahydrophenylpropionic Acid**. GEORGES DARZENS and ROST (*Compt. rend.*, 1909, 149, 681—682. Compare *Abstr.*, 1907, i, 617).—When

cyclo-hexyl methyl ketone is treated with phosphorus pentachloride, an unstable dichloro-derivative is formed, which immediately loses hydrogen chloride, yielding *a*-chlorocyclohexylethylene, $C_6H_{12} \cdot CCl:CH_2$, b. p. 70—74°/24 mm. When this is heated on an oil-bath with excess of dry potassium hydroxide, cyclohexylacetylene, $C_6H_{12} \cdot C:CH$, is obtained as a mobile liquid having a characteristic odour, b. p. 130—132°. This compound forms a sodium derivative, from which hexahydrophenylpropionic [cyclohexylpropionic] acid has been obtained by Nef's action. The new acid occurs as an oily liquid, b. p. 138—140°/6 mm.; its methyl ester has b. p. 96°/5 mm.; the ethyl ester has b. p. 105°/5 mm.

W. O. W.

Kinetics of Bromination. LUDWIK BRUNER and S. CZARNECKI (*Bull. Acad. Sci. Cracow*, 1909, 322—333).—The first part of the paper is polemical against Holleman (this vol., i, 93). In the second part an account is given of measurements of the velocity of bromination of ethylbenzene in glacial acetic acid solution in the dark. Experiments in the absence of, and in the presence of, hydrogen bromide or lithium bromide showed that these substances have no effect on the distribution of the bromine between the nucleus and the side-chain.

Toluene was also brominated electrolytically; the toluene formed a layer above a concentrated solution of hydrogen bromide, which was electrolysed between a zinc cathode and an anode either of platinum or carbon. At temperatures between 90° and 100°, substitution takes place practically only in the nucleus when the electrolysis is carried out in the dark or in a very weak light. In a bright light, however, practically only benzyl bromide is formed, no matter whether the temperature be low or high. These results are used to explain discrepancies between the observations of Cohen (*Trans.*, 1905, 87, 1034) and Holleman (*loc. cit.*).

T. S. P.

Compounds of Aluminium Bromide with Nitro-compounds of Aromatic Hydrocarbons and their Derivatives. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1053—1089).—The author has investigated the freezing-point diagrams of the systems formed by aluminium bromide with nitrobenzene, and with each of the three chloronitrobenzenes, bromonitrobenzenes, and nitrotoluenes.

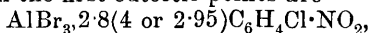
The diagram for the system $AlBr_3 - C_6H_5 \cdot NO_2$ is typical for the case of two components forming one compound. The first eutectic point ($C_6H_5 \cdot NO_2 - C_6H_5 \cdot NO_2, AlBr_3$) lies at -15°, and corresponds with a composition represented by $AlBr_3, 3C_6H_5 \cdot NO_2$. The compound $AlBr_3, C_6H_5 \cdot NO_2$, representing the crystalline phase of the second portion of the curve, forms thin, pale yellow plates, m. p. 87°, and is decomposed by water with development of heat and liberation of nitrobenzene (compare Kohler, *Abstr.*, 1901, ii, 21). The second eutectic point ($AlBr_3, C_6H_5 \cdot NO_2 - AlBr_3$) is about 20°, the composition corresponding with $AlBr_3, 0.58C_6H_5 \cdot NO_2$.

The three diagrams for the systems formed by aluminium bromide with the three chloronitrobenzenes are also typical for the formation of one definite compound between the two components. These crystalline compounds all have the formula $AlBr_3, C_6H_4Cl \cdot NO_2$,

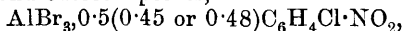
are extremely hygroscopic, and undergo instantaneous decomposition by the action of water. The m. p.'s of these compounds rise with the m. p. of the constituent chloronitrobenzene, as is seen from the following table :

	$\text{AlBr}_3, \text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$	$\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$
Ortho-.....	83.5°	32.5°
Meta-.....	103.5	44.5
Para-.....	115.0	83.0

The lack of complete proportionality between the m. p.'s of the chloronitrobenzenes and those of the compounds formed with aluminium bromide is conditioned probably by the varying stability of these compounds. This view is confirmed by comparison of the m. p.'s for the chloronitrobenzenes and their compounds with the eutectic temperatures, the greatest difference, namely, 95°, being observed between the m. p. of the compound and the second eutectic temperature for the system $\text{AlBr}_3, p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$. The first eutectic temperatures are 13.8°, 35.5°, and 60°, and the second 21°, 40°, and 20°, for the ortho-, meta- and para-compounds respectively. The compositions corresponding with the first eutectic points are



and with the second eutectic points,

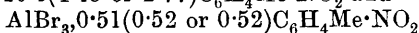


for the ortho-(meta- or para-)compound.

With aluminium bromide and the three bromonitrobenzenes, one molecular compound is formed in each case, its composition being $\text{AlBr}_3, \text{C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$. The properties of these compounds are similar to those of the corresponding chloronitrobenzene compounds. The m. p.'s of the molecular compounds are 88.5° (38°), 122° (54°), and 144° (124.5°) respectively for the ortho-, meta-, and para-derivatives, the numbers in brackets representing the m. p.'s of the bromonitrobenzenes themselves. The differences between the m. p.'s of the compounds formed by aluminium bromide with bromonitrobenzene and with chloronitrobenzene are 5°, 18.5°, and 29° for the ortho-, meta-, and para-compounds, whilst the corresponding numbers for the bromo-, nitro-, and chloronitro-benzenes themselves are 5.5°, 9.5°, and 41.5°. The first eutectic temperatures for the systems AlBr_3 -*o*-(*m*- or *p*-)bromonitrobenzene are 21°, 45.5°, and 98° respectively, these being lower than the m. p.'s of the bromonitrobenzenes by 17°, 8.5°, and 26.5° (the corresponding values for $\text{AlBr}_3, \text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ being 18.7°, 9°, and 23°); the second eutectic temperatures are 24°, 42°, and 45°, which are lower by 63.5°, 80°, and 99° (the values for $\text{AlBr}_3, \text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ being 62.5°, 63.5°, and 95°) than the m. p.'s of the corresponding compounds, $\text{AlBr}_3, \text{C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$. The compositions at the first eutectic points are $\text{AlBr}_3, 3.1(5.4 \text{ or } 2.4)\text{C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$, and at the second eutectic points, $\text{AlBr}_3, 0.5(0.36 \text{ or } 0.42)\text{C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$, for the *o*-(*m*- or *p*-)compound.

With *o*-, *m*-, and *p*-nitrotoluenes (m. p.'s - 8.5°, + 16°, and 53.5°), aluminium bromide forms the compounds $\text{AlBr}_3, \text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$, m. p.'s 90°, 96°, and 88°; the low m. p. of the para-compound probably depends on its instability. The m. p.'s of the nitrotoluenes are higher by 2.5°, 15°, and 24.5° than the first eutectic temperatures (- 11°, 1°, and 29°) of the systems AlBr_3 - $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$, whilst the m. p.'s of the

compounds $\text{AlBr}_3 \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$ are higher than the second eutectic temperatures (19° , 27° , and 27°) by 71° , 69° , and 61° respectively. The compositions corresponding with the first and second eutectic temperatures are $\text{AlBr}_3 \cdot 20.4(4.15 \text{ or } 2.77)\text{C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$ and



for the ortho-(meta- or para-)compound. The composition at the first eutectic point for the system $\text{AlBr}_3 \cdot o\text{-C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$ differs considerably from those for the meta- and para-systems, owing to the formation of the compound $\text{AlBr}_3 \cdot 2o\text{-C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$ in addition to the normal compound, $\text{AlBr}_3 \cdot o\text{-C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$. The ready decomposition of the compound $\text{AlBr}_3 \cdot p\text{-C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$ is indicated by the freezing-point diagram.

T. H. P.

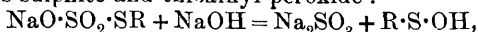
Benzyl Sulphoxide and α -Hydroxybenzyl Sulphide. EMIL FROMM and F. ERFURT (*Ber.*, 1909, 42, 3808—3812).—The constitution of benzyl sulphoxide has been established as $\text{SO}(\text{C}_6\text{H}_7)_2$, but Fromm and Ackert (*Abstr.*, 1903, i, 340) have observed the decomposition on heating to benzyl disulphide and benzaldehyde, and Smythe (*Trans.*, 1909, 95, 349) that the decomposition brought about by hydrogen chloride is very complicated. He explains this on the assumption that benzyl sulphoxide reacts in tautomeric forms, oxygen wandering from sulphur to carbon and forming α -hydroxybenzyl sulphide, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{OH}) \cdot \text{S} \cdot \text{C}_6\text{H}_7$. Pummerer (this vol., i, 580) criticises this view, but adopts another form of tautomerism.

α -Hydroxybenzyl sulphide is obtained by the addition of benzyl mercaptan to benzaldehyde in long, colourless needles, m. p. 43° . It is entirely different from benzyl sulphoxide, and cannot be converted into this. It decomposes when warmed in benzene solution into benzaldehyde benzylmercaptal, and is decomposed by sodium hydroxide, towards which benzyl sulphoxide is stable.

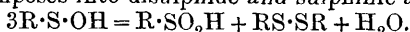
Smythe's explanation is accordingly to be rejected, and the more probable tautomeric form of benzyl sulphoxide is $\text{CHPh} \cdot \text{S}(\text{OH}) \cdot \text{CH}_2\text{Ph}$ (compare Pummerer, *loc. cit.*).

E. F. A.

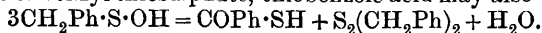
Hydrolysis of Thiosulphates and Thiosulphonates by Alkali. EMIL FROMM and F. ERFURT (*Ber.*, 1909, 42, 3816—3822).—Price and Twiss (*Trans.*, 1908, 93, 1390) have isolated sodium sulphite, benzyl disulphide, and thiobenzoic acid as products of the hydrolysis of benzyl thiosulphate by sodium hydroxide. It is now shown that benzylsulphinic acid is also formed. Accordingly, both oxidation and reduction products of the thiosulphate are formed during hydrolysis. It may be assumed (compare Gutmann, *Abstr.*, 1908, i, 497) that an oxidising agent is formed during hydrolysis. This cannot well be benzyl disulphide, as Price and Twiss (*loc. cit.*) assume, as this compound does not react when boiled with benzyl chloride and sodium hydroxide. It is now assumed that the thiosulphate forms sulphite and thioalkyl peroxide:



which last decomposes into disulphide and sulphinic acid:



In the case of benzyl thiosulphate, thiobenzoic acid may also be formed:



When sodium hydroxide is warmed with thiosulphonates, the solution is coloured yellow and contains sulphinic acids. Gutmann assumed the presence of sodium hydropersulphide, NaOSH , as an active agent in the reaction. This, however, in presence of excess of sodium hydroxide would become Na_2SO . By means of benzyl chloride it is possible to prove the presence of this substance if benzyl sulphoxide is formed. Actually by the hydrolysis of sodium *p*-tolylthiosulphonate by sodium hydroxide in presence of benzyl chloride, the following products are obtained: *p*-tolylsulphinic acid, benzyl disulphide, *p*-tolylbenzylsulphone, and *p*-tolylsulphonic acid.

E. F. A.

Action of Formaldehyde and Alkali on Sulphones. EMIL FROMM and F. ERFURT (*Ber.*, 1909, 42, 3823—3826).—Diformal-dibenzylsulphone, obtained by boiling dibenzylsulphone with formaldehyde and alkali (Fromm and Gaup, *Abstr.*, 1908, i, 970), is extremely stable. It withstands boiling with concentrated nitric acid and fusion with potassium hydroxide, and distils without decomposition; it is not attacked by bromine in chloroform, but by the action of bromine in sunlight a sparingly soluble product, m. p. 264° , is obtained. When boiled with bromine, a mixture of bromides is obtained, the most sparingly soluble of which is *dibromodiformaldibenzylsulphone*, m. p. 280° .

p-Tolylbenzylsulphone, when boiled with formaldehyde, yields *diformal-p-tolylbenzylsulphone*, m. p. 128° , which is equally stable. Phenylbenzylsulphone reacts less easily with formaldehyde, but likewise yields *diformalphenylbenzylsulphone*, m. p. 76° .

Benzylmethylsulphone, tolylmethylsulphone, or phenyltolylsulphone do not react with formaldehyde. Nitrated sulphones are decomposed by the alkali; di-*p*-nitrodiphenylsulphone, for instance, yielded stilbene, *p*-nitrophenol, and a compound, $\text{C}_{33}\text{H}_{30}\text{O}_7\text{N}_4\text{S}_3$, m. p. 322° .

Apparently, sulphones react with formaldehyde and alkali when they contain one benzyl and one aromatic residue. Two aromatic residues without the benzyl group, or a benzyl residue without a second aromatic residue, oppose the reaction.

E. F. A.

Action of *p*-Toluenesulphonyl Chloride on Thiocarbamide. EMIL FROMM and R. HEYDER (*Ber.*, 1909, 42, 3804—3807).—By the action of *p*-toluenesulphonyl chloride on thiocarbamide, Remsen and Turner (*Abstr.*, 1901, i, 270) obtained dithiocarbamide dichloride, $\text{C}(\text{NH}_2)_2\text{Cl}\cdot\text{S}\cdot\text{S}\cdot\text{CCl}(\text{NH}_2)_2$. Storch (*Abstr.*, 1891, 548) terms the same compound, which he obtained by the action of oxidising agents on thiocarbamide in acid solution, carbamido-iminodisulphide, and formulates it as $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{S}\cdot\text{S}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$, the dichloride being identical with Remsen and Turner's compound. Storch's formula is in agreement with the decomposition of the compound by water or alkalis into sulphur, thiocarbamide, and cyanamide.

p-Toluenesulphonyl chloride also acts as an oxidising agent towards arylthiocarbamides, but it acts similarly to hydrogen peroxide or bromine, liberating sulphur, and does not give disulphides. From phenylthiocarbamide and *p*-toluenesulphonyl chloride, sulphur and the *hydrochloride* of diphenyldi-iminotetrahydrodiazothiole are obtained. The

free base crystallises in colourless needles, m. p. 198° , and is identical with that described by Hector (Abstr., 1889, 872; 1890, 526; 1892, 292) with m. p. 181° . This figure is an error, as a mixture of the base prepared by both methods shows m. p. 198° . The acetate forms colourless needles, m. p. 240° (Hector, 233°); the base forms an additive product with carbon disulphide (Hector, *loc. cit.*) crystallising in yellow needles, m. p. 162° .

It is considered that the first action of toluenesulphonyl chloride is to form the disulphide; this decomposes into sulphur, phenylthiocarbamide, and phenylecyanamide, from which the diazothiole is ultimately built up. E. F. A.

Behaviour of Unsaturated Groups in Quaternary Ammonium Salts and Tertiary Sulphonamides. EDGAR WEDEKIND [with F. OBERHEIDE] (*Ber.*, 1909, 42, 3939—3941).—The author gives a brief account of certain observations similar to that of Emde (this vol., i, 565), who found that the ethylene linking of cinnamyltrimethylammonium chloride is not able to take up hydrogen and become saturated.

That the ammonium complex possesses the property of rendering a double carbon-atom linking resistant to saturation by hydrogen has already been demonstrated, for example, by the preparation of 1-allyltetrahydroquinoline from the iodoallyl derivative of quinoline by reduction with tin and hydrochloric acid. It appears also that the double linking between carbon and oxygen is protected against reduction by the ammonium residue, since attempts to reduce, by means of sodium amalgam, certain phenacylammonium salts, $\text{NR}_3\text{X}\cdot\text{CH}_2\cdot\text{COPh}$ (compare Abstr., 1908, i, 878), to the corresponding carbinol salts, $\text{NR}_3\text{X}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{OH}$, and so form an asymmetric carbon atom in addition to the asymmetric nitrogen atom, resulted in all cases in a total decomposition of the keto-ammonium salt with formation of free base; neutral reducing agents were found to be without action.

Also, with certain derivatives of tervalent nitrogen, a double carbon-atom linking exhibits unexpected behaviour. Attempts to prepare allylisobutylamine from *p*-toluenesulphoallylisobutylamide, by heating with chlorosulphonic acid at $130\text{--}140^{\circ}$ (compare Marckwald and von Droste-Huelshoff, Abstr., 1899, i, 289), show that the removal of the toluenesulphonyl residue does not take place, owing to an effect of the double linking. This reaction is, however, effected by Hinsberg's method (Abstr., 1892, 64) of heating with hydrochloric acid under pressure, toluenesulphonic acid being removed, and the hydrochloride of the amine obtained in theoretical yield.

p-Toluenesulphoallylamide, $\text{C}_{10}\text{H}_{13}\text{O}_2\text{NS}$, prepared by the action of dilute sodium hydroxide on *p*-toluenesulphonyl chloride and allylamine, forms colourless needles, m. p. $64\text{--}65^{\circ}$.

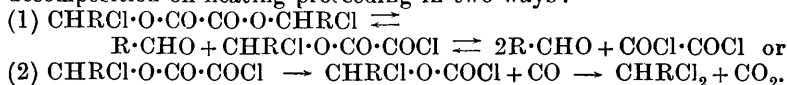
p-Toluenesulphoallylisobutylamide, prepared by the action of the calculated proportions of isobutyl bromide and alcoholic potassium hydroxide, is obtained as an oil; the hydrochloride has m. p. 230° .

p-Toluenesulphoisobutylamide, $\text{C}_{11}\text{H}_{16}\text{O}_2\text{NS}$, has m. p. 78° .

T. H. P.

Oxalyl Chloride. III. Its Action on Carbonyl Compounds.

HERMANN STAUDINGER (*Ber.*, 1909, 42, 3966—3985. Compare *Abstr.*, 1908, i, 938; this vol., i, 796).—Oxalyl chloride behaves towards many carbonyl compounds like an inorganic acid chloride, such as phosphorus pentachloride, does, the carbonyl group being converted into $\cdot\text{CCl}_2$, thus: $\text{CR}^1\text{R}^2\text{:O} + \text{COCl}\cdot\text{COCl} = \text{CR}^1\text{R}^2\text{:Cl}_2 + \text{CO} + \text{CO}_2$. The reaction has been studied for the following groups of ketonic derivatives: (1) Dibenzylideneacetone, dianisylideneacetone, benzylideneacetophenone, cinnamaldehyde, and benzylideneacetone; (2) benzaldehyde and benzophenone; (3) dimethylaminobenzaldehyde, dimethylaminobenzophenone, and tetramethyldiaminobenzophenone; (4) tetramethyldiaminodibenzylideneacetone and dimethylaminobenzylideneacetophenone. The ketochlorides of nearly all these compounds can be readily prepared by means of the above reaction, which proceeds in some cases in the cold and in others only on heating. An intermediate product is obtained only with cinnamaldehyde, its decomposition on heating proceeding in two ways:

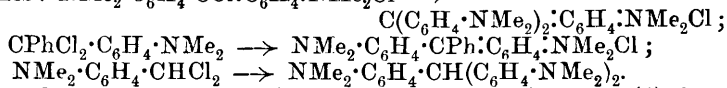


The ketochlorides corresponding with the compounds of group (1) are formed more readily than those of group (2), the cinnamenyl group increasing the reactivity of the carbonyl group towards oxalyl chloride. In other cases, also, a special influence of the cinnamenyl residue on neighbouring groups has been observed (compare Staudinger, *Abstr.*, 1908, i, 411; von Baeyer and Villiger, *Abstr.*, 1902, i, 380; von Baeyer, *Abstr.*, 1905, i, 281; Straus and Hüsey, this vol., i, 490). Also, the compounds of group (3) react far more readily than those of group (2), and the members of group (4) more readily than those of group (1), a dimethylamino-group in the para-position causing a marked increase in the reactivity of the carbonyl group.

The action of carbonyl chloride on the carbonyl group is similar to, but far less ready than, that of oxalyl chloride, the same products being obtained: $\text{CR}^1\text{R}^2\text{:O} + \text{COCl}_2 = \text{CR}^1\text{R}^2\text{Cl}_2 + \text{CO}_2$; in no case is an intermediate product observed. Only the highly reactive compounds of groups (3) and (4) react readily with carbonyl chloride.

Of the various ketochlorides, only those with two dimethylamino-groups have a quinonoid character; the author ascribes to these compounds formulæ analogous to those suggested by von Baeyer for the triphenylmethane dyes (*Abstr.*, 1907, i, 757; compare also Schlenck, this vol., i, 808).

The ketochlorides of group (3) are regarded as intermediate products in the formation of triphenylmethane dyes, and, indeed, they react extremely readily with dimethylaniline according to the following schemes: $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CCl}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{Cl} \rightarrow$



The analogous conversion of the ketochlorides of group (4) into phenyldistyrylmethane and diphenylstyrylmethane dyes is to be investigated later.

The condensation product of oxalyl chloride and cinnamaldehyde: $\text{CHPh}:\text{CH}:\text{CHCl}\cdot\text{O}\cdot\text{CO}\cdot\text{CO}\cdot\text{O}\cdot\text{CHCl}:\text{CH}:\text{CHPh}$, forms white leaflets, m. p. $106.5-107^\circ$ (decomp.), at which temperature it slowly, but almost quantitatively, loses CO and CO_2 . It is extremely resistant to the action of water, but when heated with it, it yields oxalic acid; with aniline (6 mols.) in dichloroethylene, it gives oxanilide almost quantitatively, whilst with methyl alcohol it forms methyl oxalate and cinnamaldehyde.

Distyryldichloromethane, prepared from dibenzylideneacetone and oxalyl chloride in dichloroethylene solution, was obtained in pale yellow leaflets, m. p. $72-74^\circ$ (von Baeyer and Villiger, Abstr., 1901, i, 658, gave 78° , and Straus and Ecker, Abstr., 1906, i, 859, 77°).

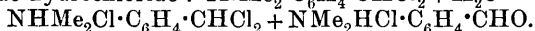
$\beta\beta$ -Dichloro- α -dianisylidenepropene, $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH})_2\text{CCl}_2$, prepared from dianisylideneacetone and oxalyl chloride, forms white or faintly yellow crystals, m. p. $86-87^\circ$, and is stable when dry, but when moist, or in solution, immediately changes to a bluish-violet decomposition product, which is converted into the original compound by boiling with oxalyl chloride in ether or light petroleum.

Styryldichloromethane, prepared from cinnamaldehyde, has b. p. $124/13$ mm., m. p. $57.5-58.5^\circ$ (compare Charon and Dugoujon, Abstr., 1903, i, 240).

Phenylstyryldichloromethane, $\text{CHPh}:\text{CH}:\text{CPhCl}_2$, prepared from benzylideneacetophenone, has b. p. $190-192/16$ mm., m. p. $37.5-38^\circ$.

Benzylideneacetone (2 mols.) and oxalyl chloride (1 mol.) react slowly in the cold, forming brownish-red needles, m. p. $145-146^\circ$ (decomp.), the composition of which does not correspond with any simple product.

Dimethylaminobenzylidene chloride, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHCl}_2$, obtained by the action of oxalyl chloride or carbonyl chloride on dimethylaminobenzaldehyde, forms colourless or faintly yellow plates, decomp. at $60-65^\circ$ with evolution of hydrogen chloride, or at $100-110^\circ$ in a sealed tube. It is extremely sensitive to the action of moisture, which changes it first to green and then to a yellow mixture of dimethylaminobenzylidene chloride hydrochloride and dimethylaminobenzaldehyde hydrochloride: $2\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHCl}_2 + \text{H}_2\text{O} =$

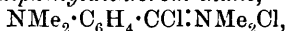


The action of moisture on the ethereal or light petroleum solution of dimethylaminobenzylidene chloride yields a dark green product, m. p. $100-110^\circ$ (decomp.), which in some cases is composed of 1 mol. of dimethylaminobenzylidene chloride and 1 mol. of its hydrochloride, and is probably a quinhydrone-like compound formed by the union of the chloride in its quinonoid form, $\text{NMe}_2\text{Cl}:\text{C}_6\text{H}_4\cdot\text{CHCl}$, with its hydrochloride. With aniline (3 mols.), dimethylaminobenzylidene chloride yields dimethylaminobenzylideneaniline (compare Sachs and Lewin, Abstr., 1903, i, 37), whilst with dimethylaniline it gives a deep blue compound, which, with water, yields the white leucobase of crystal-violet, m. p. 173° . Dimethylaminobenzylidene chloride hydrochloride (*vide supra*), m. p. $150-155^\circ$ (decomp.), is distinctly more stable than the free base. Dimethylaminobenzaldehyde hydrochloride (*vide supra*) forms white crystals, m. p. $107-109^\circ$, forms a

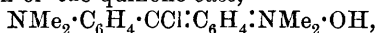
colourless solution in water, which decomposes it into the aldehyde, and does not react with dimethylaniline.

Di- α -chlorophenyldimethylaminophenylmethane, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPhCl}_2$, prepared from dimethylaminobenzophenone, is readily acted on by moisture, and is obtained only in solution. Its *hydrochloride*, $\text{C}_{15}\text{H}_{16}\text{NCl}_3$, m. p. 110—120° (decomp.), is white and dissolves in water to a deep orange-red solution. *Dimethylaminobenzophenone hydrochloride*, $\text{C}_{15}\text{H}_{16}\text{ONCl}$, forms white crystals, m. p. 129—130°.

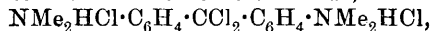
Tetramethyldiaminodiphenyldichloromethane,



prepared from tetramethyldiaminobenzophenone, best by the action of carbonyl chloride, separates in bluish-black, hygroscopic leaflets with green reflection, sinters at 125—140°, and decomp. at 150°. In water or alcohol it gives a deep blue solution, the colour disappearing gradually in the cold and rapidly on heating, the original ketone being formed. Addition of sodium hydroxide to its dilute solution results in the precipitation of the quinone *base*,



in violet-red flocks, m. p. (impure) 150—160° (decomp.). With dimethylaniline the ketochloride reacts instantaneously, giving crystal-violet. With aqueous hydrochloric acid, it forms a green *acid salt*, $\text{NMe}_2\text{HCl} \cdot \text{C}_6\text{H}_4 \cdot \text{CCl} : \text{C}_6\text{H}_4 : \text{NMe}_2\text{Cl}$, whilst with dry hydrogen chloride it yields the white *salt* of the true ketochloride,



which turns dark blue at 150°, decomposes at 185°, and gives a deep blue aqueous solution.

On passing hydrogen chloride into a benzene or dichloroethylene solution of tetramethyldiaminobenzophenone, the solution at first turns brown, owing to the formation of the quinonoid mono-hydrochloride, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) : \text{C}_6\text{H}_4 : \text{NMe}_2\text{Cl}$, and almost immediately afterwards colourless, consequent on the formation of the dihydrochloride, which decomposes at 150° in a vacuum, giving the ketone and hydrogen chloride; the dihydrochloride exhibits no inclination towards the quinonoid structure.

Tetramethyldiaminodistyryldichloromethane, prepared by the action of oxalyl chloride or carbonyl chloride on tetramethyldiaminodibenzylideneacetone, separates in the quinonoid form as a violet precipitate, dilute solutions of which are dark green and are changed to red by dilute hydrochloric acid.

Phenyldimethylaminostyryldichloromethane, prepared from dimethylaminobenzylideneacetophenone, has as yet only been obtained in solution.

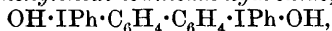
T. H. P.

Homologue of Diphenyleneiodonium Hydroxide: Ditolyleneiodonium Hydroxide. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 190—194).—Diazotisation of 2 : 2'-diamino-4 : 4'-dimethyldiphenyl (compare von Niementowski, *Abstr.*, 1902, i, 21), followed by treatment with potassium iodide, yields: (1) a small proportion of 2 : 2'-di-iodo-4 : 4'-dimethyldiphenyl, which could not be purified, and (2) *ditolyleneiodonium iodide*, $\text{C}_6\text{H}_3\text{Me}_2 > \text{I} \cdot \text{I}$, which forms

yellow crystals, m. p. 206° (decomp.) (compare Abstr., 1907, i, 1021; this vol., i, 94). T. H. P.

Derivatives of 4:4'-Diiododiphenyl with Polyvalent Iodine and the Iodination of Diphenyl. CONRAD WILLGERODT and GUSTAV HILGENBERG (*Ber.*, 1909, 42, 3826—3833).—4:4'-Diiododiphenyl (prepared by diazotising benzidine and decomposing the diazo-compound with potassium iodide) crystallises in colourless platelets, m. p. 202°. The *bisiododichloride*, $\text{ICl}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{ICl}_2$, forms an amorphous, yellow precipitate (decomp. 154°); 4:4'-*di-iodosodiphenyl* was not obtained pure, the product exploded about 198°. 4:4'-*Di-iodoxydiphenyl*, $\text{IO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{IO}_2$, obtained by boiling the iodochloride with sodium hypochlorite, is amorphous; it explodes at 218°, and, like the above compounds, gives only di-iododiphenyl when recrystallised.

Diphenyl-4:4'-diphenylenedi-iodinium hydroxide,



could only be obtained in aqueous solution of weak alkaline reaction. A number of salts are described: the *iodide* is a bright yellow, amorphous precipitate (decomp. 158°); the *bromide* is colourless, sinters at 170°, m. p. 185°; the *chloride* is also colourless, m. p. 185°; the *dichromate* is yellow and blackens at 80°; the *mercurichloride* is a colourless, amorphous compound, m. p. 170°; the *platinichloride* crystallises in golden-yellow needles, m. p. 168°.

The following salts of *di-p-tolyl-4:4'-diphenylenedi-iodinium hydroxide* have been prepared. The *iodide* is a light yellow, amorphous compound, m. p. 145°; the *bromide* is colourless, sinters at 180°, m. p. 186°; the *chloride* decomposes at 190°; the yellow *dichromate* sinters at 90°, m. p. 122°; the *mercurichloride* has m. p. 185°; the *platinichloride* is a yellowish-red precipitate, m. p. 173°.

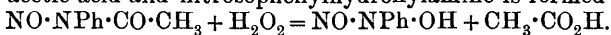
Di-as-m-xylyl-4:4'-diphenylene-di-iodinium hydroxide was obtained in solution with an alkaline reaction; the *iodide* forms a yellow, amorphous precipitate, m. p. 152°.

The dry iodinium compounds, when heated above their melting point, decompose into 4:4'-di-iododiphenyl and aryl iodides. This confirms their composition as diphenylene compounds, and not diphenyl-iodinium derivatives. Further, diphenyldi-iodochloride and mercury diphenyl give the same diphenyldiphenylenedi-iodinium chloride as obtained from di-iodosodiphenyl and iodobenzene.

When diphenyl is warmed in light petroleum solution with sulphur iodide and nitric acid, D 1.34, the product is di-iododiphenyl. When, however, nitric acid (D 1.5) is employed, the product is *p*-di-iodobenzene. This product also results when iodine and nitric acid (D 1.5) are used to introduce the halogen into diphenyl. E. F. A.

Action of Hydrogen Peroxide on Nitrosoacetanilide and Spontaneous Decomposition of the Latter. EUGEN BAMBERGER and OSCAR BAUDISCH (*Ber.*, 1909, 42, 3582—3591).—When hydrogen chloride is passed into a light petroleum solution of nitrosoacetanilide, acetanilide is formed, together with a small amount of a diazo-salt, but when the nitroso-derivative is oxidised with hydrogen peroxide at

—20° under suitable conditions, the acetyl group is eliminated in the form of acetic acid and nitrosophenylhydroxylamine is formed :



If the conditions which are described in detail are adhered to strictly, the yield of nitrosophenylhydroxylamine can be as high as 94% of the theoretical, but otherwise nitroso- and even nitro-benzene are formed by the oxidation of the nitrosohydroxylamine.

The hydroxylamine can be isolated in the form of its ammonium salt (compare this vol., i, 978) by passing a rapid stream of ammonia into a dry ethereal solution.

In a few of the experiments, hydrogen peroxide was practically without action on nitrosoacetanilide. *p*-Chloro- and *p*-bromo-nitrosoacetanilides are oxidised by hydrogen peroxide in much the same manner as nitrosoacetanilide.

p-Bromonitrosoacetanilide, $\text{NO} \cdot \text{NAc} \cdot \text{C}_6\text{H}_4\text{Br}$, decomposes at 86—87°, and *p*-bromophenylnitrosohydroxylamine, $\text{NO} \cdot \text{N}(\text{OH}) \cdot \text{C}_6\text{H}_4\text{Br}$, has m. p. 86—87°.

Diphenyl is obtained when a benzene solution of nitrosoacetanilide is kept at the ordinary temperature (Abstr., 1898, i, 366), but when an ethereal solution is kept at 0°, a small amount of benzenediazonium nitrate is formed.

J. J. S.

Amic Acids. V. Action of Amines on Dibasic Aliphatic Acids. J. BISHOP TINGLE and S. J. BATES (*J. Amer. Chem. Soc.*, 1909, 31, 1233—1242).—In earlier papers (Tingle and Cram, Abstr., 1907, i, 692; Tingle and Lovelace, Abstr., 1907, i, 1044; Tingle and Rolker, this vol., i, 28; Tingle and Brenton, this vol., i, 798), experiments have been described on the interaction of amines with phthalic acid and its derivatives. The present paper gives an account of an extension of the work to aliphatic dibasic acids.

It has been found that the aliphatic amic acids, $\text{NHR} \cdot \text{CO} \cdot \text{X} \cdot \text{CO}_2\text{H}$, behave quite differently from the corresponding aromatic compounds. Under conditions in which the phthalamic acids are readily converted into imides, the aliphatic compounds are quite stable and cannot be transformed into the imides even by prolonged heating at a high temperature. The cause of this difference is discussed, and it is shown that it can only be due to the inherent nature of the benzene nucleus.

Oxanilic acid is not affected at 100° by ethyl alcohol, methyl alcohol, or toluene, but is converted by aniline into aniline oxanilate. *Quinoline oxanilate*, m. p. 122—123°, and the *pyridine* salt, m. p. 132—133°, form colourless crystals; the β -*naphthylamine* salt, m. p. 151°, forms pink crystals. *Potassium hydrogen oxanilate* was also prepared.

β -Naphthylloxamic acid (Friedländer, Heilpern, and Spielfogel (Abstr., 1899, i, 708) could not be prepared. β -Naphthylsuccinamic acid melts at 184—185°, instead of 190—192°, as stated by Pellizzari and Matteucci (Abstr., 1888, 1303), and is not changed when heated at 100° with aniline, quinoline, or β -naphthylamine in presence of alcohol or toluene.

Fumaric acid combines with aniline at the ordinary temperature to

form *aniline hydrogen fumarate*, m. p. 185°, which forms colourless crystals. At 160—170°, aniline and fumaric acid yield anilino-succinylphenylimide (phenylasparaginil). Fumarilic acid could not be obtained by Bischoff's method (Abstr., 1891, 1220), but was prepared by the action of fumaryl chloride on an ethereal solution of aniline. When either this compound or maleilic acid is heated with aniline at 100°, phenylasparaginil is produced.

When a mixture of malic acid and aniline is distilled under reduced pressure, maleilic acid and phenylasparaginil are produced. Malilic acid could not be prepared by Arppe's method (*Annalen*, 1856, 96, 111), but by warming the anil with strong potassium hydroxide solution and adding hydrochloric acid to the well-cooled product, small quantities of the acid were obtained, m. p. 155°; its *aniline* salt has m. p. 110°.

ψ -Itaconilic acid is not affected by aniline at 100°. Citraconic acid reacts with aniline to form a compound, m. p. 170—171°, which is probably anilino-pyrotartaric acid. The statement of Gottlieb (*Annalen*, 1852, 77, 284), that when aniline and citraconic acid are heated together at 100° the anilic acid is produced, could not be confirmed.

Tartranilic acid yields salts with all the amines studied. The *aniline* and *quinoline* salts melt at 149—150° and 129—130° respectively. The β -*naphthylamine* salt, m. p. 176—177°, when heated at 180°, is converted into a compound, probably *phenyl- β -naphthyltartramide*, $\text{NHPh}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, m. p. 240—242°, which forms colourless crystals. *β -Naphthyltartramic acid*, $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$,

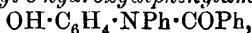
m. p. 180°, is obtained in small yield by heating β -naphthylamine with tartaric acid for three hours at 180—200°, and when heated at its m. p. is converted into the β -*naphthylamide*, m. p. 220°; the *aniline* salt melts at 172—174° with formation of phenyl- β -naphthyltartramide.
E. G.

[Preparation of Methylenebis-3-chloro-6-nitroaniline.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 212594).—*Methylenebis-3-chloro-6-nitroaniline*, $\text{CH}_2(\text{NH}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{NO}_2)_2$, is prepared by heating 5-chloro-*o*-nitroaniline with formaldehyde at 70—80°. F. M. G. M.

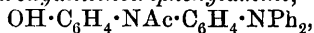
Electrochemical Reduction of Condensation Products of Aldehydes with Amines. WALTER LÖB (*Ber.*, 1909, 42, 3987).—Brand (this vol., i, 784) has overlooked the work of the author (Abstr., 1899, i, 122) and of Goecke (Abstr., 1903, i, 615) on this subject.
T. H. P.

Diphenylamine and Acylperoxides. STEPHAN GAMBARJAN (*Ber.*, 1909, 42, 4003—4013).—Attempts have been made to prepare diphenylhydroxylamine by the oxidation of diphenylamine. Hydrogen peroxide is without action on the amine, and Caro's acid does not give definite products. With benzoyl peroxide in chloroform solution, the

chief product is *N*-benzoyl-*o*-hydroxydiphenylamine,

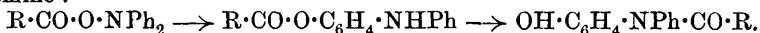


and with acetyl peroxide the products are *N*-acetyl-*o*-hydroxydiphenylamine, *N*-acetyl-*o*-hydroxyanilinotriphenylamine,

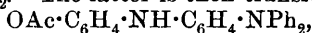


and tetraphenylhydrazine.

The acyl peroxide probably reacts with the amine, yielding free acid and acyldiphenylhydroxylamine, $\text{R} \cdot \text{CO} \cdot \text{O} \cdot \text{O} \cdot \text{CO} \cdot \text{R} + \text{HNPh}_2 = \text{R} \cdot \text{CO} \cdot \text{OH} + \text{R} \cdot \text{CO} \cdot \text{O} \cdot \text{NPh}_2$, the latter then undergoes molecular rearrangement, yielding an *o*-acyloxy-derivative of diphenylamine, and this, by a second rearrangement, yields an *o*-hydroxy-*N*-acyldiphenylamine:



The formation of the triphenylamine derivative can be accounted for by the following series of reactions. Two molecules of acetyldiphenylhydroxylamine undergo condensation, yielding acetic acid and $\text{OAc} \cdot \text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NPh}_2$. The latter is then transformed into



and this into $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NAc} \cdot \text{C}_6\text{H}_4 \cdot \text{NPh}_2$. The tetraphenylhydrazine is probably formed by the condensation of acetyldiphenylhydroxylamine with the excess of diphenylamine: $\text{NPh}_2 \cdot \text{OAc} + \text{HNPh}_2 = \text{AcOH} + \text{NPh}_2 \cdot \text{NPh}_2$. *N*-Benzoyl-*o*-hydroxydiphenylamine dissolves in hot glacial acetic acid, and has m. p. 214° . When hydrolysed with methyl-alcoholic potassium hydroxide at 140° it yields *o*-hydroxydiphenylamine (Deninger, Abstr., 1894, i, 511), which, on acetylation, gives *N*-acetyl-*o*-hydroxydiphenylamine, m. p. 144 — 146° . The same acetyl compound is formed by the action of acetyl peroxide on diphenylamine, and crystallises from benzene. It dissolves in aqueous alkalis, but is precipitated by carbon dioxide.

N-Acetyl-*o*-hydroxyanilino-triphenylamine has m. p. 218 — 220° , and crystallises from glacial acetic acid.

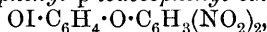
Diphenylamine and perbenzoic acid yield benzoic acid and an orange-red compound, m. p. 138 — 142° . J. J. S.

Preparation and Hydrolysis of Phenylthiocarbimide Oxide. EMIL FROMM and R. HEYDER (*Ber.*, 1909, 42, 3800—3803).—By the action of bromine on phenylthiocarbimide in chloroform solution in presence of aqueous ethyl alcohol, Freund and Bachrach (Abstr., 1895, i, 576, 578) obtained a bromine additive product of phenylthiocarbimide, and from this, phenylthiocarbimide oxide in small quantities. It is now found that the main product is a substance, $\text{C}_9\text{H}_9\text{O}_2\text{NBr}_2$, soluble in chloroform, crystallising in colourless needles. When methyl alcohol is used in the condensation, a corresponding compound, $\text{C}_8\text{H}_7\text{O}_2\text{NBr}_2$, m. p. 96° , is obtained, which is identical with methyl 2 : 4-dibromocarbaniolate, described by Hentschel (Abstr., 1887, 143). The ethyl derivative is accordingly *ethyl* 2 : 4-dibromocarbaniolate.

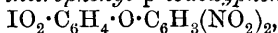
Phenylthiocarbimide oxide behaves on hydrolysis in agreement with the formula, $\text{NPh} \begin{array}{c} \text{CO} \text{---} \text{S} \\ \diagdown \quad \diagup \\ \text{C}(\text{NPh}) \cdot \text{S} \end{array}$, assigned to it by Hantzsch and Wolve-

kamp (Abstr., 1904, i, 720). Potassium hydroxide in cold concentrated solution hydrolyses it to sulphur, diphenylcarbamide, and alkali sulphide. Phenylhydrazine gives rise to hydrogen sulphide and diphenylthiosemicarbazide. E. F. A.

Derivatives of Aromatic *p*-Monoiodophenyl Ethers with Polyvalent Iodine. CONRAD WILLGERODT and GUSTAV WIEGAND (*Ber.*, 1909, 42, 3763—3769).—as-m-*Dinitrophenyl p*-iodophenyl ether, prepared by adding potassium *p*-iodophenoxide to a cold alcoholic solution of chlorodinitrobenzene (1 mol.), forms pale yellow, lustrous needles of m. p. 156°. as-m-*Dinitrophenyl p*-iodochloride phenyl ether, $\text{ICl}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, is obtained in the form of yellow needles by acting on a cold solution of the iodo-compound in chloroform with chlorine; it is very stable, and on heating it decomposes at 123°. as-m-*Dinitrophenyl p*-iodosophenyl ether,

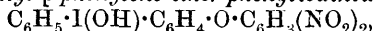


prepared by acting on the iodochloride with dilute sodium carbonate at the ordinary temperature, is a yellow, amorphous powder which decomposes at 131°. Attempts to prepare the iodoso-acetate were unsuccessful. as-m-*Dinitrophenyl p*-iodoxyphenyl ether,

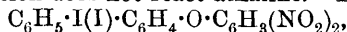


is obtained only in small quantities by boiling the iodoso-compound with water. A better result is obtained by digesting the iodochloride with sodium hypochlorite and acetic acid for one or two days at room temperature, and the yield is almost quantitative when the reaction mixture is boiled for ten to fifteen minutes instead. The pure iodoxy-compound is very stable; it crystallises in small, white needles, and explodes at 193°. This new method for preparing iodoxy-compounds was found to be equally satisfactory in the case of iodoxybenzene and *p*-iodoxytoluene.

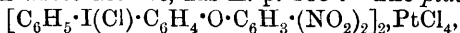
as-m-*Dinitrophenyl-p*-phenylene-ether-phenyliodinium hydroxide,



is best prepared in solution by treating equimolecular quantities of dinitrophenyl *p*-iodoxyphenyl ether with silver oxide and water at 40—60°. The solution does not react alkaline. The *iodide*,



is prepared by rendering the solution of the base weakly alkaline with sodium carbonate, and then adding a concentrated solution of potassium iodide; it forms yellow needles of m. p. 159°. The *chloride*, similarly prepared, crystallises in white needles, and has m. p. 178°. The *bromide*, also in white needles, has m. p. 183°. The *platinichloride*,



obtained by mixing the aqueous solutions, has m. p. 180°. The *mercurichloride* of similar constitution has m. p. 185°. On mixing solutions of the iodinium hydroxide and potassium dichromate, a *pyrochromate*, $[\text{C}_6\text{H}_5 \cdot \text{I} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2]_2, \text{Cr}_2\text{O}_7$, is precipitated; it has m. p. 112° (decomp.).

Picryl p-iodophenyl ether, prepared in a similar way to the dinitrophenyl ether, crystallises in large, yellow prisms, and has m. p. 136°. *Picryl-p*-iodochloridephenyl ether, $\text{Cl}_2\text{I} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3$, was obtained in small, yellow needles, which decomposed at 151°. Iodoso-

and iodoxy-compounds of picryl *p*-iodophenyl ether could not be prepared.

p-Iodophenyl acetate, $C_6H_4I \cdot OAc$, was obtained from the interaction of potassium iodophenoxide and acetyl chloride in white, prismatic needles, which were so unstable that analysis was not possible. When the acetate was at once dissolved in chloroform and treated with chlorine, *phenyl-p-iodochloride acetate* was precipitated in small, yellow needles, which were as unstable as the iodo-compound itself, and were not analysed.

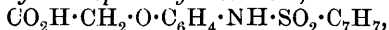
p-Iodophenyl benzoate, prepared from potassium iodophenoxide and benzoyl chloride, forms silvery, rhombic laminæ, and has m. p. 125° . *Phenyl-p-iodochloride benzoate* forms small, yellow needles, which decompose at 132° .

p-Iodosophenyl benzoate was not obtained in a pure state.

p-Iodoxyphenyl benzoate forms small, rhombic plates, which explode at 221° . Iodinium compounds could not be obtained. R. V. S.

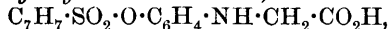
Nitration of Certain Derivatives of *p*-Aminophenol. FRÉDÉRIC REVERDIN [with A. DE LUC] (*Ber.*, 1909, 42, 4109—4184.* Compare this vol., i, 377; *Abstr.*, 1907, i, 695).—Derivatives are now studied which contain the groups $SO_2 \cdot C_7H_7$, $CO \cdot C_6H_5$, and $CH_2 \cdot CO_2H$, introduced two at a time alternately into the hydroxyl and amino-groups.

p-Toluenesulphonylaminophenoxyacetic acid,



prepared by heating *p*-toluenesulphonyl chloride, *p*-aminophenoxyacetic acid, and sodium acetate in alcoholic solution, forms colourless plates, m. p. 187° . The *ethyl* ester also forms colourless plates, m. p. 90° .

p-Toluenesulphonyloxyanilinoacetic acid,

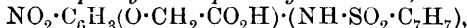


formed on heating *p*-hydroxyphenylglycine with *p*-toluenesulphonyl chloride and sodium hydroxide, crystallises in colourless needles, m. p. 161° . The *ethyl* ester has m. p. 205° ; it is hydrolysed by alkali to *ethyl p*-hydroxyanilinoacetate, crystallising in colourless plates, m. p. 69° .

p-Benzoylaminophenoxyacetic acid, $CO_2H \cdot CH_2 \cdot O \cdot C_6H_4 \cdot NH \cdot CPh$, prepared by the interaction of benzoyl chloride and *p*-aminophenoxyacetic acid, forms slightly violet-hued plates, m. p. 197° .

p-Benzoyloxyanilinoacetic acid, $OBz \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CO_2H$, forms colourless, prismatic, mother of pearl-like crystals, m. p. 165 — 171° .

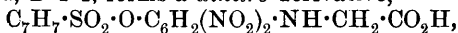
3-Nitro-4-toluenesulphonylaminophenoxyacetic acid,



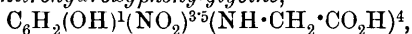
produced on nitrating with nitric acid, D 1.4, in acetic acid solution, forms almost colourless crystals, m. p. 158° , from alcohol. It crystallises from benzene in bright yellow, flat, prismatic needles. When hydrolysed by heating with concentrated sulphuric acid, 3-nitro-4-aminophenoxyacetic acid is obtained, crystallising in lustrous, brown needles, m. p. 185° . This is isomeric with the 2-nitro-compound obtained by Howard (*Abstr.*, 1898, i, 29). The *barium* salt forms bunches of lustrous, orange-coloured needles.

* and *Arch. Sci. phys. nat.*, 1909, [iv], 28, 439—459.

p-Toluenesulphonyloxyanilinoacetic acid, when warmed at 60—70° with nitric acid, D 1.4, forms a dinitro-derivative,

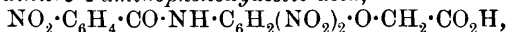


crystallising in almost colourless or light yellow, matted needles, m. p. 222° (decomp.). It is hydrolysed by sulphuric acid to a compound, assumed to be *dinitrohydroxyphenylglycine*,



which crystallises in blackish-brown needles with a metallic lustre, m. p. 176—177° (decomp.), and dissolves in dilute sodium hydroxide with a reddish-violet coloration. When nitric acid, D 1.52, is used for nitration, a *trinitro*-compound is formed, crystallising in matted needles, m. p. 194°. This yields the above-described dinitro-*p*-oxyphenylglycine on hydrolysis; accordingly, the third nitro-group is in the toluenesulphonyl nucleus, and the trinitro-derivative has the formula $\text{NO}_2\cdot\text{C}_7\text{H}_6\cdot\text{SO}_2\cdot\text{O}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The dinitro-derivative is obtained on nitration in acetic acid solution.

Nitric acid (D 1.4) acts on *p*-benzoylaminophenoxyacetic acid, forming a *mononitro*-derivative, $\text{C}_6\text{H}_3(\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})^1(\text{NO}_2)^3(\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5)^4$, crystallising in minute, citron-yellow needles, m. p. 176—177°; on hydrolysis with sulphuric acid, it yields 3-nitro-4-aminophenoxyacetic acid. When nitration is effected in sulphuric acid solution by means of a mixture of nitric and sulphuric acids, a *trinitro*-derivative, *nitrobenzoyl*-2 : 5-dinitro-4-aminophenoxyacetic acid,



is formed, crystallising in citron-yellow needles, m. p. 206°, which yields 2 : 5-dinitro-4-aminophenoxyacetic acid, m. p. 170° (Reverdin and Bucky, Abstr., 1906, i, 748), on hydrolysis with sulphuric acid.

Nitration with acetic anhydride and nitric acid leads to a *trinitro*-compound, which was not obtained crystalline, probably containing the third nitro-group in the benzoyl radicle, since it yields 2 : 6-dinitro-4-aminophenoxyacetic acid, $\text{C}_6\text{H}_2(\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})(\text{NO}_2)(\text{NH}_2)$, crystallising in yellowish-brown plates, m. p. 176°, on hydrolysis.

p-Benzoyloxyanilinoacetic acid, when nitrated with nitric acid (D 1.4), forms a compound crystallising in citron-yellow needles, m. p. 189°, which, on hydrolysis, yields dinitro-*p*-hydroxyphenylglycine, m. p. 176—177°. A mixture of nitric and sulphuric acids yields products, m. p. 189° and 197°, which are a mixture of di- and tri-nitro acids. The chief product is *nitrobenzoyldinitrohydroxyanilinoacetic acid*. On hydrolysis, dinitro-*p*-hydroxyphenylglycine and nitrobenzoic acid are obtained.

The series of papers on the nitration of *p*-aminophenyl are briefly summarised. Nitration with nitric acid alone or in presence of acetic acid leads to mono- and dinitro-derivatives, which contain the nitro groups in positions 3 and 3 : 5. Acetyl and benzoyl derivatives give dinitro-compounds with the nitro-groups in 2 : 6. Compounds containing the radicles $\text{Ph}\cdot\text{CO}$, $\text{CH}_3\cdot\text{CO}$, CH_3 , or $\text{CH}_2\cdot\text{CO}_2\text{H}$, yields mixtures of dinitro-derivatives with the nitro-groups in positions 3 : 5, 2 : 5, or 2 : 6.

E. F. A.

Preparation of Arylalkyl-*p*-aminophenols. CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 211869).—When the con-

condensation products from aromatic aldehydes and *p*-aminophenols are reduced with zinc in alkaline solution, they yield products which are employed for photographic purposes.

Benzyl-p-aminophenol, m. p. 89° , is obtained when benzylidene-*p*-aminophenol (30 parts) is reduced with zinc dust (15 parts) in alkaline solution, and the mixture afterwards acidified and extracted with ether. The *hydrochloride*, *sulphate*, and *acetate* are described.

Anisyl-p-aminophenol, m. p. $102-103^{\circ}$, is prepared in an analogous way from anisylidene-*p*-aminophenol; its *sodium* derivative separates in glistening, golden scales.

Salicyl-p-aminophenol has m. p. $122-123^{\circ}$.

F. M. G. M.

Intramolecular Changes of Acylated Compounds. KARL AUWERS and FRITZ EISENLOHR (*Annalen*, 1909, 369, 209—245. Compare this vol., i, 222, 436).—It has been shown that the transformation $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OAc} \rightarrow \text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, which occurs during the reduction of the corresponding nitro-*O*-acetate, does not always take place at once; in fact, the labile *O*-ester has been isolated in a few cases. It seemed probable, therefore, that the *O*-esters which have not been isolated are also capable of existing for a definite interval of time, but the velocity of transformation into the isomeric *N*-ester is so great as to render their separation impracticable. It should be possible, however, to prevent the migration of the acyl group by causing the amino-group to take part in an intermolecular reaction proceeding with a velocity greater than that of the intramolecular transformation of the *O*-acyl compound. That this is possible follows from the fact that *o*-nitro-*p*-tolyl benzoate when boiled with glacial acetic acid, acetic anhydride, and zinc dust yields *o*-acetyl-amino-*p*-tolyl benzoate. The observation that the latter substance when treated with a dilute alcoholic solution of sodium hydroxide yields *o*-benzoylamino-*p*-cresol, led to the study of the behaviour of mixed esters of amino-phenols when hydrolysed cautiously. A displacement of one acyl group by another does not take place when mixed esters of *m*- and *p*-aminophenols are hydrolysed; only the radicle attached to oxygen is eliminated. In the case of *o*-aminophenol derivatives, however, the radicle attached to nitrogen is displaced by that joined to oxygen provided the latter is much heavier than the former.

The action of alkali on *p*-benzoquinonebenzoylphenylhydrazone has also been investigated (compare Willstätter and Veraguth, *Abstr.*, 1907, i, 453). When a cold dilute alcoholic solution of this substance (1 mol.) is treated with a *N*/10-solution of sodium hydroxide (0.1 mol.), it yields benzeneazophenyl benzoate, although occasionally, for some unknown reason, this reaction does not take place; a one-hundredth molecular proportion of sodium hydroxide does not produce this change. The action of hot aqueous sodium hydroxide on *p*-benzoquinonebenzoylphenylhydrazone is remarkable, in that only small quantities of benzeneazophenol and benzoic acid and relatively large quantities of benzanilide are produced; a true explanation of the formation of the latter substance cannot yet be given.

The transformation of *p*-benzoquinonebenzoylphenylhydrazone into benzeneazophenyl benzoate cannot be effected by boiling with

toluene, xylene, or pyridine. The hydrazone is hydrolysed quantitatively by hot glacial acetic acid, yielding benzeneazophenol; the benzoyl group must be eliminated during its migration from the nitrogen to the oxygen, since benzeneazophenyl benzoate is not affected by boiling glacial acetic acid.

Benzeneazophenyl benzoate is decomposed very slowly when boiled with alcohol, acetic acid, and zinc, although the formation of aniline may be detected soon after the commencement of the experiment. The benzoyl- and acetyl-phenylhydrazones of *p*-benzoquinone when treated in the same manner do not yield even traces of aniline, a fact in accord with the work of Auwers and Eckhardt (Abstr., 1908, i, 480) and of Auwers and Hirt (Abstr., 1908, i, 438).

A solution of *p*-benzoquinonebenzoylphenylhydrazone in acetone, when treated with zinc dust and acetic acid, yields a substance which crystallises in small, colourless crystals, m. p. 137—140°.

o-Amino-*p*-cresol is obtained in quantitative yield by the electrolytic reduction of *o*-nitro-*p*-cresol; the *diacetyl* derivative, $C_{11}H_{13}O_3N$, crystallises in large leaflets and flat needles, m. p. 145°. *o*-Benzoyl-amino-*p*-tolyl acetate, $C_{16}H_{15}O_3N$, prepared by the action of acetyl chloride (5 mols.) on *o*-benzoylamino-*p*-cresol (1 mol.) in pyridine, forms pearly leaflets and flat needles, m. p. 134°.

o-Acetyl-amino-*p*-tolyl benzoate, $C_{16}H_{15}O_3N$, is most readily prepared by the action of an ethereal solution of benzoyl chloride on sodium *o*-acetyl-amino-*p*-tolyl-oxide in the presence of anhydrous potassium carbonate; it forms colourless needles and compact prisms, m. p. 146°, and is converted by (1) boiling acetic anhydride into the *diacetyl*-benzoyl derivative, $OAc \cdot C_6H_3Me \cdot NAcBz$, m. p. 101—102°, and (2) an alcoholic solution of an equivalent quantity of sodium hydroxide into *o*-benzoylamino-*p*-cresol.

o-Propionyl-amino-*p*-cresol, $C_{10}H_{13}O_2N$, crystallises in small, glistening, white needles, m. p. 95—96°; the *propionate*, $C_{13}H_{17}O_3N$, forms slender, colourless, pearly leaflets, m. p. 91—92°. *o*-Acetyl-amino-*p*-tolyl *propionate*, $C_{12}H_{15}O_3N$, crystallises in flat, white needles, m. p. 104—105°, and is converted to a small extent by an alcoholic solution of an equivalent quantity of sodium hydroxide into *o*-propionyl-amino-*p*-cresol.

o-Valeryl-amino-*p*-cresol, $C_{12}H_{17}O_2N$, crystallises in small, slender needles, m. p. 106°; the *benzoate*, $C_{19}H_{21}O_3N$, forms long, slender needles, and softens at 128°, m. p. 142°; when treated with a dilute alcoholic solution of sodium hydroxide, it yields a mixture of *o*-valeryl-amino-*p*-cresol (9 parts), and *o*-benzoylamino-*p*-cresol (1 part).

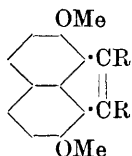
o-Heptylamino-*p*-cresol, $C_{14}H_{21}O_2N$, forms colourless crystals, m. p. 103—104°; the *benzoate*, $C_{21}H_{25}O_3N$, forms very small crystals, m. p. 87—89°, and when treated with alcoholic sodium hydroxide yields *o*-heptylamino-*p*-cresol.

o-Benzoyloxybenzylacetamide $OBz \cdot C_6H_4 \cdot CH_2 \cdot NHAc$, forms colourless crystals, m. p. 108—109°. 3 : 5-Dibromo-2-benzoyloxybenzylacetanilide, $OBz \cdot C_6H_3Br_2 \cdot CH_2 \cdot NPhAc$, crystallises in glistening prisms, m. p. 147°. 3 : 5-Dibromo-2-benzoyloxybenzyl-*p*-nitroacetanilide, $OBz \cdot C_6H_2Br_2 \cdot CH_2 \cdot NAc \cdot C_6H_4 \cdot NO_2$, is a faintly yellow, crystal-

line substance, m. p. 153·5—154°. *o*-Benzoyloxybenzaldehydeacetylphenylhydrazone, $\text{OBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{N} \cdot \text{AcPh}$, crystallises in white needles, m. p. 128°. The four substances just described are hydrolysed by sodium hydroxide solution with elimination of the benzoyl group.

W. H. G.

2:7-Dimethoxy-9:10-diphenylacenaphthylene and the Corresponding Dianisyl Compounds. ERICH BESCHKE [with O. BEITLER and S. STRUM] (*Annalen*, 1909, 369, 184—208).—An investigation on the chemical behaviour of substituted acenaphthylenes having the annexed general formula; the preparation of these substances has been described (this vol., i, 961).



2:7-Dimethoxy-1:8-dibenzoylnaphthalene, $\text{C}_{26}\text{H}_{20}\text{O}_4$, is prepared by oxidising a solution of 2:7-dimethoxy-9:10-diphenylacenaphthylene in acetic acid with chromic acid or lead peroxide; it crystallises in colourless, slender needles, m. p. 257°, and is reduced by zinc dust and an alcoholic solution of potassium hydroxide to 2:7-dimethoxy-9:10-diphenylacenaphthene glycol, $\text{C}_{26}\text{H}_{22}\text{O}_4$, crystallising in colourless, slender needles, m. p. 188—189°. The latter substance in hot glacial acetic acid is converted by concentrated hydrochloric acid into 2:7-dimethoxy-9:9-diphenylacenaphthenone,

$\text{C}_{10}\text{H}_4(\text{OMe})_2 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CPh}_2 \end{smallmatrix}$; the same substance is formed by treating

1:8-dibenzoyl-2:7-dimethoxynaphthalene with zinc dust and strong acetic acid, also by oxidising 2:7-dimethoxy-9:10-diphenylacenaphthylene with bromine or concentrated nitric acid in glacial acetic acid; it crystallises in long, pale yellow needles, m. p. 224°, and, when boiled with a 10% alcoholic solution of potassium hydroxide, yields an isomeric substance, $\text{C}_{26}\text{H}_{20}\text{O}_3$, crystallising in long, pale yellow needles, m. p. 200°. Either of these isomerides is converted by a 10% alcoholic solution of potassium hydroxide under pressure at 130—140° into 2-hydroxy-7-methoxy-9:9-diphenylacenaphthenone,

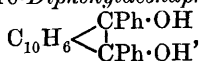
$\text{C}_{25}\text{H}_{18}\text{O}_3$, crystallising in yellow needles, m. p. 237—238°; the benzoate,

$\text{C}_{32}\text{H}_{22}\text{O}_4$, forms long needles, m. p. 232—233°.

The following compounds are prepared by the same methods from 2:7-dimethoxy-9:10-di-*p*-anisylacenaphthylene: 2:7-dimethoxy-1:8-di-*p*-methoxybenzoylnaphthalene, $\text{C}_{28}\text{H}_{24}\text{O}_6$, colourless needles, m. p. 206—207°; 2:7-dimethoxy-9:10-di-*p*-anisylacenaphthene glycol,

$\text{C}_{28}\text{H}_{26}\text{O}_6$, colourless, slender needles, m. p. 157°; 2:7-dimethoxy-9:9-di-*p*-anisylacenaphthenone, $\text{C}_{28}\text{H}_{24}\text{O}_5$, pale yellow prisms, m. p. 177°.

[With M. KITAJ.]—9:10-Diphenylacenaphthene glycol,



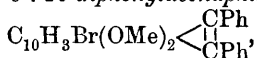
prepared by the action of magnesium phenyl bromide on acenaphthene quinone in ethereal solution, crystallises in small, colourless needles, m. p. 155—156°, and is oxidised by chromic acid in glacial acetic acid, yielding 1:8-dibenzoylnaphthalene, $\text{C}_{24}\text{H}_{16}\text{O}_2$, which forms colour-

less, lancet-like crystals, m. p. 189—190°. The glycol, when boiled with glacial acetic acid and concentrated hydrochloric acid, yields 9 : 9-diphenylacenaphthenone, $C_{10}H_6 \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CPh}_2 \end{smallmatrix}$, which forms almost colourless crystals, m. p. 174°, and is converted by a boiling 10% solution of potassium hydroxide in 90% alcohol into 8-diphenylmethylnaphthalene-1-carboxylic acid, $C_{10}H_6 \begin{smallmatrix} \text{CHPh}_2 \\ \diagup \diagdown \\ \text{CO}_2\text{H} \end{smallmatrix}$, colourless needles, m. p. 225—226°.

2 : 7-Dimethoxy-9 : 10-diphenylacenaphthene, $C_{10}H_4(\text{OMe})_2 \begin{smallmatrix} \text{CHPh} \\ \diagup \diagdown \\ \text{CHPh} \end{smallmatrix}$, prepared by heating an alcoholic solution of the corresponding acenaphthylene with acetic acid and sodium amalgam, crystallises in colourless needles, m. p. 165°. In the absence of acetic acid, 7-methoxy-9 : 10-diphenyl-3 : 4-dihydroacenaphthene, $C_{25}H_{22}O$, is formed ; it crystallises in colourless needles, m. p. 159°, forms an additive product with 2 atoms of bromine, and, when boiled with amyl alcohol and sodium, yields 7-methoxy-9 : 10-diphenyl-1 : 2 : 3 : 4-tetrahydroacenaphthene, $C_{25}H_{24}O$, which forms colourless, slender needles, m. p. 165°.

2 : 7-Dimethoxy-9 : 10-di-p-anisylacenaphthene, $C_{28}H_{26}O_4$, prepared in the same way as the analogous phenyl compound, forms colourless, slender needles, m. p. 150°. 7-Methoxy-9 : 10-di-p-anisyl-4 : 9-dihydroacenaphthylene, $C_{27}H_{24}O_3$, prepared by treating a hot alcoholic solution of 2 : 7-dimethoxy-9 : 10-di-p-anisylacenaphthylene with sodium amalgam, crystallises in glistening, bright yellow leaflets, m. p. 191—192° ; when reduced with amyl alcohol and sodium, it yields 7-methoxy-9 : 10-di-p-anisyl-1 : 2 : 3 : 4-tetrahydroacenaphthene, $C_{27}H_{28}O_3$, crystallising in felted, white needles, m. p. 133—134°.

Bromo-2 : 7-dimethoxy-9 : 10-diphenylacenaphthylene,



prepared by the action of bromine (1 mol.) on a hot solution of the corresponding acenaphthylene in glacial acetic acid, has m. p. 212° ; a tribromo-derivative, $C_{26}H_{17}O_2\text{Br}_3$, is formed when excess of bromine is used ; it crystallises in brick-red needles, m. p. 205°. The bromo-derivative is oxidised by chromic acid in glacial acetic acid to the corresponding diketone, $C_{26}H_{19}O_4\text{Br}$, colourless crystals, m. p. 162°.

W. H. G.

Synthesis of 3 : 4 : 8-Trihydroxyphenanthrene Derivatives. LUDWIG KNORR and HEINRICH HÜRLEIN (*Ber.*, 1909, 42, 3497—3503. Compare Abstr., 1907, i, 547, 789).—During the conversion of codeine into ψ -codeine, a wandering of the alcoholic hydroxyl group from position 6 to 8 occurs, and a like change occurs during the conversion of thebaine into thebenine. Attempts have been made to synthesise these compounds in order to prove the validity of these conclusions, but so far without success. The starting point of the work was to prepare 5-bromo-2-methoxybenzyl alcohol, $C_8H_9O_2\text{Br}$, from bromosaligenin (Auwers and Büttner, Abstr., 1899, i, 36), potassium hydroxide, and methyl iodide in methyl

alcohol; it crystallises in slender needles, m. p. 75°. This, on treatment with phosphorus pentachloride, yields *5-bromo-2-methoxybenzyl chloride* as an oil, and by boiling an alcoholic solution of the chloride with potassium cyanide for five hours, the corresponding *nitrile*, C_9H_8ONBr , is obtained in almost colourless needles, m. p. 65°. Hydrolysis of the nitrile with potassium hydroxide leads to the formation of *5-bromo-2-methoxyphenylacetic acid*, $C_9H_9O_3Br$, which crystallises in needles, m. p. 135°. The *sodium* salt when heated with *o*-nitrovanillin methyl ether and acetic anhydride in a sealed tube at 100—110° for twenty-four hours yields *2-nitro-3:4-dimethoxy- α -(5-bromo-2-methoxyphenyl)cinnamic acid*, $C_{18}H_{16}O_7NBr$, m. p. 208°. The *ammonium* salt, $C_{18}H_{19}O_7N_2Br$, is sparingly soluble, and serves for the separation of the acid from the *bromonitrotrimethoxystilbene*, $C_{17}H_{11}O_5NBr$, which is also formed; it crystallises in yellow rhombohedra, m. p. 136—138°. Reduction of the nitro-acid by ferrous sulphate and ammonia yields the corresponding *amino-acid* in an 80% yield. It forms yellow flakes.

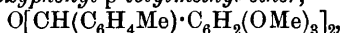
The sodium salt of this acid, after treatment with sodium nitrite and sulphuric acid, gives, on warming, *5-bromo-3:4:8-trimethoxyphenanthrene-9-carboxylic acid*, $C_{18}H_{15}O_5Br$; it crystallises from alcohol in rectangular leaflets, decomp. about 230°; the *methyl* ester, $C_{19}H_{17}O_5Br$, has m. p. 132°.

Neither the ethereal solution of this ester nor the other bromo-compounds described above, react with magnesium. W. R.

Phenyl-*o*-tolylcarbinol. ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1116—1117. Compare this vol., i, 778).—*Phenyl-*o*-tolylcarbinol*, $C_6H_4Me \cdot CHPh \cdot OH$, prepared by the action of benzaldehyde on the organo-magnesium compound obtained from *o*-bromotoluene and magnesium, forms well developed prisms, m. p. 95°, and on distillation decomposes apparently into a mixture of phenyltolylmethane and phenyl tolyl ketone. With concentrated sulphuric acid, it forms a bright red solution. T. H. P.

Abnormal Behaviour of Asarylaldehyde. TIBOR SZÉKI (*Reprint from Naturw. Museumsheften*, 1909, 4, Part I, 1—7).—It has been found previously (Fabinyi and Széki, *Abstr.*, 1906, i, 424) that asarylaldehyde reacts with some magnesium alkyl haloids to form complex ethers, instead of the expected secondary alcohols. In the present paper it is shown that this peculiarity is not exhibited with all magnesium alkyl haloids, but that with certain of these substances the reaction proceeds normally.

Asarylaldehyde reacts with magnesium anisyl iodide to form *p*-methoxyphenyl-2:4:5-trimethoxyphenylcarbinol (*anisylasarylcarbinol*), $HO \cdot CH(C_6H_4 \cdot OMe) \cdot C_6H_2(OMe)_3$, m. p. 90°, which forms colourless crystals from hot alcohol and dissolves in sulphuric acid with a red coloration. Magnesium *p*-tolyl bromide reacts with the aldehyde to give 2:4:5-trimethoxyphenyl-*p*-tolylmethyl ether,



m. p. 175°, which crystallises from a mixture of benzene and light petroleum, and gives a deep red coloration with sulphuric acid. By

condensation with magnesium *o*-tolyl bromide, no crystalline product could be obtained by the ordinary procedure, but by heating the components suspended in a mixture of benzene and light petroleum during three hours, a colourless, crystalline *substance*, m. p. 85°, having the empirical formula $C_{33}H_{32}O_5$ was obtained.

With magnesium α -naphthyl bromide and asarylaldehyde, 2 : 4 : 5-*trimethoxyphenyl- α -naphthylcarbinol*, m. p. 132°, was obtained. This gives a bluish-violet coloration with sulphuric acid. Magnesium propyl iodide condenses with the aldehyde to form 2 : 4 : 5-*trimethoxyphenylpropylcarbinol*, m. p. 84°, which separates from benzene in colourless crystals, and dissolves in sulphuric acid with a yellow coloration. Magnesium *isobutyl* iodide, on the contrary, reacts with the aldehyde analogously to magnesium ethyl iodide (*loc. cit.*), and gives $\delta\epsilon$ -di-2 : 4 : 5-*trimethoxyphenyl- $\beta\eta$ dimethyl- Δ^7 -octene*,

$CHMe_2 \cdot CH_2 \cdot CH[C_6H_2(OMe)_3] \cdot C[C_6H_2(OMe)_3] : CH \cdot CHMe_2$,
m. p. 81°, which crystallises from alcohol in colourless needles, and dissolves in sulphuric acid with an orange-red colour. T. A. H.

Cholesterol. XII. ADOLF WINDAUS (*Ber.*, 1909, 42, 3770—3775. Compare Abstr., 1908, i, 264, 728).—By oxidising cholesterol with potassium hypobromite, and further oxidising the product with permanganate, a saturated diketotricarboxylic acid, $C_{27}H_{40}O_8$, was obtained. The author now finds that further oxidation of this acid with potassium hypobromite results in the formation of a *monoketotricarboxylic acid*, $C_{26}H_{40}O_7$, which is intermediate between the original acid and the tricarboxylic acid, $C_{25}H_{40}O_6$, obtained when chromic acid is employed. The new acid is a colourless, amorphous substance, which yields, however, a *potassium hydrogen salt*, $C_{26}H_{39}O_7K$, crystallising in four-sided laminae. The acid regenerated from this salt was not crystalline, but gave satisfactory analyses. It does not react with hydroxylamine, but chromic acid readily converts it into the tricarboxylic acid, $C_{25}H_{40}O_6$.

The tricarboxylic acid, $C_{25}H_{40}O_6$, is further oxidised by hot chromic acid (in acetic acid), with production of traces of an odoriferous substance, already noticed by other observers, acetone, and a new *tetracarboxylic acid*, $C_{22}H_{32}O_8$. The yield of this acid is only 8—10%. It crystallises in rosettes of prisms with $1H_2O$, and has m. p. 194° (softens 190°). The *rubidium hydrogen salt*, $C_{22}H_{31}O_8Rb$, and a similar *caesium hydrogen salt* were prepared and analysed. The acid is stable towards chromic acid, concentrated nitric acid, potassium permanganate, and ozone. It is suggested that the odoriferous substance previously mentioned may be methyl *isoamyl* ketone. R. V. S.

Liquid Crystals of Compounds of Cholesterol and Ergosterol with Carbamide. PAUL GAUBERT (*Compt. rend.*, 1909, 149, 608—610. Compare Abstr., 1908, i, 882).—On heating cholesterol on a glass slip with a carbamide, or an alkyl- or thio-carbamide, interaction occurs in a few seconds with formation of anisotropic liquid substances which solidify on cooling. The liquid crystals in the case of thiocarbamide, thiosinnamine, and phenylthiocarbamide are lozenge-shaped, whereas carbamide and the alkylcarbamides give spherulites or birefringent liquid drops. On solidifying, bundles of

crystals or very irregular spherulites are formed. The monobenzyl carbamide of cholesterol is remarkable on account of the large size and uniformity of its solid spherulites, the fineness of the fibres, and the variation of its birefringence with temperature. With the thiocarbamides the optic axis of the lozenge-shaped liquid crystals, which are uniaxial, is perpendicular to the glass slip. Crystals differently oriented appear to dissolve again.

With carbamide, on cooling the isotropic liquid very small spherulites with a dark cross are produced. These coalesce together to form individuals as large as 0.1 mm. in diameter, showing beautiful polarisation tints in concentric circles.

Superfusion was only noticed in the compound of thiosinamine which can be completely solidified at the ordinary temperature without modification of the liquid crystals. True crystallisation is obtained in this substance by reheating.

Ergosterol yields compounds with the carbamides exhibiting the same peculiarity as the cholesterol compounds, but having in general a higher melting point.
R. J. C.

Preparation of *iso*Propyl *p*-Aminobenzoate. FARBENFABRIKEN VORM F. BAYER & Co. (D.R.-P. 211801).—When *p*-aminobenzoic acid (or its salts) is treated with *isopropyl* alcohol or iodide, products of therapeutic value are obtained.

isoPropyl p-aminobenzoate, m. p. 85–86°, is prepared by saturating a moist *isopropyl*-alcoholic solution of *p*-aminobenzoic acid with hydrogen chloride, and heating for several hours at 100°, or by heating *p*-aminobenzoic acid (42 parts), sodium (7 parts), and *isopropyl* alcohol (500 parts) with *isopropyl* iodide (50 parts) during twenty hours; the *sulphate* crystallises in leaflets.

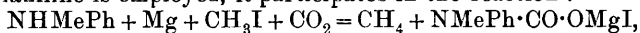
isoPropyl p-nitrobenzoate, m. p. 110–111°, dark yellow needles, is prepared in the same way from *p*-nitrobenzoic acid; on reduction with aluminium and moist ether, or with tin and alcoholic hydrochloric acid, the foregoing compound is obtained.

isoPropyl p-β-naphtholazobenzoate, $\text{CO}_2\text{Pr}^\beta \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, m. p. 169°, red needles, is prepared by the esterification of *p*-β-naphtholazobenzoic acid.
F. M. G. M.

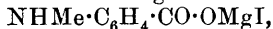
Synthesis of Aromatic Amino-acids by Rearrangement.

II. JOSEF HOUBEN and ARNOLD SCHOTTMÜLLER (*Ber.*, 1909, 42, 3729–3750).—The authors have continued their attempts to effect the transference of a carboxyl group from the nitrogen atom to the nucleus in aromatic amino-compounds. The *p*-methylaminobenzoic acid mentioned in a former paper (*Abstr.*, 1904, i, 1014) has been found to consist mainly of *p*-dimethylaminobenzoic acid. When sodium phenylacetylcarbamate (from sodioacetanilide and carbon dioxide) is heated, only sodium malonate is formed. The corresponding derivative of formanilide yields similarly sodium oxanilate, whilst sodium phenylbenzoylcarbamate (from sodiobenzanilide) loses carbon dioxide when heated. Experiments with the sodium derivatives of the aromatic amines (compare Titherley, *Trans.*, 1897, 71, 462) were also unsuccessful. Magnesium iodide phenylmethylcarbamate when heated in a sealed tube is converted into *p*-dimethylaminobenzoic acid. When

the rearrangement is effected by heating in a stream of carbon dioxide in dimethylaniline solution, the same acid is produced, but the yield is much better (40%). If safrole or quinoline is employed as solvent, secondary products are obtained. When, instead of dimethylaniline, methylaniline is employed, it participates in the reaction :



and the product then suffers rearrangement into



an almost quantitative yield of *p*-monomethylaminobenzoic acid being obtained. The methylaniline may be replaced by a mixture of aniline and dimethylaniline, and dimethylaniline hydriodide may be used instead of a mixture of methylaniline and methyl iodide. *Dimethylaniline hydriodide* has m. p. 150°.

Methylation of *p*-aminobenzoic acid with methyl sulphate in aqueous alcohol yielded a mixture of products from which *p*-dimethylaminobenzoic acid was isolated. Methylation in glacial acetic acid (compare Houben and Brassert, Abstr., 1906, i, 845) gave a considerable quantity of *p*-aminobenzoic acid sulphate. On treating the mother liquor with sodium nitrite, a nitroso-compound was obtained, which had m. p. 202—203°. It gave an ammonium salt, which was golden-yellow in colour and seemed to have m. p. 215—217°, and when decomposed with dilute acetic acid yielded pure *p*-methylnitrosoaminobenzoic acid.

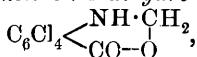
[With WALTER BRASSERT.]—On digesting this acid with alcoholic hydrogen chloride at the ordinary temperature, the nitroso-group is eliminated and *ethyl p*-methylaminobenzoate hydrochloride is obtained. When treated with sodium nitrite, this yields *ethyl p*-methylnitrosoaminobenzoate, which crystallises in groups of needles, and has m. p. 57°. *p*-Methylaminobenzoic acid forms brush-like clusters of needles, and has m. p. 160° (decomp.); its *ethyl* ester has m. p. 65—67°.

Magnesium iodide phenylethylcarbamate was prepared in ether, and was then heated in a current of carbon dioxide at 200°. The main product had m. p. 195°, and was found to be *p*-methylethylaminobenzoic acid. By nitrosylating the mother liquor, *p*-ethylnitrosoaminobenzoic acid was obtained. The other methods mentioned above were applied to similar reactions with ethylaniline and diethylaniline.

R. V. S.

Tetrachloroanthranilic Acid. VICTOR VILLIGER and LOUIS BLANGEY (*Ber.*, 1909, 42, 3549—3552. Compare Tust, Abstr., 1887, 1046; 1888, 836).—This acid can be obtained in a crystalline condition from tetrachlorophthalic anhydride by first converting it into the acid amide by treatment with ammonia, which then, when treated with sodium hypochlorite and sodium hydroxide, yields the tetrachloroanthranilic acid; this crystallises from alcohol in long needles, m. p. 182—183°. It is a strong acid and yields well characterised salts, and, on heating above its m. p., is decomposed quantitatively into 2 : 3 : 4 : 5-tetrachloroaniline. Tust's acid was probably impure.

5 : 6 : 7 : 8-Tetrachloro-1-keto-3 : 4-dihydro-2 : 4-benzoxazine,



obtained by the condensation of the acid with formaldehyde, crystallises in leaflets, m. p. 216° . Hot sodium carbonate regenerates the acid, and potassium cyanide yields tetrachloro- ω -cyanomethyl-anthranilic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{Cl}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CN}$, needles, m. p. 178° .

Tetrachloroaniline has m. p. 121° (Beilstein and Kurbatoff, Abstr., 1879, 143, give 118°). W. R.

Preparation of *o*-Alkylthiolbenzoic Acids and their Derivatives. FARBERWERKE VORM MEISTER, LUCIUS & BRÜNING (D.R.-P. 211679. Compare Abstr., 1908, i, 648, 797; this vol., i, 231).—It has now been found that in the preparation of *o*-alkylthiolbenzoic acids it is not necessary to start from thiolbenzoic acid itself, but the more accessible *o*-xanthylbenzoic acid may be used. This on methylation yields methyl *o*-methylthiolbenzoate. *o*-Methylthiolbenzoic acid is obtained when *o*-diazobenzoic acid is heated successively with potassium xanthate at $70-80^{\circ}$ and sodium methyl sulphate in alkaline solution at $100-120^{\circ}$. When methyl anthranilate is employed, methyl *o*-xanthylbenzoate, $\text{OEt}\cdot\text{CS}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, a pale brown oil, is obtained; this on treatment with alkaline sodium alkyl sulphate is converted into the corresponding alkylthiolbenzoate. F. M. G. M.

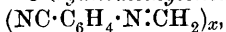
Nitrile Oxides. IV. Relations of Nitrile Oxides to the Reactions of Hoffmann and Curtius. HEINRICH WIELAND (*Ber.*, 1909, 42, 4207—4209).—The author has shown (this vol., i, 216) that, when heated in indifferent solvents, the nitrile oxides undergo rearrangement to the isomeric carbimides: $\text{O} < \overset{\text{CR}}{\underset{\text{N}}{\parallel}} \rightarrow \text{R}\cdot\text{N}\cdot\text{C}\cdot\text{O}$. The

assumption that, when the polymeric nitrile oxides, the probable constitution of which has been already given (*loc. cit.*), undergo this change, they are first de-polymerised to the simple nitrile oxides, is supported by the observation that benzonitrile oxide is converted partly into phenylcarbimide when heated in xylene solution. In this case, however, this change does not proceed readily, since before the temperature (about 110°) at which the isomeric change occurs is reached, the more favoured polymerisation to diphenylfuroxan takes place; this reaction is not, however, observed with the tri-nitrile oxides, for which the conditions of spontaneous decomposition into simple molecules are also those of the isomeric change.

Unsuccessful attempts were made to obtain benzonitrile oxide: (1) by the removal of hydrogen bromide from benzoylbromamide, which forms the first product of the action of hypobromite on benzamide, and (2) by the removal of nitrogen from benzoylazoimide. The author, therefore, agrees with Schroeter (this vol., i, 617) that the nitrile oxides do not stand in causal relation either with Hoffmann's reaction or with Curtius' azoimide reaction (this vol., i, 216). T. H. P.

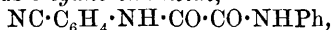
***o*-Aminobenzonitrile.** ARNOLD REISSERT and F. GRUBE (*Ber.*, 1909, 42, 3710—3721).—Numerous experiments have been made on the reduction of *o*-nitrobenzonitrile in the hope of obtaining *o*-cyanophenylhydroxylamine, but they have yielded only the reduction

products previously known. For the preparation of *o*-aminobenzonitrile, the authors revert to stannous chloride, by means of which a yield of 80% is obtained. *o*-Cyanomethyleneaniline,



from *o*-aminobenzonitrile (dissolved in acetone) and formaldehyde solution, serves to identify the nitrile; it forms needles, m. p. 211—212°.

Di-o-cyanoxanilide, $\text{NC}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CN}$, is obtained on heating equal weights of *o*-aminobenzonitrile and methyl oxalate at 140—150°; it crystallises in almost colourless, slender needles, m. p. 318° (decomp.). When warmed with alcoholic potassium hydroxide or concentrated sulphuric acid, the compound is hydrolysed; on long-continued boiling with aqueous alkali, 4-hydroquinazoline-2-carboxylic acid (see below) is produced in small amount. When *o*-aminobenzonitrile is heated for three hours in a reflux apparatus with three times its weight of methyl oxalate, *methyl o-cyanoxanilate*, $\text{NC}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{Me}$, is produced; it crystallises in long, colourless needles of m. p. 139°, and is hydrolysed on boiling with water. With aniline it yields *o-cyano-oxanilide*,



which forms pale yellow needles, m. p. 197·5°. *o*-Cyano-oxanilic acid forms long, silky needles, m. p. 126°; when boiled with water it decomposes into the nitrile and oxalic acid. When kept at the ordinary temperature in dilute acid solution, it changes into an isomeric acid which is identical with the 4-hydroquinazoline-

2-carboxylic acid, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \diagup \quad \diagdown \\ \text{N}=\text{C}\cdot\text{CO}_2\text{H} \end{smallmatrix}$ or 4-hydroxyquinazoline-

2-carboxylic acid, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{C}(\text{OH})\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{N}=\text{C}\cdot\text{CO}_2\text{H} \end{smallmatrix}$, first prepared by Griess.

Diazotisation of the nitrile and subsequent reduction did not yield *o*-cyanophenylhydrazine as expected, but the isomeric 3-aminoindazole of m. p. 153—154° (Bamberger and Goldberger, Abstr., 1899, i, 545).

o-Aminothiobenzamide, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CS}\cdot\text{NH}_2$, is prepared by dissolving *o*-aminobenzonitrile in alcohol, adding aqueous 25% ammonia, and then passing hydrogen sulphide. The compound crystallises in plates with serrated edges, has m. p. 121·5° (sinters previously), and is not changed at 200°, thus differing from the *m*-compound. The *hydrochloride* decomposes at 203°. The ortho-compound reacts with an alcoholic solution of iodine analogously to the meta-compound (Wanstrat, Ber., 1873, 6, 333), the *hydriodide* of the base, $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}$, being produced. It forms long, lanceolate crystals, which have m. p. 197—198° (decomp.). The salt is remarkably stable towards cold alkali. The base, $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}$, liberated by means of silver oxide, forms colourless needles, which have m. p. 170° (sintering previously). The *hydrochloride*, $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}\cdot 2\text{HCl}$, has m. p. 118°; from it the base is easily set free by alkali. The *nitrate*, $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}\cdot 2\text{HNO}_3$, decomposes at 175°. The *sulphate*, $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}\cdot \text{H}_2\text{SO}_4$, has m. p. 210°. The *platinichloride*, $[\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}]\cdot \text{H}_2\text{PtCl}_6$, and the *mercurichloride* (decomposing at 223°) were also prepared. Diazotisation of *o*-aminothiobenzamide in strongly acid solution yields 4-thiol-

1:2:3-*benzotriazine*, $C_6H_4 \begin{smallmatrix} C(SH):N \\ N \equiv N \end{smallmatrix}$ (compare Finger, Abstr., 1888, 948), which crystallises in golden-yellow needles, m. p. 187.5° (decomp.). It gives a *benzoyl* compound, m. p. 163° (decomp.), and an *acetyl* compound, $C_7H_4N_3SAc$, m. p. 144° (decomp.). A *methyl* compound, $C_7H_4N_3SMe$, is produced when thiolbenzotriazine is heated with a methyl-alcoholic solution of sodium methoxide and a little methyl iodide in a sealed tube at 120°. It forms yellow crystals, m. p. 101—102° (previously sintering). Oxidation with permanganate converts it into 4-*hydroxy*-1:2:3-*benzotriazine*, white needles, decomposing at 212—213°. R. V. S.

Reactivity of the Methylene Groups in Ethyl *p*- and *o*-Nitrophenylacetates. WALTHER BORSCHKE (*Ber.*, 1909, 42, 3596—3602. Compare this vol., i, 232).—A 50—60% yield of *p*-nitrophenylacetic acid can be obtained by nitrating a solution of phenylacetic acid in concentrated sulphuric acid with a mixture of concentrated nitric and sulphuric acids. The ethyl ester has b. p. 196—197°/20 mm. A benzoyl derivative could not be obtained by the action of sodium ethoxide and benzoyl chloride on the ester, and although sodium ethoxide and 2:4-dinitrobromobenzene reacted with the ester, only tarry products were obtained. A condensation product with benzenediazonium chloride could not be obtained in either acetic acid or alkaline solution. With amyl nitrite and sodium ethoxide the ester yields the *oximino*-derivative,



and the *oxime* of *ethyl p-nitrophenylglyoxylate*, which crystallises from dilute alcohol in slender needles, m. p. 181—182° (decomp.). The corresponding *acid*, $C_8H_6O_5N_2$, crystallises from water in colourless needles, m. p. 160—161° (decomp.). When heated, the acid yields carbon dioxide, water, and *p*-nitrobenzonitrile.

Ethyl *p*-nitrophenylacetate condenses with benzaldehyde in the presence of a few drops of piperidine, yielding a thin, dark brown oil, which, on hydrolysis with sulphuric acid, yields *α-p*-nitrophenylcinnamic acid. When *p*-nitrobenzaldehyde is used, *ethyl α-p-nitrophenyl-p-nitrocinnamate*, $NO_2 \cdot C_6H_4 \cdot CH:C(CO_2Et) \cdot C_6H_4 \cdot NO_2$, m. p. 164°, is obtained. The corresponding *acid*, $C_{15}H_{10}O_6N_2$, forms yellow crystals from ethyl acetate, and has m. p. 264° (decomp.).

α-p-Nitrophenylcoumarin (Abstr., 1900, i, 438) can be obtained in a similar manner from the nitro-ester, salicylaldehyde, and piperidine.

Ethyl *o*-nitrophenylacetate is most readily prepared by Reiser's method (*Ber.*, 1897, 30, 1043). It does not react with benzenediazonium chloride or bromo-2:4-dinitrobenzene, but with amyl nitrite and sodium ethoxide yields ethyl *o*-nitro-oximinophenylglyoxylate (Gabriel, Abstr., 1883, 920), but no ethyl benzisooxazole-*α* carboxylate. The *o*-nitro-ester does not condense with aldehydes as readily as the isomeric *p*-compound.

α-o-Nitrophenylcoumarin, $C_{15}H_9O_4N$, forms pale yellow crystals, begins to sinter at 160°, and has m. p. 215°. Sodium *o*-nitrophenylacetate, benzaldehyde, and acetic anhydride yield *α-o*-nitrophenylcinnamic acid, $CHPh:C(CO_2H) \cdot C_6H_4 \cdot NO_2$, m. p. 193°. J. J. S.

Chlorides of Certain Acylamino-acids. JULES MAX (*Annalen*, 1909, **369**, 276—286).—A number of chlorides of acylamino-acids have been prepared by the action of acetyl chloride and phosphorus pentachloride on acylamino-acids (compare Fischer, *Abstr.*, 1905, i, 263). Certain of the compounds prepared have been described recently by Mohr and Stroschein (this vol., i, 581).

Benzoylalanyl chloride forms slender, white leaflets, sinters at 125°, m. p. 130° (decomp.); with methyl alcohol it yields *benzoylalanine methyl ester*, $C_{11}H_{13}O_3N$, crystallising in small, white, striated rods, m. p. 80·5—81·5° (corr.).

Benzoyl-leucyl chloride, $C_4H_9\cdot CH(NHBz)\cdot COCl$, crystallises in small needles and decomposes at 80—90°; *benzoyl-leucine methyl ester*, $C_{14}H_{19}O_3N$, has m. p. 95—96° (corr.); the *ethyl ester*, $C_{15}H_{21}O_3N$, crystallises in cubes and rods, m. p. 73—75°; *benzoyl-leucinamide*, $C_{13}H_{18}O_3N_2$, crystallises in glistening, hexagonal, striated plates, m. p. 171° (corr.).

Benzoylphenylalanyl chloride, $CH_2Ph\cdot CH(NHBz)\cdot COCl$, forms colourless, rhombic plates, and decomposes at 123—125°; *benzoylphenylalanine methyl ester*, $C_{17}H_{17}O_3N$, has m. p. 86·5—87·5° (corr.); the corresponding *ethyl ester*, $C_{18}H_{19}O_3N$, forms tufts of small, colourless needles, m. p. 95—95·5° (corr.); *benzoylphenylalaninamide*, $C_{16}H_{16}O_2N_2$, crystallises in stellate aggregates of matted needles, m. p. 198° (corr.).

Benzoylaspartyl chloride, $COCl\cdot CH(NHBz)\cdot CH_2\cdot COCl$, sinters at 100° and decomposes just above this temperature; *methyl benzoyl-aspartate*, $CO_2Me\cdot CH(NHBz)\cdot CH_2\cdot CO_2Me$, crystallises in long, colourless needles, m. p. 94—95° (corr.); the *ethyl ester*, $C_{15}H_{19}O_5N$, forms long, glistening needles, m. p. 97—98° (corr.), $[\alpha]_D^{20} - 23\cdot9^\circ$ (in alcohol); the corresponding *diamide*, $C_{11}H_{13}O_3N_3$, turns brown at 250°, m. p. 264° (decomp., corr.).

Formylglycyl chloride, $CHO\cdot NH\cdot CH_2\cdot COCl$, decomposes at 100°; the analogous *acetyl* compound, $NHAc\cdot CH_2\cdot COCl$, crystallises in small plates and decomposes at 115—118°. W. H. G.

Catalytic Action of Colloidal Metals of the Platinum Group. VIII. Progressive Reduction of Phenyl Propiolic Acid. CARL PAAL and WILHELM HARTMANN (*Ber.*, 1909, **42**, 3930—3939. Compare *Abstr.*, 1908, i, 599; this vol., i, 358, 381, 545).—By the partial reduction of phenylpropiolic acid, by shaking with hydrogen (1 mol.) and palladium hydrosol, *allocinnamic acid* was obtained. In early experiments made in cold weather, the acid, m. p. 42° (*isocinnamic acid*), was obtained, and this is regarded as the primary form. At higher temperatures, Liebermann's *allocinnamic acid*, m. p. 68°, was formed. Subsequently, all experiments, even in the cold, led to the formation of the *allo-acid*. From preparations made in another laboratory, Liebermann's *isocinnamic acid*, m. p. 57—58°, was at first obtained; subsequently here, too, only *allocinnamic acid* could be prepared (compare Biilmann, this vol., i, 155, 382; Liebermann, this vol., i, 155).

Cinnamic acid, m. p. 132—133°, is formed in small quantity during the reduction.

Total reduction of phenylpropionic acid by the same method leads to β -phenylpropionic acid, m. p. 47—48°. E. F. A.

Influence of Constitution on the Rotatory Power of Optically Active Substances. HANS RUPE (*Annalen*, 1909, 369, 311—369. Compare Abstr., 1903, i, 565).—An investigation of the effect on the optical rotatory power produced by the introduction of a methyl or phenyl group into the menthyl esters of various acids. The results obtained may be summarised as follows:

(1) The replacement of a methyl by a phenyl group is usually accompanied by a marked decrease in the optical rotatory power; for example, menthyl crotonate has $[\alpha]_D^{20} - 91.06^\circ$, whilst menthyl cinnamate has $[\alpha]_D^{20} - 76.95^\circ$ (compare paragraph 4).

(2) The optical rotatory power is diminished by an assemblage of strong negative groups (phenyl): thus, menthyl cinnamate has $[\alpha]_D^{20} - 76.95^\circ$, whilst menthyl β -phenylcinnamate has $[\alpha]_D^{20} - 37.92^\circ$.

(3) The optical rotatory power of esters of acids with optically active alcohols is increased by substituting an α -hydrogen atom by a negative group, whilst it is decreased if the group be introduced at some distance from the α -carbon atom.

(4) The influence exerted by a phenyl group on the optical rotatory power becomes greater as it becomes more distant from the asymmetric carbon atom ("*Hebelwirkung*"); in this it differs from the ethylene linking, which has but a small effect on the optical rotatory power when greatly removed from the asymmetric carbon atom; for example, the menthyl esters of valeric acid, $\Delta^{\beta\gamma}$ -pentenoic acid, and $\Delta^{\gamma\delta}$ -pentenoic acid have the values $[\alpha]_D^{20} - 69.05^\circ$, -72.51° , and -67.32° respectively, whilst the menthyl esters of propionic acid, phenylacetic acid, butyric acid, β -phenylpropionic acid, hexoic acid, and δ -phenylvaleric acid have the values $[\alpha]_D^{20} - 75.51^\circ$, -69.57° (difference = 6), -70.46° , -58.48° (difference = 12), -64.86° , and -33.86° (difference = 31) respectively.

The menthyl esters are prepared by acting on the acid chloride with a solution of menthol and pyridine in benzene; the acid chloride is obtained by treating the dry sodium salt of the acid with a solution of phosphoryl chloride in benzene.

In certain cases the menthyl ester obtained from a racemic acid is the ester of one of the optically active antipodes; for example, menthyl *l*- β -phenylbutyrate was obtained from *dl*- β -phenylbutyric acid.

[With E. BUSOLT.]—Menthyl cinnamate, prepared from cinnamic acid obtained from storax, is a colourless oil, b. p. 111—112°/0.25 mm., $[\alpha]_D^{20} - 76.95^\circ$ (in benzene). Menthyl β -phenylpropionate forms long, white prisms, m. p. 32°, b. p. 197—198°/12 mm., $[\alpha]_D^{20} - 58.48^\circ$ (in benzene). Menthyl α -methylcinnamate forms long, slender, white needles, m. p. 52°, $[\alpha]_D^{20} - 62.60^\circ$. Menthyl β -phenyl- α -methylpropionate, $C_{20}H_{30}O_2$, forms glistening, white needles, m. p. 41°, $[\alpha]_D^{20} - 50.73^\circ$. Menthyl β -methylcinnamate, $C_{20}H_{28}O_2$, crystallises in white leaflets, m. p. 82°, $[\alpha]_D^{20} - 65.89^\circ$. 1- β -Phenylbutyric acid is a colourless, viscous oil, b. p. 157.25—157.75°/12 mm., $[\alpha]_D^{20} - 57.23^\circ$; the chloride has b. p. 112—113°/11.5 mm.; the menthyl ester, $C_{20}H_{30}O_2$, crystallises in long,

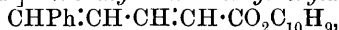
transparent prisms, m. p. 47—48°, $[\alpha]_D^{20} - 76.26^\circ$; the corresponding *d*-compounds could not be obtained in a pure state. *Menthyl α -phenylcinnamate*, $C_{25}H_{30}O_2$, forms silvery leaflets, m. p. 81—82°, $[\alpha]_D^{20} - 53.44^\circ$. *Menthyl $\alpha\beta$ -diphenylpropionate*, $C_{25}H_{32}O_2$, forms long, slender, silky needles, m. p. 67—68°, $[\alpha]_D^{20} - 86.04^\circ$. *Menthyl β -phenylcinnamate* crystallises in small, glistening, white needles, m. p. 66—67°, $[\alpha]_D^{20} - 37.92^\circ$. *Menthyl $\beta\beta$ -diphenylpropionate* forms small, slender, white needles, m. p. 40—41°, $[\alpha]_D^{20} - 61.72^\circ$. *Menthyl phenylpropiolate*, $C_{19}H_{24}O_2$, forms long, pale yellow needles, m. p. 67°, $[\alpha]_D^{20} - 71.77^\circ$.

Menthyl phenylacetate has b. p. 94—95°/0.25 mm., $[\alpha]_D^{20} - 67.57^\circ$. *Menthyl atropate (α -phenylacrylate)*, $C_{19}H_{26}O_2$, is an unstable, pale yellow, limpid oil, which changes into a viscid, gummy substance when kept, $[\alpha]_D^{20} - 63.03^\circ$. *Menthyl α -phenylpropionate*, $C_{19}H_{28}O_2$, is a colourless oil, b. p. 90—91°/0.25 mm., $[\alpha]_D^{20} - 61.87^\circ$. *Menthyl methylatropate (α -phenylcrotonate)*, $C_{20}H_{28}O_2$, is a yellow oil, which decomposes when distilled in a vacuum, $[\alpha]_D^{20} - 46.13^\circ$ (?). *Menthyl α -phenylbutyrate*, $C_{20}H_{30}O_2$, b. p. 112—114°/0.5 mm., could not be obtained quite pure, $[\alpha]_D^{20} - 26.78^\circ$ (?).

Menthyl methacrylate, $C_{14}H_{24}O_2$, is a colourless, limpid oil, b. p. 125—126°/14 mm., $[\alpha]_D^{20} - 91.76^\circ$. *Menthyl isobutyrate* has b. p. 116—117°/12 mm., $[\alpha]_D^{20} - 72.05^\circ$. *Menthyl crotonate* has b. p. 134°/11 mm., $[\alpha]_D^{20} - 91.06^\circ$. *Menthyl butyrate* has b. p. 126°/12.5 mm., $[\alpha]_D^{20} - 70.56^\circ$. *Menthyl α -methylcrotonate*, $C_{15}H_{26}O_2$, is a colourless, limpid oil, b. p. 140—141°/10.25 mm., $[\alpha]_D^{20} - 84.38^\circ$. *Menthyl α -methylbutyrate*, $C_{15}H_{28}O_2$, is a colourless liquid, b. p. 130°/9 mm., $[\alpha]_D^{20} - 63.97^\circ$. *Menthyl β -methylcrotonate* is a slightly yellow liquid, b. p. 144—145°/13 mm., $[\alpha]_D^{20} - 88.60^\circ$. *Menthyl β -methylbutyrate* is a colourless, limpid liquid, b. p. 129°/9 mm., $[\alpha]_D^{20} - 64.02^\circ$.

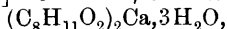
[With P. HÄUSSLER.]—*Menthyl diphenylacetate*, $C_{24}H_{30}O_2$, forms small, slender, white needles, m. p. 52—53°, $[\alpha]_D^{20} - 66.70^\circ$.

[With F. MÜNTER.]—*Menthyl cinnamenylacrylate*,



is a viscid, gelatinous substance, which commences to decompose in a vacuum at 80°, $[\alpha]_D^{20} - 75.14^\circ$ (in benzene). *Menthyl δ -phenyl- $\Delta^{\beta\gamma}$ -pentenoate*, $C_{21}H_{30}O_2$, is a pale yellow oil, b. p. 217—218°/11.5 mm., $[\alpha]_D^{20} - 47.54^\circ$. *Menthyl δ -phenylvalerate*, $C_{21}H_{32}O_2$, is a viscid, pale yellow oil, b. p. 206—207°/11.5 mm., $[\alpha]_D^{20} - 33.86^\circ$.

[With WALTHER LOTZ.]—*Calcium $\beta\delta$ -dimethylsorbate*,



crystallises in tufts of small, white needles; the *barium* salt ($2H_2O$) forms aggregates of glistening needles; the *menthyl* ester, $C_{18}H_{30}O_2$, is a colourless oil, b. p. 183—184°/14 mm., $[\alpha]_D^{20} - 59.80^\circ$ (in alcohol). The lactone of γ -hydroxy- $\beta\delta$ -dimethyl- Δ^{α} -hexenoic acid, $C_8H_{12}O_2$, is a colourless, limpid liquid, b. p. 111—113°/14 mm.; the *barium* and *silver* salts of the acid were analysed. $\beta\delta$ -Dimethyl- Δ^{β} -hexenoic acid, $CHMe_2:CH:CH:CH_2:CO_2H$, is a colourless liquid, b. p. 119.5—120.5°/14 mm.; the *cadmium* salt ($2H_2O$) forms glistening, white needles; the *menthyl* ester, $C_{18}H_{32}O_2$, has b. p. 169—170°/14 mm., $[\alpha]_D^{20} - 68.51^\circ$ (in alcohol). $\beta\delta$ -Dimethylhexoic acid, $C_8H_{16}O_2$, has b. p. 118.5—119.5°/14 mm.; the *menthyl* ester, $C_{18}H_{34}O_2$, is a colourless oil, b. p. 168.5—169.5°/14 mm., $[\alpha]_D^{20} - 57.38^\circ$.

[With C. DORSCHKY.]—*Amyl α-phenylcinnamerylacrylate*, $\text{CHPh}:\text{CH}:\text{CH}:\text{CPh}\cdot\text{CO}_2\text{C}_6\text{H}_{11}$, has b. p. 170—172°/0·25 mm., $[\alpha]_{\text{D}}^{20} + 3\cdot87^\circ$ (in alcohol); *amyl αδ-diphenyl-Δ^{8γ}-pentoate* and *amyl αδ-diphenyl-Δ^α-pentoate*, $\text{C}_{22}\text{H}_{26}\text{O}_2$, are colourless oils, having $[\alpha]_{\text{D}}^{20} + 7\cdot15^\circ$ and $+4\cdot84^\circ$ (in alcohol) respectively.

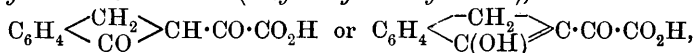
[With C. LIECHTENHAN.]—*αδ-Diphenylvaleric acid*, $\text{C}_{17}\text{H}_{18}\text{O}_2$, crystallises in colourless, hexagonal plates, m. p. 77—78°; the *amyl ester*, $\text{C}_{22}\text{H}_{28}\text{O}_2$, is a colourless oil with a slight fluorescence, b. p. 140—141°/0·5 mm., $[\alpha]_{\text{D}}^{20} + 4\cdot85^\circ$ (in alcohol). W. H. G.

Solubilities of Salicylates of the United States Pharmacopœia in Aqueous Alcohol Solution at 25°. ATHERTON SEIDELL (*J. Amer. Chem. Soc.*, 1909, 31, 1164—1168).—A redetermination of the solubility of the salicylates of ammonium, lithium, phenyl, quinine, sodium, strontium, and bismuth, also of free salicylic acid in aqueous alcohol solutions at 25°. The results obtained are tabulated, and curves given in the original. L. DE K.

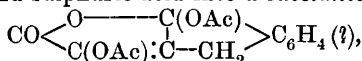
Condensation Products of o-Phthalaldehyde. II. JOHANNES THIELE and JOSEF SCHNEIDER (*Annalen*, 1909, 369, 287—299).—Pyruvic acid condenses with o-phthalaldehyde in a similar manner to acetone and acetophenone, yielding hydrindoneoxalic acid (compare Thiele and Falk, *Abstr.*, 1906, i, 750). The condensation of methyl ketones with o-phthalaldehyde leads not only to the formation of hydrindones, but also of a yellow substance (*loc. cit.*), which is now shown to be o-phenylene-ββ-naphthylene ketone (*isochrysoketone*). Ethyl acetonedicarboxylate also condenses with o-phthalaldehyde, yielding ethyl benzocycloheptadienonedicarboxylate.

Aniline reacts with o-phthalaldehyde, yielding phenylphthalimidine (compare Hessert, *Abstr.*, 1878, 66) or phenylphthalimidinil, according to the proportions of the reacting substances used.

Hydrindoneoxalic acid (3-hydroxy-2-oxalyindene),

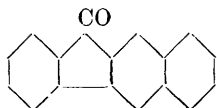


crystallises in silky, pale yellow needles, m. p. 211—212°; the *methyl ester*, $\text{C}_{12}\text{H}_{10}\text{O}_4$, forms long, white needles, m. p. 99·5°. The acid may also be obtained by the action of potassium hydroxide on a solution of α-hydrindone and methyl oxalate in methyl alcohol; it is converted by acetic anhydride and sulphuric acid into a substance,



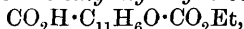
which forms colourless crystals, m. p. 149—150° (decomp.).

o-Phenylene-ββ-naphthylene ketone, annexed formula, prepared by the interaction of o-phthalaldehyde and α-hydrindone in alcoholic solution in the presence of potassium hydroxide, crystallises in pale yellow needles, m. p. 152°; the *phenylhydrazone*, $\text{C}_{23}\text{H}_{16}\text{N}_2$, forms yellow crystals, m. p. 174°.



Ethyl benzocycloheptadienonedicarboxylate,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \cdot \text{C}(\text{CO}_2\text{Et}) \\ \text{CH} \cdot \text{C}(\text{CO}_2\text{Et}) \end{smallmatrix} \text{CO}$, crystallises in colourless leaflets, m. p. 95.5° , and is converted by (1) a dilute methyl-alcoholic solution of potassium hydroxide into the *ethyl hydrogen ester*,



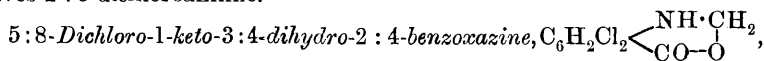
crystallising in small, slender, white needles, m. p. 185° ; (2) hot 20% sulphuric acid into the corresponding *acid*, $\text{C}_{13}\text{H}_8\text{O}_5$, m. p. 210° (decomp.); (3) an alcoholic solution of phenylhydrazine into the *additive product*, $\text{C}_{23}\text{H}_{24}\text{O}_5\text{N}_2$, colourless needles, m. p. 138° ; the corresponding *dimethyl ester* forms colourless needles, m. p. 181° .

Benzocycloheptadienonecarboxylic acid, $\text{C}_{12}\text{H}_8\text{O}_3$, is formed when the dicarboxylic acid is heated at its m. p., or when the diethyl ester is boiled with aqueous sodium hydroxide; it crystallises in long, white needles, m. p. 172° .

Phenylphthalimidinil, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{NPh}) \\ \text{CH}_2 \end{smallmatrix} \text{NPh}$, crystallises in colourless needles, turns brown at 135° , m. p. $142-143^\circ$; the *platinichloride*, $\text{C}_{40}\text{H}_{32}\text{N}_4 \cdot \text{H}_2\text{PtCl}_6$, is a reddish-yellow, crystalline powder, m. p. $212-213^\circ$ (decomp.). W. H. G.

Dichlorophthalic and Dichloroanthranilic Acids. VICTOR VILLIGER (*Ber.*, 1909, 42, 3529—3549).—Only two of the four possible dichloro-*o*-phthalic acids have been described, the 3:6-acid by Graebe and Gourevitz (*Abstr.*, 1900, i, 547), and the 3:5-acid by Crossley and Le Sueur (*Trans.*, 1902, 81, 1533). Neither of these acids was prepared by the direct chlorination of the phthalic acid. If, however, phthalic anhydride is dissolved in fuming sulphuric acid (23% SO_3) and chlorine is passed into the liquid, iodine being used as the carrier, the following reaction occurs: $\text{C}_8\text{H}_4\text{O}_3 + 2\text{Cl}_2 + 2\text{SO}_3 = \text{C}_8\text{H}_2\text{O}_3\text{Cl}_2 + 2\text{ClSO}_3\text{H}$, so that the reaction can be controlled by weighing. The reaction is finished after forty hours at $40-60^\circ$. The chlorinated anhydride is obtained as a white, crystalline powder by pouring the reaction liquid on to ice and filtering off as soon as possible. The anhydride is hydrolysed by hot water, the sulphuric acid removed, and the acid converted into the zinc salt. The filtrate from the precipitated zinc salt is treated with calcium chloride until no precipitate of calcium salt is obtained. The zinc salt consists of a mixture of the 3:4- and 4:5-dichlorophthalates; the calcium salt is nearly pure 3:6-salt. The 3:6-acid is the chief product of the reaction; the 3:4-acid amounts to 30—35%, and the 4:5-acid to 15—20% of the mixture.

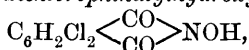
Graebe and Gourevitz's work on 3:6-dichlorophthalic acid is confirmed, and the *potassium, sodium, ammonium, calcium, barium, zinc, and silver* salts have been prepared. 3:6-Dichloroanthranilic acid, prepared from the corresponding phthalic acid, has m. p. $151-153^\circ$ [Graebe and Gourevitz (*loc. cit.*) found 142° . Bamberger and Demuth, *Abstr.*, 1901, i, 392, $154.5-155^\circ$ (corr.)] This acid, when heated, gives 2:5-dichloroaniline.



prepared by heating dichloroanthranilic acid and formaldehyde in methyl alcohol during one hour, crystallises in long needles, m. p. $159-161^\circ$. It

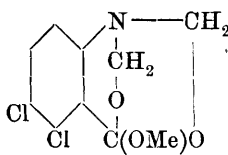
does not dissolve in alkaline carbonate, but is hydrolysed by sodium hydroxide into its components. On digestion with potassium cyanide and acidification, 3 : 6-dichlorophenylglycinenitrile-2-carboxylic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CN}$, is obtained; it crystallises in needles, m. p. 120—123°. The dicarboxylic acid is obtained by hydrolysing the nitrile; m. p. 159—160°.

The mixture of dichlorophthalic acids, obtained from the zinc precipitate, is converted into the anhydride, distilled, and the distillate crystallised from toluene, whereby nearly pure 4 : 5-dichloroanhydride is obtained, leaving the 3 : 4-substance in the mother liquor. To obtain the pure 3 : 4-dichlorophthalic acid, the crude 3 : 4-anhydride is first converted into the 3 : 4-dichlorophthalylhydroxylamine,



which crystallises in long needles, m. p. 218—219°. It is easily hydrolysed by dilute mineral acid to hydroxylamine and 3 : 4-dichlorophthalic acid, $\text{C}_8\text{H}_4\text{O}_4\text{Cl}_2$, which separates from water in small, rectangular plates, m. p. quickly heated about 195°. The alkali, calcium, barium, copper, zinc, and silver salts have been prepared. The anhydride, $\text{C}_8\text{H}_2\text{O}_3\text{Cl}_2$, has m. p. 120—121°, b. p. 329°.

When the dichlorophthalylhydroxylamine is heated with sodium carbonate solution, it is converted into a mixture of 5 : 6- (60—70%) and 3 : 4-dichloroanthranilic acids; these are separated by taking advantage of the zinc 3 : 4-dichloro-salt being less soluble than the 5 : 6-compound. 3 : 4-Dichloroanthranilic acid, $\text{C}_7\text{H}_5\text{O}_2\text{NCl}_2$, crystallises in needles, m. p. 237—238°; by heating for two hours at 240° in an atmosphere of carbon dioxide, it is partly converted into 2 : 3-dichloroaniline. By heating crude 5 : 6-dichloroanthranilic acid with formaldehyde, it is converted into a complex tricyclic compound

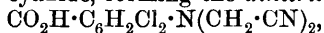


termed by the author 5 : 6-dichloroanthranilic diformalide methyl ether (annexed formula), which crystallises in needles, m. p. 152·5°.

When heated with ethyl alcohol, the ethyl ether, $\text{C}_{11}\text{H}_{11}\text{O}_3\text{NCl}_3$, crystallises out in needles, m. p. 123—124°. It is insoluble in alkali carbonates,

but easily hydrolysed on heating. Potassium cyanide converts it into the compound,

$\text{C}_6\text{H}_2\text{Cl}_2 \begin{array}{c} \text{N}(\text{CH}_2\cdot\text{CN}) \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{O} \text{CH}_2$, of m. p. 170—173°, which yields the carboxylic acid on hydrolysis; decomp. 200°. It reacts a second time with potassium cyanide, forming the dinitrile,



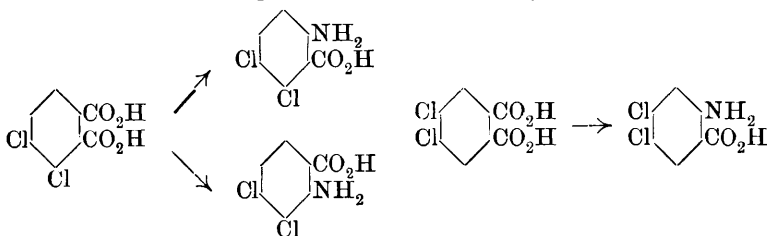
which yields the corresponding acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{N}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, decomp. 190°.

Acetaldehyde and benzaldehyde also give condensation products with this dichloroanthranilic acid, m. p. 142° (decomp.) and 179—180° respectively.

5 : 6-Dichloroanthranilic acid, $\text{C}_7\text{H}_5\text{O}_2\text{NCl}_2$, obtained by the hydrolysis of the formaldehyde compound, crystallises in long needles, m. p. 176—177° (decomp.), and has been characterised by preparation of metallic salts and its easy conversion into 3 : 4-dichloroaniline.

4:5-Dichlorophthalic acid, $C_8H_4O_4Cl_2$, crystallises in long, flat needles, m. p. on quickly heating 200° ; the anhydride, $C_8H_2O_3Cl_2$, forms prisms, m. p. $185-187^\circ$; the ethyl hydrogen ester, needles, m. p. $133-134^\circ$; the 4:5-dichlorophthalylhydroxylamine, m. p. $195-197^\circ$. The anhydride on treatment with aqueous ammonia and sodium hypochlorite yields only 4:5-dichloroanthranilic acid, $C_7H_5O_2NCl_2$, needles, m. p. $213-214^\circ$; on heating the acid, it yields 3:4-dichloroaniline. 4:5-Dichloroanthranilic diformalide methyl ether, $C_{10}H_9O_3NCl_2$, forms needles, m. p. $118-121^\circ$; the ethyl ether is formed by heating with ethyl alcohol, m. p. $95-97^\circ$, and it reacts with two molecules of potassium cyanide.

The preparation of these three dichloroanthranilic acids is a proof of the constitution assigned to the new dichlorophthalic acids, thus:



This also receives complete support by the chlorination of the two monochlorophthalic acids in fuming sulphuric acid. 3-Chlorophthalic acid gave 3:6- and 3:4-dichloro-acids; 4-chlorophthalic acid gave only 3:4- and 4:5-dichloro-acids. It is to be remarked that the monochlorophthalic acids cannot be obtained by the chlorination of the anhydride in sulphuric acid.

W. R.

[Preparation of Phenolphthalein Esters.] KNOLL & Co. (D.R.-P. 212892).—The utility of phenolphthalein diacetate when employed therapeutically has been restricted by its ready hydrolysis, whilst the dibenzoate and dibenzenesulphonate from their stability have proved useless. The employment of substituted and higher paraffin acids, or of aromatic acids, gives rise to phenolphthalein derivatives of intermediate stability and therapeutic value. *Phenolphthalein diisovalerate*, m. p. 110° , is a colourless, crystalline powder insoluble in, but slowly decomposed by, hot sodium hydroxide.

Phenolphthalein dibutyrate is an amorphous powder; it is decomposed by hot alkali carbonates.

Phenolphthalein disalicylate has m. p. $195-198^\circ$. *Phenolphthalein carbonate*, m. p. $200-210^\circ$ (decomp.), is prepared by heating phenolphthalein with phenyl carbonate or with guaiacol carbonate in the presence of sodium hydroxide under diminished pressure. *Phenolphthalein dicinnamate*, m. p. 181° , is a crystalline powder.

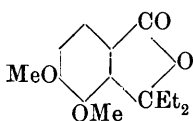
F. M. G. M.

Action of Organic Magnesium Compounds on Dicarboxylic Acids and a Method of Converting a $\cdot CO_2H$ Group into $\cdot CO\cdot R$. HUGO SIMONTS and K. ARAND (*Ber.*, 1909, 42, 3721—3728).—The

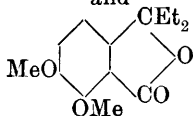
interaction of magnesium alkyl halides and phthalic acid leads to the formation of both ketonic and tertiary alcoholic derivatives. In the former the $\cdot\text{CO}_2\text{H}$ group has been converted into $\cdot\text{COR}$ by the following series of changes: $\cdot\text{CO}_2\text{H} \rightarrow \cdot\text{CO}_2\text{Mg}\cdot\text{X} \rightarrow \cdot\text{C}(\text{OMgX})_2\cdot\text{R} \rightarrow \cdot\text{C}(\text{OH})_2\cdot\text{R} \rightarrow \cdot\text{CO}\cdot\text{R}$. Magnesium ethyl bromide (8 mols.) and phthalic acid (1 mol.) in ethereal solution yield diethylphthalide,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{OEt})_2 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$, and propiophenone *o*-carboxylic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COEt} \\ \diagup \quad \diagdown \\ \text{CO}_2\text{H} \end{smallmatrix}$. The

latter has at first the m. p., 91° , previously given by Gabriel and Michael, but this rises on recrystallisation to 97° . 5:6-Dibromo-3:3-diethylphthalide, m. p. 103° , is similarly obtained from 4:5-dibromophthalic acid; 3:4-dibromopropiophenone *o*-carboxylic acid, m. p. 113° , is also formed. The action of magnesium propyl bromide on phthalic acid is similar; the m. p. of the 3:3-dipropylphthalide, which has b. p. $170^\circ/13\text{ mm.}$, was found to be 68° , whilst Bauer has previously given 76° for this compound. 3:4-Dimethoxyphthalic acid (hemipinic acid) yields with magnesium ethyl bromide a mixture of the two possible isomeric dimethoxydiethylphthalides (annexed formulæ) in the form of an oil, and a mixture of the two corresponding dimethoxypropiophenone *o*-carboxylic acids, which were also not separated, although selected crystals had different m. p. (85° and 113° respectively).

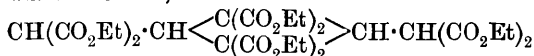


and



R. V. S.

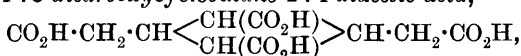
cycloButane Derivatives as Products of the Polymerisation of Ethyl Dicarboxyglutaconate. MAX GUTHZEIT, ARNO WEISS, and WALTER SCHAEFFER (*J. pr. Chem.*, 1909, [ii], 80, 393—449).—The nature of the isomerism of the two bimolecular esters, m. p. 103° and 88° , derived from ethyl dicarboxyglutaconate still remains unsolved, but further evidence has been obtained which supports the view that the ester, m. p. 103° , is the ethyl ester of 1:1:3:3-tetracarboxycyclobutane-2:4-dimalonic acid,



(compare Guthzeit and Weiss, *Abstr.*, 1901, i, 314).

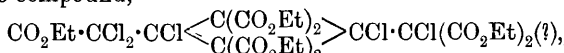
Four isomeric tetracarboxylic acids, $\text{C}_{10}\text{H}_{12}\text{O}_8$, have been obtained during the investigation, namely, two from the ester, m. p. 103° , a third from the isomeric ester, m. p. 88° , and a fourth from the bimolecular ester derived from ethyl isoaconitate (*loc. cit.*); they are isomeric 1:3-dicarboxycyclobutane-2:4-diacetic acids, but the nature of the isomerism is not known.

Ethyl 1:1:3:3-tetracarboxycyclobutane-2:4-dimalonic acid, m. p. 103° , when boiled with concentrated hydrochloric acid yields a mixture of 1:3-dicarboxycyclobutane-2:4-diacetic acid,

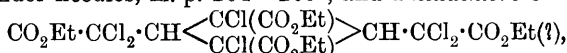


m. p. 197 — 198° , the methyl ester of which, $\text{C}_{14}\text{H}_{20}\text{O}_8$, is an oil, and 1:3-dicarboxycyclobutane-2:4-diacetic acid, m. p. 234° , the methyl ester

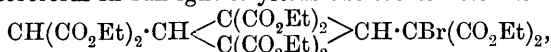
of which forms long, compact prisms, m. p. 76—77°. The ester, m. p. 103°, undergoes the following changes: (1) It is converted by aniline at 140—150° into malonanilide and ethyl β -anilinoethylene-*aa*-dicarboxylate, and by a concentrated alcoholic solution of ammonia into malonamide and ethyl aminoethylenedicarboxylate; (2) when treated with ethyl iodide and zinc, it yields ethyl diethylcarboxyglutaconate and ethyl diethylmalonate, the latter being a decomposition product of the former; (3) it is converted by chlorine at 130—150° into a *pentachloro* compound,



small, slender needles, m. p. 204—205°, and a *hexachloro*-compound,



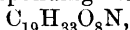
small prisms, m. p. 178—180°; (4) when acted on by bromine in boiling chloroform in sunlight it yields the *bromo*-derivative,



which crystallises in large, compact prisms, m. p. 78—80°, and the analogous *dibromo*-derivative, $\text{C}_{30}\text{H}_{42}\text{O}_{16}\text{Br}_2$, colourless prisms, m. p. 147—148°. A *pentabromo*-compound, $\text{C}_6\text{Br}_5(\text{CO}_2\text{Et})_7$, crystallising in prisms, m. p. 215—217°, is formed when bromine is added to a hot solution of the ester in glacial acetic acid.

The *cyclobutane* ester, m. p. 88°, when boiled with concentrated hydrochloric acid yields a *dicarboxycyclobutanediacetic acid*, $\text{C}_{10}\text{H}_{12}\text{O}_8$, m. p. 184°.

The interaction of equivalent quantities of ethyl dicarboxyglutaconate and piperidine results in the formation of the *piperidinium* salt, $\text{C}(\text{CO}_2\text{Et})_2 \cdot \text{CH} \cdot \text{C}(\text{CO}_2\text{Et}) \cdot \text{C}(\text{OEt}) \cdot \text{O} \cdot \text{C}_5\text{NH}_{12}$, which crystallises in yellow needles, m. p. 94°, and is probably an intermediate product in the transformation of ethyl dicarboxyglutaconate into the bimolecular ester, m. p. 103°. The corresponding *diethylammonium* salt,



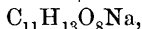
forms yellow needles, m. p. 131—132°; ethyl dicarboxyglutaconate does not polymerise under the influence of diethylamine. The *mercuric* salt, $\text{C}_{30}\text{H}_{42}\text{O}_{16}\text{Hg}$, is a yellowish-green, viscid oil. The complex *mercury* compound, $\text{C}_{15}\text{H}_{20}\text{O}_8\text{Hg}(\text{OH})_3 \cdot 3\text{Hg} \cdot \text{OAc} (?)$, crystallising in small, slender, white needles, is formed by the action of mercuric acetate on the sodium derivative of the ester.

The bimolecular ester derived from ethyl *isoaconitate*, in analogy to the esters obtained from ethyl dicarboxyglutaconate, must have the formula $\text{CH}(\text{CO}_2\text{Et})_2 \cdot \text{CH} \left\langle \begin{array}{c} \text{CH}(\text{CO}_2\text{Et}) \\ \text{CH}(\text{CO}_2\text{Et}) \end{array} \right\rangle \text{CH} \cdot \text{CH}(\text{CO}_2\text{Et})_2$; when boiled with 10% hydrochloric acid it yields a *dicarboxycyclobutanediacetic acid*, $\text{C}_{10}\text{H}_{12}\text{O}_8$, identical with von Pechmann's bimolecular glutaconic acid (compare Abstr., 1899, i, 870).

Methyl dicarboxyglutaconate,

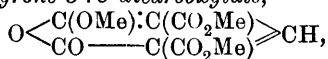


a colourless viscid oil, is obtained as the *sodium* derivative,



m. p. 247—248°, by the interaction of methyl malonate and chloro-

form in the presence of sodium methoxide; the analogous *copper* derivative, $(C_{11}H_{13}O_8)_2Cu$, forms microscopic prisms, m. p. 245—246°; the *mercuric* derivative, $(C_{11}H_{13}O_8)_2Hg$, crystallises in prisms, m. p. 156°; the *mercuriacetate*, $C_{11}H_{13}O_7 \cdot O \cdot Hg \cdot OAc$, crystallises in stellate groups of small needles, m. p. 147—148°, is obtained when an excess of mercuric acetate is used in the preparation of the normal mercuric salt; the *mercurichloride*, $C_{11}H_{13}O_7 \cdot OHgCl$, forms tufts of prisms, m. p. 178—180°. The parent substance when treated with an ethereal solution of piperidine yields the *methyl* ester of 1:1:3:3-tetracarboxy-cyclobutane-2:4-dimalonic acid, $C_{22}H_{28}O_{16}$, glistening prisms, m. p. 221—222°, and when heated at 220° under a pressure of 20 mm. yields *methyl 6-methoxy-2-pyrone-3:5-dicarboxylate*,



very small prisms, m. p. 128—129°.

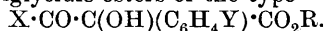
The action of chlorine on ethyl ethane- $\alpha\alpha\beta\beta$ -tetracarboxylate and ethyl cyclobutane-1:1:3:3-tetracarboxylate was investigated for purposes of comparison; the latter compound yields a *tetrachloro*-derivative, $(CO_2Et)_2C \begin{array}{c} \diagup CCl_2 \\ \diagdown CCl_2 \end{array} C(CO_2Et)_2$, obtained as a viscid syrup; the first named yields a chlorinated product with elimination of an ethylcarboxy-group.

W. H. G.

Identity of Helianthic Acid and Chlorogenic Acid. K. GORTER (*Arch. Pharm.*, 1909, 247, 436—438).—The properties ascribed by Ludwig and Kromeyer to helianthic acid, isolated from sunflower seeds, show the greatest similarity to those of chlorogenic acid (this vol., i, 588). The author therefore has isolated helianthic acid in a crystalline form, and proved its identity with chlorogenic acid by a comparison of the m. p.'s, specific rotations, calcium salts, and acetyl derivatives.

C. S.

New General Methods for the Synthesis of Aromatic Aldehydes. ALFRED GUYOT (*Compt. rend.*, 1909, 149, 789—790).—The $\alpha\beta$ -diketonic esters (Bouveault, *Abstr.*, 1904, i, 556; 1907, i, 217) combine with aromatic hydrocarbons, phenols, and tertiary amines, forming acidylphenylglycidic esters of the type



Condensation occurs in the para-position to the substituent, or where this is already occupied, in the ortho-position. Zinc chloride is employed to effect condensation in the case of the phenols, and sulphuric acid in the case of amines. In the latter instance the product is accompanied by compounds of the type $X \cdot CO \cdot C(C_6H_4Y)_2 \cdot CO_2R$, arising from further condensation.

The acidylphenylglycollic esters prepared in this way undergo quantitative decomposition when treated by any of the following methods: (1) On warming with excess of concentrated sulphuric acid, when the following reaction occurs: $X \cdot CO \cdot C(OH)(C_6H_4Y) \cdot CO_2R + 2H_2O = Y \cdot C_6H_4 \cdot CH(OH) \cdot CO_2H + X \cdot CO_2H + R \cdot OH$. The hydroxy-acid then loses water and carbon monoxide, and gives the aldehyde, $Y \cdot C_6H_4 \cdot CHO$. (2) On boiling with an aqueous solution of a copper

salt, when oxidation occurs with formation of a phenylglyoxylic acid; this loses carbon dioxide when boiled with dimethyl-*p*-toluidine, forming the aldehyde. (3) On hydrolysis with aqueous potassium hydroxide, the corresponding phenylglycollic acid is formed; this need not be isolated, since the aldehyde is readily obtained by oxidising the solution with potassium ferricyanide.

The $\alpha\beta$ -diketonic esters used in the foregoing syntheses can be replaced by mesoxalic esters (compare this vol., i, 159, 236, 306).

W. O. W.

Benzaldehydesulphoxylate and Acetonesulphoxylate. EMIL FROMM and F. ERFURT (*Ber.*, 1909, 42, 3812—3816).—Formaldehyde reacts with sodium hyposulphite to form formaldehydesulphoxylate (rongalite). According to Bazlen (*Abstr.*, 1905, ii, 240), sodium benzaldehydesulphoxylate, $\text{NaSO}_3\text{C}_7\text{H}_7$, is formed by the action of benzaldehyde and sodium hyposulphite in presence of sodium hydroxide. This product is now shown to be benzaldehyde bisulphite; in addition, the hyposulphite is in part oxidised to sulphite and in part reduced to disulphite. Acetone acts similarly to benzaldehyde; formaldehyde is the only compound which forms sulphoxylate.

E. F. A.

Action of Sodium Disulphide on Ring-Substituted *p*-Nitrotoluenes. JAN. J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 899—913).—Ring-substituted *p*-nitrotoluenes are converted by an alcoholic solution of sodium disulphide into the corresponding ring-substituted *p*-aminobenzaldehydes and *p*-toluidines, the latter being volatile with steam. The amino-groups in the resulting aldehydes are replaceable by halogen atoms or other groups, thus affording a means of preparing substitution products of benzaldehyde.

Bromine water converts *p*-aminobenzaldehyde into 3:5-dibromo-4-aminobenzaldehyde, which forms colourless crystals, m. p. 150°. 2-Chloro-4-aminobenzaldehyde changes in a few hours to an infusible modification, insoluble in water, alcohol, or ether. Both forms are converted by acetic anhydride into 2-chloro-4-acetylaminobenzaldehyde, m. p. 152°, which is transformed by acetic anhydride and a small proportion of concentrated sulphuric acid into 2-chloro-4-acetylaminobenzylidene diacetate, $\text{NHAc}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CH}(\text{OAc})_2$, m. p. 122°. Warming with alcoholic hydrochloric acid decomposes this substance into 2-chloro-4-aminobenzaldehyde and acetic acid. 2-Chloro-4-acetylaminobenzoic acid, which forms colourless crystals, m. p. 206°, is obtained by oxidising 2-chloro-4-acetylaminobenzaldehyde or 2-chloro-aceto-*p*-toluidide with potassium permanganate. Boiling with hydrochloric acid converts it into 2-chloro-4-aminobenzoic acid, whilst bromine water precipitates 3-chloro-2:4:6-tribromoaniline.

2-Chloro-*p*-toluidine is separated by steam distillation from the products of the interaction of sodium disulphide and 2-chloro-4-nitrotoluene. With acetic anhydride it yields 2-chloroaceto-*p*-toluidide, m. p. 104°. Wynne and Greeves (*Proc.*, 1895, 11, 151) give 86°, but their compound contained $1\text{H}_2\text{O}$. Glacial acetic acid and acetic anhydride

convert 2-bromo-4-aminobenzaldehyde into 2-bromo-4-acetylaminobenzaldehyde, crystallising in pale yellow needles, m. p. 135°. 2-Bromo-*p*-toluidine and acetic anhydride yield 2-bromoaceto-*p*-toluidide, which forms colourless crystals, m. p. 113°. Boiling with potassium permanganate in aqueous solution converts the last compound into 2-bromo-4-acetylaminobenzoic acid, colourless crystals, m. p. 206°, which on boiling with hydrochloric acid yields 2-bromo-4-aminobenzoic acid, crystallising in colourless needles, m. p. 202° (decomp.). Bromine water converts this acid into 2 : 3 : 4 : 6-tetrabromoaniline.

2-Iodo-4-nitrotoluene is converted by sodium disulphide into 2-iodo-*p*-toluidine, volatile with steam. It forms colourless crystals, m. p. 38°, and with acetic anhydride yields 2-iodoaceto-*p*-toluidide (Willgerodt and Gartner, Abstr., 1908, i, 876). The residue from the steam distillation of 2-iodo-*p*-toluidine contains 2-iodo-4-aminobenzaldehyde, which crystallises in yellow needles, m. p. 136°. It changes more rapidly than the corresponding chloro- and bromo-derivatives to an infusible, insoluble modification, which is converted by glacial acetic acid and acetic anhydride into 2-iodo-4-acetylaminobenzaldehyde, yellow crystals, m. p. 144°.

By the Sandmeyer reaction, *p*-aminobenzaldehyde yields *p*-chlorobenzaldehyde (von Walther and Raetze, Abstr., 1902, i, 466), *p*-bromobenzaldehyde (Jackson and White, Abstr., 1878, 728), and *p*-iodobenzaldehyde (Hantzsch, Abstr., 1894, i, 331). The same reaction converts 2-chloro-4-aminobenzaldehyde into 2 : 4-dichlorobenzaldehyde (Erdmann and Schwechten, Abstr., 1891, 448), and 2-bromo-4-aminobenzaldehyde into 2 : 4-dibromobenzaldehyde, colourless crystals, m. p. 80°, which is oxidised by potassium permanganate to 2 : 4-dibromobenzoic acid.

3 : 5-Dibromobenzaldehyde is obtained by diazotisation of 3 : 5-dibromo-4-aminobenzaldehyde, and is volatile with steam. It forms colourless crystals, m. p. 90°, and is oxidised by permanganate to 3 : 5-dibromobenzoic acid.

2 : 4-Diiodobenzaldehyde is obtained by treating diazotised 2-iodo-4-aminobenzaldehyde (soluble form) with potassium iodide. It forms colourless crystals, m. p. 129°, which quickly become pale yellow.

A. J. W.

Bromine Derivatives of *o*-Amino- and of *o*-Hydroxy-benzaldehyde. JULIUS MÜLLER (*Ber.*, 1909, 42, 3695—3703).—5-Bromosalicylaldehyde has been the only known monobrominated salicylaldehyde. The author now describes isomerides containing the bromine in positions 3 and 4, and incidentally mentions other new compounds.

4-Bromosalicylaldehyde, m. p. 52°, is produced by reducing 4-bromo-2-nitrobenzaldehyde by ferrous sulphate and ammonium hydroxide to 4-bromo-2-aminobenzaldehyde, m. p. 85°, which is dissolved in 50% acetic acid and diazotised by sodium nitrite and sulphuric acid, the solution being subsequently heated to 90°. It has a pleasant, aromatic odour, gives a reddish-violet coloration with ferric chloride, dissolves in sodium hydroxide, and forms a sodium hydrogen sulphite compound,

phenylhydrazone, m. p. 145°, *oxime*, m. p. 151°, and an *acetyl* derivative, m. p. 92°.

4-Bromo-2-aminobenzaldoxime, m. p. 194°, is obtained by the interaction of the corresponding aldehyde, hydroxylamine hydrochloride, and anhydrous sodium carbonate in the presence of alcohol, or by reducing an alcoholic solution of 4-bromo-2-nitrobenzaldoxime by ammonium sulphide. 4-Bromo-2-aminobenzaldehydophenylhydrazone has m. p. 215°.

3-Bromosalicylaldehyde, m. p. 49°, is obtained by adding finely-powdered 3-nitrosalicylaldehyde to a cold solution of stannous chloride in hydrochloric acid, isolating the yellow stannichloride obtained by warming, and suspending it in dilute hydrochloric acid; the suspension is diazotised and added to a hot solution of cuprous bromide. The aldehyde is volatile with steam, soluble in sodium hydroxide or carbonate, and forms an *oxime*, m. p. 165°; *phenylhydrazone*, m. p. 100°; and *semicarbazone*, m. p. 266°.

3-Bromo-2-acetoxybenzonitrile, m. p. 49—50°, obtained by heating 3-bromosalicylaldoxime, anhydrous sodium acetate, and acetic anhydride at 160—170° for four hours, is rapidly hydrolysed by cold concentrated sulphuric acid, yielding 3-bromosalicylamide, m. p. 165°, which is converted by boiling moderately concentrated hydrochloric acid into 3-bromosalicylic acid, m. p. 184°, identical with Lellmann and Grothmann's compound. C. S.

Condensation of Aldehydes and Hydroxyaldehydes with Phenols. P. DANCKWORTT (*Ber.*, 1909, 42, 4163—4171).—With the object of ascertaining the molecular proportions in which aldehydes condense with phenols in the presence of hydrochloric acid, *p*-nitrobenzaldehyde, nitrovanillin, the monobrominated *o*-, *m*-, and *p*-hydroxybenzaldehydes, bromopiperonal, and bromocinnamaldehyde have been submitted to the following process. The aldehyde (1 mol.) and a phenol (2 mols.) are dissolved in glacial acetic acid and treated with concentrated hydrochloric acid. Sooner or later a precipitate is formed in the cold, which is collected, washed with water, and finally with ether, benzene, or chloroform to remove unchanged material. The products are amorphous, and usually exhibit halochromy. In the cold, bromovanillin unites with phenol itself in the proportion 1 : 2, and with polyhydric phenols in equal molecular proportions, a second molecule of the phenol being added after long warming. *p*-Nitrobenzaldehyde combines always with 2 mols. of a phenol. 5-Bromosalicylaldehyde combines with 1 mol. of resorcinol, the isomeric *m*- and *p*-compounds with 2 mols. Bromopiperonal condenses with 1 mol. of resorcinol, and bromocinnamaldehyde with 2 mols. C. S.

Phenyl Vinyl Ketone and some of its Homologues. ELMER P. KOHLER (*Amer. Chem. J.*, 1909, 42, 375—401).—By the action of acrylyl chloride on benzene in presence of aluminium chloride, Moureu (*Abstr.*, 1894, i, 30) obtained a small quantity of a colourless substance which he regarded as phenyl vinyl ketone. Klages (*Chem. Zeit.*, 1908, 33, 318), however, did not accept this conclusion, and stated that phenyl vinyl ketone and its homologues can be obtained

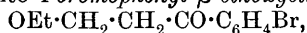
by the action of alcoholic potassium hydroxide on α -bromo-ketones. It has already been shown (this vol., i, 394) that Klages' products are mixtures which do not contain any unsaturated ketone.

The author has now repeated Moureu's work, and finds that his supposed phenyl vinyl ketone is α -hydrindone. This is doubtless formed from phenyl vinyl ketone, since the latter is readily converted into α -hydrindone by the action of aluminium chloride. It has been found that phenyl vinyl ketone can be obtained by the action of potassium iodide on $\alpha\beta$ -dibromopropiophenone, but the product of this reaction always contains β -ethoxypropiophenone, owing to the fact that in presence of minute quantities of acid, phenyl vinyl ketone is capable of uniting with the alcohol employed as a solvent. This method has been extended to the preparation of phenyl propenyl ketone and phenyl *isobutenyl* ketone.

An improved method is described for the preparation of $\alpha\beta$ -dibromopropionic acid. $\alpha\beta$ -Dibromopropionyl chloride reacts with benzene in presence of aluminium chloride to form $\alpha\beta$ -dibromopropiophenone, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{COPh}$, m. p. 58° , which crystallises in large needles or plates, and on reduction with zinc dust is converted into a mixture of propiophenone and dibenzoylbutane; the latter substance melts at 112° , and its oxime at 232° (compare Etaix, Abstr., 1898, i, 125).

Phenyl vinyl ketone, $\text{CH}_2\text{:CH}\cdot\text{COPh}$, b. p. $115^\circ/18$ mm., is very reactive; it instantaneously reduces potassium permanganate, combines energetically with bromine, hydrogen halides, and primary and secondary amines, and polymerises when exposed to sunlight or when gently heated. The ketone reacts readily with phenylhydrazine with formation of 1:3-diphenylpyrazoline, $\text{CPh}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{N} \quad \text{NPh} \end{smallmatrix}$ (or possibly the

1:5-compound), m. p. 158° , which forms large, yellow needles. *Ethoxypropiophenone*, $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COPh}$, m. p. about 12° , b. p. $135^\circ/18$ mm., yields a *phenylhydrazone*, m. p. 86° . β -Chloropropiophenone, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{COPh}$, m. p. 57° , obtained by the combination of phenyl vinyl ketone with hydrogen chloride, crystallises in large plates. Phenyl vinyl ketone unites readily with sodium hydrogen sulphite with formation of *sodium benzoylethanesulphonate*, which separates in large, colourless plates containing $1\text{H}_2\text{O}$. β -Benzoylethanesulphonic acid, $\text{COPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, m. p. 95° , forms colourless needles. By the action of magnesium methyl iodide on phenyl vinyl ketone, phenyl propyl ketone is obtained, and by the action of magnesium phenyl bromide, β -phenylpropiophenone is produced. 4-Bromophenyl $\alpha\beta$ -dibromoethyl ketone, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Br}$, m. p. 74° , prepared from bromopropionyl chloride and bromobenzene by Friedel and Crafts' reaction, forms large prisms, and by the action of potassium iodide is converted into 4-bromophenyl β -ethoxyethyl ketone,



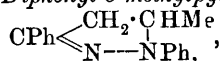
m. p. 54° , which crystallises in large, colourless plates, and yields a *phenylhydrazone*, m. p. 108° .

$\alpha\beta$ -Dibromobutyryl chloride, $\text{CHMeBr}\cdot\text{CHBr}\cdot\text{COCl}$, b. p. $112^\circ/20$ mm., prepared from the dibromobutyric acid obtained by treating crotonic acid with bromine, reacts with benzene in presence of aluminium chloride to form $\alpha\beta$ -dibromobutyrophenone $\text{CHMeBr}\cdot\text{CHBr}\cdot\text{COPh}$,

m. p. 112°, which crystallises in needles. The latter compound is converted by potassium iodide into *phenyl propenyl ketone*,



b. p. 135°/20 mm., which can also be prepared by treating *crotonyl chloride*, $\text{CHMe}:\text{CH}\cdot\text{COCl}$, b. p. 126°, with benzene in presence of aluminium chloride. 1:3-*Diphenyl-5-methylpyrazoline*,



m. p. 108°, obtained by the action of phenylhydrazine on phenyl propenyl ketone, forms thin, yellow plates. The ketone reacts with magnesium methyl iodide to form *isovalerophenone*, and with magnesium phenyl bromide to form β -phenylbutyrophenone.

Bromophenyl propenyl ketone, $\text{CHMe}:\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Br}$, m. p. 47°, reacts with phenylhydrazine to form 1-phenyl-5-bromophenyl-3-methyl-

pyrazoline, $\text{C}_6\text{H}_4\text{Br}\cdot\text{C} \begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ \diagdown \quad \diagup \\ \text{N} \text{---} \text{NPh} \end{array}$, m. p. 136°, and unites with

bromine with production of 4-bromophenyl $\alpha\beta$ -dibromopropyl ketone,



m. p. 76°, which crystallises in needles.

Dibromoisovaleryl chloride, $\text{CMe}_2\text{Br}\cdot\text{CHBr}\cdot\text{COCl}$, b. p. 126—130°/20 mm., prepared from the dibromo-acid obtained by treating $\beta\beta$ -dimethylacrylic acid with bromine, is converted by Friedel and Crafts' reaction into *dibromoisovalerophenone*, $\text{CMe}_2\text{Br}\cdot\text{CHBr}\cdot\text{COPh}$, m. p. 81°, which crystallises in needles. This dibromo-ketone is converted by potassium iodide into *phenyl isobutenyl ketone*, $\text{CMe}_2:\text{CH}\cdot\text{COPh}$, b. p. 148°/22 mm., a colourless liquid, which yields a *phenylhydrazone*, m. p. 88°, and reacts with magnesium phenyl bromide with formation of β -phenylisobutyrophenone and an unsaturated compound, and, on oxidation with potassium permanganate, is converted into benzophenone. β -Phenylisobutyrophenone yields a *phenylhydrazone*, m. p. 94°, and two *oximes*, m. p. 85° and 111°, which crystallise in needles and plates respectively. E. G.

[Condensation Products of Amino- and Chloro-anthraquinones.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 212470).—By the condensation of substituted 1-aminoanthraquinones with substituted 2-chloroanthraquinones at high temperatures or under pressure, substituted $\alpha\beta$ -dianthraquinoneimides are obtained. Condensation products from the following compounds are mentioned in the patent. 6-Chloro-1-methylaminoanthraquinone, prepared from 6-chloro-1-nitroanthraquinone and methylamine; 7-chloro-1-methylaminoanthraquinone; 1-amino-6- and 1-amino-7-methylaminoanthraquinone from 6(7)-chloro-1-aminoanthraquinone and methylamine; 2-chloroanthraquinone; 2-chloro-5- and 2-chloro-8-methylaminoanthraquinones; 2-chloro-5- and 2-chloro-8-aminotolylanthraquinones, obtained from 2-chloro-5- and 2-chloro-8-nitroanthraquinone and *p*-toluidine; 2-chloro-5- and 2-chloro-8-methoxyanthraquinones, obtained from 2-chloro-5- or 2-chloro-8-nitroanthraquinone; 2-chloro-5- and -8-oxyanthraquinones, prepared from sodium 5-nitro-2-anthraquinonesulphonate; 2-chloro-8-acetylaminoanthraquinone, prepared from 2-chloro-8-aminoanthraquinone. The

product obtained by fusing 6(or 7)-chloro-1-acetylaminanthraquinone with phosphoryl chloride. 5- or 8-Aminanthraquinone-2:3-quinoline, obtained by the nitration and subsequent reduction of anthraquinonyl-2:3-quinoline; 5- or 8-aminanthraquinonyl-2:1-quinolines, obtained in the same way from anthraquinonyl-2:1-quinoline; 5- or 8-amino-2:3-anthraquinoline; 2-chloro-5-acetylaminanthraquinoline.

F. M. G. M.

Preparation of Xanthopurpurin. FARBERWERKE VORM MEISTER, LUCIUS & BRÜNING (D.R.-P. 212697).—A quantitative yield of 1:3-dihydroxyanthraquinone (xanthopurpurin) is obtained when a 20% aqueous suspension of purpurin mixed with ammonium hydroxide is treated at the ordinary temperature with sodium hyposulphite until the red colour disappears.

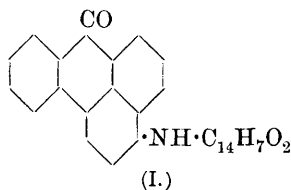
F. M. G. M.

Preparation of Dithioanthraquinones. FARBENFABRIKEN VORM FRIEDR. BAYER & Co. (D.R.-P. 212857).—Sodium thiolanthraquinone disulphide (this vol., i, 496) can be prepared by boiling an alcoholic solution of potassium anthraquinone- α -sulphonate with sodium hydrosulphide.

Sodium 1:5-dithiolanthraquinone, dark brown needles, is prepared by boiling sodium anthraquinone-1:5-disulphonate with sodium sulphide in aqueous solution.

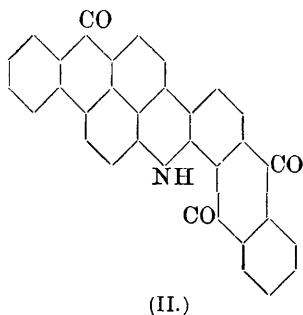
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[Preparation of Benzanthranyl-1-aminoanthraquinone Derivatives.]

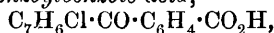


BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 212471).—The condensation of 1-aminoanthraquinone with halogenated benzanthrones at high temperatures leads to the formation of 1-benzanthranylaminanthraquinones (formula I). These on further condensation lose two atoms of hydrogen and yield compounds (formula II) which on treatment with alkaline hyposulphite produce vat dyes.

F. M. G. M.



[Preparation of Substituted ω -Halogenmethylantraquinones.] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 211967).—*o*-Chloromethylbenzoylbenzoic acid,



m. p. 173° , is prepared by adding aluminium chloride to a warm solution

of phthalic anhydride in *o*-chlorotoluene and heating at 70° during half an hour. By heating the foregoing acid at 110 — 135° with sulphuric acid, two isomeric chloromethylantraquinones are formed. These form yellow needles, m. p. 215° and 165° respectively.

Bromomethylantraquinone is obtained in an analogous manner from

o-bromotoluene. *Dichloromethylantraquinone*, m. p. 205°, is prepared by chlorinating chloromethylantraquinone at 210–220°. These compounds, when fused with sulphur, are used for the preparation of dyes.
F. M. G. M.

History of the Terpenes. IWAN KONDAKOFF (*J. pr. Chem.*, 1909, [ii], 80, 455–468).—Polemical. A criticism of Wallach's work, *Terpene und Campher*.
W. H. G.

***l*-Pinene and its Isomeric Change into Dipentene.** WLADIMIR A. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 996–1004. Compare Abstr., 1908, i, 278).—According to Flawitzky's investigations (Abstr., 1887, 968), the action of sulphuric acid on *l*-pinene results first in the rupture of the 4-carbon atom ring with formation of optically active terpene hydrate (terpineol), the latter then undergoing dehydration to *l*-isoterpene (limonene), which is subsequently converted into dipentene.

The author has followed polarimetrically the action of alcoholic sulphuric acid and water (1 mol.) on *l*-pinene (1 mol.). The rotation of the mixture at first increases to a maximum, and then gradually diminishes. Fractionation of the products at a stage where the rotation had not quite reached the maximum value revealed the presence of an ether, $C_{10}H_{17}\cdot OEt$, b. p. 216–217°/740 mm., $D_{47.5}^{20}$ 0.9010, $n_{D}^{17.5}$ 1.4649, $[\alpha]_D - 66.95^\circ$. Later, when the rotation had reached its maximum value, the products were found to contain, in addition to this ether, the corresponding alcohol, $C_{10}H_{17}\cdot OH$, formed by hydrolysis of the ether.

Fractionation of *l*-pinene always yields a large part boiling considerably below 155°, the b. p. of *l*-pinene. The conclusion is drawn that *l*-pinene is not a chemical individual, but consists of a mixture of hydrocarbons, possibly of pinene and fenchene. This conclusion is also indicated by the results of Bouchardat and Lafont (Abstr., 1894, i, 612; 1898, i, 442; 1899, i, 156) and of Barbier and Grignard (Abstr., 1908, i, 94, 852), who found that, in the hydration of *l*-pinene, fenchyl alcohol and borneol are formed in addition to the normal product, terpineol. The author has confirmed these results, and has also demonstrated the presence of fenchene in *l*-pinene, which probably contains camphene as well.
T. H. P.

Constituents of Ethereal Oils. Carvenene, $C_{10}H_{16}$, and "Terpinene." FRIEDRICH W. SEMMLER (*Ber.*, 1909, 42, 4171–4174. Compare this vol., i, 110; Wallach, *ibid.*, i, 726; Auwers, *ibid.*, i, 592, 596).—The α -terpinene, obtained by Auwers from *o*-cresol, does not agree with other terpinenes in its physical data; probably intramolecular change occurs during one or other of the many reactions by which it is produced. Wallach's statement, that a relatively pure chloroterpinene (chlorocarvenene) can only be obtained with the greatest difficulty by the action of phosphorus pentachloride on carvenone, is refuted, since the author finds that a very smooth reaction occurs when the two substances are shaken for about one hour in light petroleum. Carvenene prepared by the author's process is free from cymene, and is oxidised by cold alkaline potassium permanganate to

$\alpha\delta$ -dihydroxy- α -methyl- δ -isopropyladipic acid, m. p. 189°. Carvenene is therefore $\Delta^{1:3}$ -dihydrocymene (Wallach's α -terpinene), and is claimed by the author to be the purest sample hitherto obtained. C. S.

Terpenes of Rosin Spirit. CARLO GRIMALDI (*Chem. Zeit.*, 1909, 33, 1157).—The only terpenes previously recorded as present in "rosin spirit" are pinene and dipentene. The author confirms the presence of both these substances, and in addition has found camphene in "spirits" prepared from American and Austrian rosins. No phellandrene, sylvestrene, or limonene was found. T. A. H.

***l*-Camphene.** P. G. GOLUBEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1004—1014).—The author has succeeded in isolating from the ethereal oil of the Siberian fir, pure natural *l*-camphene, m. p. 50°, b. p. 159—160°, $[\alpha]_D - 92.37^\circ$ (compare Abstr., 1905, i, 74), in the form of opaque, volatile crystals, which gradually become transparent.

The action of a mixture of acetic acid and 50% sulphuric acid, in the proportions employed by Bertram and Walbaum (Abstr., 1894, i, 204), on this pure camphene yields, after three hours at 50—60°, 75.1% of *isoborneol* acetate, $C_{10}H_{17}OAc$; after six hours at 50—60°, 75.81%; after nine hours at 50—60°, 81.3%, and after two hours at 70—80°, 79.45% of the acetate. After heating at 50—60°, the hydrolysed products are slightly dextrorotatory, whilst at 70—80° they become inactive. The *isoborneol* obtained from the acetate is optically inactive, and has the same crystalline form as the *isoborneol* prepared from artificial camphene. On oxidation with permanganate, this *isoborneol* gives a camphor identical with that obtained by Bertram and Walbaum (*loc. cit.*) by oxidising the *isoborneol* yielded by artificial camphene and exhibiting all the ordinary characters of Japan camphor, from which it differs only in being optically inactive.

Beside the principal product, *isoborneol*, of the action of sulphuric and acetic acids on *l*-camphene, there are formed also *i*-camphene, identical in its chemical properties with *l*-camphene, and, probably, cymene. T. H. P.

Carrot Oil, the Ethereal Oil of the Fruit of *Daucus Carota*. ERWIN RICHTER (*Arch. Pharm.*, 1909, 247, 391—413).—The ethereal oil is a pale golden-yellow liquid with a characteristic, not unpleasant odour, and has $D_{15} 0.9439$ and $[\alpha]_D^{15} - 13.38^\circ$. It does not contain sulphur, nitrogen, or methoxyl groups. The acid number is 2.04, ester number 18.22, saponification number 20.26; after acetylation the saponification and ester numbers are 95.5 and 69.97 respectively. It contains 0.04% of *isobutyric* acid and 0.8% of *palmitic* acid. The presence of aldehydes cannot be established with certainty. After being treated with sodium carbonate, potassium hydroxide, and sodium hydrogen sulphite, the oil is hydrolysed by 5% alcoholic potassium hydroxide; the volatile acids thereby obtained are acetic and probably formic acids. The oil, after hydrolysis, is dried and fractionally distilled. Fractions I and II, b. p. 150—160° and 160—170°

respectively, contained terpenes, but these could not be isolated. A fresh portion of the oil, therefore, was distilled with alcohol, whereby the terpenes were removed, whilst the higher-boiling sesquiterpenes and oxygenated substances remained in the distilling vessel. The mixture of terpenes thus obtained was proved to contain *d*-pinene and *l*-limonene.

The higher-boiling fractions, b. p. 100—125°/18 mm., 125—155°/18 mm., 155—160°/18 mm., and 160—180°/18 mm., solidify more or less completely by cooling, and contain an alcohol, which is isolated by the xanthogenic method.

The alcohol, *daucol*, $C_{15}H_{26}O_2$, m. p. 115°—116°, is a colourless, odourless, tasteless substance, which forms an *acetate*, $OAc \cdot C_{15}H_{25}O$, m. p. 79°; the function of the other oxygen atom remains undecided; it does not appear to be ketonic. Oxidation of the alcohol does not lead to definite results.

The residue of the higher-boiling fractions consists of sesquiterpenes, which have not been exhaustively examined. C. S.

Camomile Oil. C. HARTWICH and A. JAMA (*Chem. Zentr.*, 1909, 80, [ii], 823; from *Apoth. Zeit.*, 1909, 24, 585—586).—The florets of camomile (*Matricaria chamomilla*) yield 0.35% of a deep blue, viscid volatile oil, D_{20}^{15} 0.954, n_D^{21} 1.3637344 in alcoholic solution, $[\alpha]_D = 0$, saponification value 74.4, which shows no absorption spectrum, and after saponification retains the characteristic odour of camomile. The flower disks yield 0.51% of a slightly green oil, D_{20}^{15} 0.949, n_D^{21} 1.3637166 in alcohol, $[\alpha]_D = 0$, saponification number 33.7, which readily loses its colour and becomes yellow. After saponification, it develops an odour recalling that of lavender oil. It is suggested that camomile oil should be distilled from the florets only, and not from the flower-heads (florets and disks) as at present. T. A. H.

Composition of Oil of Cloves. Alcoholic and Aldehydic Constituents. HENRI MASSON (*Compt. rend.*, 1909, 149, 630—632, 795—797).—The following new constituents have been isolated from the fraction of oil of cloves (*Eugenia caryophyllata*) boiling below 125°/10 mm.: Methylamylcarbinol, methylheptylcarbinol, benzyl alcohol, furfuryl alcohol, together with an unsaturated compound, b. p. 190—195°, possibly a methylfurfuryl alcohol.

The fraction of oil of cloves b. p. 65—90°/15 mm. contains small quantities of α -methylfurfuraldehyde. The fraction having b. p. 105—120°/15 mm. contains a still smaller amount of *dimethylfurfuraldehyde*, $C_7H_8O_2$, b. p. 206—208°. This develops an intense violet coloration with α -naphthol and sulphuric acid, and on oxidation yields *dimethylpyromucic acid*, $C_7H_8O_3$, b. p. 129—130°.

Methyl salicylate has been isolated from the fraction of oil of cloves b. p. 105—120°/15 mm. (compare Erdmann, Abstr., 1898, i, 37).

W. O. W.

Volatile Oils. ROURE-BERTRAND FILS (*Chem. Zentr.*, 1909, 80, [ii], 1055—1056; from *Wiss. industr. Ber. Roure-Bertrand Fils*, 1909, [ii], 929—944).—Peppermint oil distilled from plants grown at Grasse remained liquid at -17° . Oil prepared in 1907, containing 10.6% combined menthol and 6.4% menthone, was hydrolysed, and

then yielded on fractionation *isovaleraldehyde*, *isoamyl alcohol*, *l*-pinene, a *hydrocarbon*, b. p. 165—167°, *i*-cineol, and *sec*-*l*-menthol, as well as *d*-menthone. *Schinus molle* oil is also described (this vol., i, 817). T. A. H.

Composition and Fractionation of Samphire Oil. F. BORDE (*Chem. Zentr.*, 1909, 80, ii, 1335; from *Bull. Sci. Pharm.*, 1909, 16, 393. Compare *ibid.*, 132, and Delépine, this vol., i, 642).—In continuation of previous work (*loc. cit.*), the author finds that the oil distilled from the stems and leaves contains (1) a *terpene*, b. p. 158—160°, D_4^{20} 0.8703, $[\alpha]_D + 44^\circ 37'$, iodine number 336, which is probably *d*-pinene; (2) a *hydrocarbon* (or a mixture of hydrocarbons), $C_{10}H_{16}$, b. p. 176—180°, D_4^{20} 0.8957, iodine number 175.5; (3) a *substance*, $C_{11}H_{16}O(?)$, b. p. about 210°, D 0.95023, $[\alpha]_D + 1^\circ 4'$, iodine number 156, and (4) an *isomeride* of apiole, $C_{12}H_{14}O_4$, b. p. 285—295°, D 1.1753, $[\alpha]_D = 0$, iodine number 119 (compare Delépine, *loc. cit.*). The quantities of these four products in oils from the fruit, stem and leaf, and the whole plant are given in the original. T. A. H.

Main Constituent of Japanese Lac. II. Oxidation of Urushiol Dimethyl Ether by Ozone. RIKO MAJIMA (*Ber.*, 1909, 42, 3664—3673. Compare this vol., i, 402).—The supposition that urushiol, $C_{20}H_{30}O_2$, is a dihydric phenol containing an unsaturated aliphatic group, $C_{14}H_{25}$, is more or less supported by the behaviour of urushiol dimethyl ether and ozone in chloroform. When a gas containing 15% of ozone is used at 0°, a very explosive, viscous *tetraozonide*, $C_{22}H_{34}O_{14}$, is obtained, in which it is probable that two mols. of ozone have entered the phenolic nucleus, since eugenyl methyl ether under the same conditions yields a *triozonide*, $C_{11}H_{14}O_{11}$. When urushiol dimethyl ether is ozonised by 6% ozone, a *diozonide*, $C_{22}H_{34}O_8$, or a *triozonide*, $C_{22}H_{34}O_{11}$, is obtained, according to the duration of the action. Both of these are decomposed by hot water, yielding carbon dioxide, acetaldehyde, heptaldehyde, azelaic and oxalic acids, and a *substance*, $C_{15}H_{22}O_3$, containing two methoxyl groups.

The formation of a *triozonide* suggests that the side-chain may be $C_{14}H_{23}$, and contain three double linkings.

Urushiol diacetate, $C_{24}H_{34}O_4$, is a yellow, viscous liquid, obtained by boiling "urushic acid" with acetic anhydride; it is easily hydrolysed by alcoholic potassium hydroxide. C. S.

Extractum Tanacetii. HERMANN MATTHES and HERMANN SERGER (*Arch. Pharm.*, 1909, 247, 418—431).—In recent years it has been shown repeatedly that the methods of estimating extracts are not satisfactory. The authors select the dried flowers of the tansy and show how the extract, by suitable treatment with alcohol, water, and ether, can be separated into pure resin, resin powder, resin soluble in ether, and fats. The solubilities, colour reactions, acid numbers, ester numbers, saponification numbers, and iodine numbers of these are tabulated.

The resins are separately hydrolysed by alcoholic potassium hydroxide, and thus converted into resin acids soluble in ether, resin acids

insoluble in ether, resin alcohols, and unsaponifiable matter. The fats are examined by the usual methods. A simpler apparatus than Farnsteiner's for the conversion of oleic acid into elaidic acid by a measured quantity of nitrogen peroxide is described and figured.

C. S.

Soluble Chitin from *Limulus polyphemus*, and its Osmotic Behaviour. CARL L. ALSBERG and C. A. HEDBLÖM (*J. Biol. Chem.*, 1909, 6, 483—497).—Chitin was first separated from the skeletal structures of the king crab (*Limulus*) by Halliburton, and in the present research it was found to have the properties he described, which are the same (percentage composition included) as that from other animals. Prolonged treatment with weak hydrochloric acid in the cold causes it first to gelatinise and then to form a colloidal solution with water. This change cannot be brought about if strong potassium hydroxide is employed in its preparation. The explanation advanced of the colloidal solution is that it combines with solvent water, and is perhaps also hydrolysed. It depresses the freezing point so slightly that its molecular weight is probably very great. It dialyses, and has the peculiar property of carrying the water in which it is dissolved through the membrane.

W. D. H.

Aloe-Emodin. OTTO A. OESTERLE and G. RIAT (*Arch. Pharm.*, 1909, 247, 413—417).—The results of previous work (Abstr., 1906, i, 973) indicate that aloetic acid is not, as formerly supposed, tetranitro-anthraquinone, but is nitrated aloe-emodin, probably a mixture of the di- and tri-nitro-derivatives. However, it is oxidised by chromic and acetic acids to a substance, decomposing at about 320°, which is reduced by potassium hydrogen sulphide to a blue substance. By treating a boiling alcoholic suspension of the last with sulphuric acid and sodium nitrite, amino-groups are replaced by hydrogen, and a dihydroxyanthraquinone, $C_{14}H_8O_4$, m. p. 190—191° (probably chrysazin), is obtained, which crystallises in glistening, brownish-yellow leaflets and forms an acetate, m. p. 232—234°. Aloe-emodin has been hitherto regarded as trihydroxymethylanthraquinone, but the preceding results confirm Robinson and Simonsen's formula (*Trans.*, 1909, 95, 1085), in which one of the hydroxyl groups is in the side-chain.

C. S.

Chemical Examination of Elaterium and the Characters of Elaterin. FREDERICK B. POWER and CHARLES W. MOORE (*Pharm. J.*, 1909, [iv], 29, 501—504).—Elaterium consists of a sediment deposited by the juice of the fruit of the "squirting cucumber" (*Ecballium Elaterium*). Previous work on it has been confined mainly to the isolation and examination of the supposed active principle, elaterin, to which a number of different empirical formulæ have been assigned (compare Berg, Abstr., 1898, ii, 447; 1906, i, 596; 1907, i, 146; 1909, i, 248, 587; Pollak, *ibid.*, 1906, i, 973; von Hemmelmayr, *ibid.*, 1906, i, 973).

Elaterium of English origin contained 5.3% moisture, and yielded, on ignition, 6.7% of ash. It furnished no volatile oil on steam distillation. The portion soluble in boiling water amounted to 6%, and included some starch and dextrose in addition to brown amorphous

matter, devoid of purgative properties. The portion insoluble in water was extracted successively by hot chloroform and alcohol, and in this way 57% of it dissolved. The residue from this treatment was physiologically inert.

The mixed chloroform-alcohol extract was exhausted successively with light petroleum and ether. The residue from this treatment consisted mainly of brown resin. The light petroleum extract gave a small amount of a colourless, crystalline substance, m. p. 170—180°, and, after hydrolysis with potassium hydroxide, a mixture of fatty acids with some phytosterol-like substance. The ether extract consisted mainly of a colourless, crystalline product, m. p. 217—220°, corresponding with the "elaterin" of the Pharmacopœias. This was not homogeneous, but consisted of at least two colourless substances, each crystallising in a different form, neither of which was obtained in an undoubtedly pure state. The one had m. p. 230° (decomp.) and $[\alpha]_D - 52.9^\circ$, and the other had a lower melting point and was dextro-rotatory, $[\alpha]_D + 13.9^\circ$. Both these substances proved to be of similar empirical composition, but the first was physiologically inert, whilst the second showed marked physiological activity. Examination of "commercial elaterin" showed that this also consisted mainly of varying mixtures of these two substances, and this variation probably accounts for the marked difference in medicinal value of commercial specimens of elaterin.

T. A. H.

The Chlorophyll Group. IV. Zinc Chlorophyll and Zinc Prophyllotaonin. HENRYK MALARSKI and LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1909, 21, 523—547. Compare this vol., i, 174).—Zinc chlorophylls have been prepared from the chlorophyllans of stinging nettle and maple leaves. These zinc compounds give the Krause reaction, and have spectra similar to that of chlorophyll.

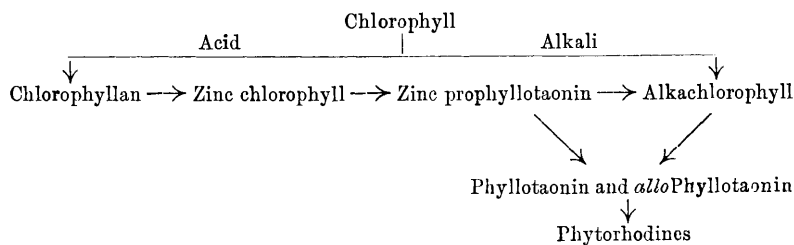
The chlorophyllans are not homogeneous substances; one constituent reacts more readily with zinc hydroxide and carbon dioxide than the other. The former is termed *allochlorophyllan*, and is regarded as a product formed by the action of acids on *allochlorophyll* (Sorby's yellow chlorophyll). When treated with concentrated hydrochloric acid, it yields phylloxanthin as chief product. The function of the carbon dioxide in the formation of the zinc chlorophyll has not been determined; carbon dioxide is not eliminated when the zinc compounds are acidified.

With alkalis the zinc chlorophylls yield two compounds, α - and β -zinc-prophyllotaonins, which are similar to *allochlorophylls*. The α -compound reacts with hydrochloric acid, yielding *allophyllotaonin* whereas the β -compound yields *phyllotaonin* together with other substances. With boiling alcoholic hydrochloric acid, the zinc prophyllotaonins yield *pythorhodines*. In the action of alkalis on the zinc chlorophyll, ammonia is not evolved.

It is pointed out that the products obtained by the action of acids on chlorophyll and *allochlorophyll* are different; the former yields chlorophyllan and *allochlorophyllan*, and ultimately *phyllocyanin* and *phylloxanthin*, whereas the latter yields *phyllotaonin* and *allophyllotaonin* and their ethers.

Willstätter's results can be explained by the fact that phyllotaonins are readily converted into phytorhodines.

The following scheme is given :



J. J. S.

The Chlorophyll Group. V. The Identity of Chlorophyllpyrrole and Hæmopyrrole. L. BARABASZ and LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1909, 21, 548—550).—The identity of chlorophyllpyrrole and hæmopyrrole has been established by showing that the former reacts with benzenediazonium chloride, yielding two dyes identical with those obtained from hæmopyrrole (Abstr., 1908, i, 710).

J. J. S.

The Kaempherol from Robinin. NICOLAI WALIASCHKO (*Arch. Pharm.*, 1909, 247, 447—462).—The object of the present research is to ascertain whether robigenin, the yellow colouring matter obtained by the hydrolysis of robinin (Abstr., 1904, i, 606), is actually identical with kaempherol, as stated by Perkin (*Trans.*, 1902, 81, 473). This object has been attained, the identity of both substances being proved by a comparison of the tetra-acetates and tetramethyl ethers.

The reaction between kaempherol, ethyl iodide, and potassium hydroxide leads to the formation of *kaempheryl triethyl ether*, m. p. 103—104°.

Kaempherol yields several methylated derivatives. By treatment with methyl iodide and potassium hydroxide, the tetramethyl ether, m. p. 175—176°, and Ciamician and Silber's trimethyl ether, m. p. 139—140°, are obtained, whereas the action of methyl-alcoholic potassium hydroxide and methyl sulphate produces the *dimethyl ether*, m. p. 142—143°, *heptamethyldikaempherol*, $C_{15}H_8O_6Me_2, C_{15}H_5O_6Me_5$, m. p. 144—145°, and *pentamethylkaempherol*, $C_{15}H_5O_6Me_5$, m. p. 155—156°.

When warmed with 12% nitric acid, kaempherol yields 3-nitro-*p*-hydroxybenzoic acid, oxalic acid, and a *substance*, m. p. 130—131°.

C. S.

Constitution of Tannin. VI. MAXIMILIAN NIERENSTEIN (*Ber.*, 1909, 42, 3552—3553).—A reply to Iljin (this vol., i, 503). Tannin, a mixture of digallic and hydroxygallic acids, is decomposed by one of Iljin's methods of purification. *Gallalphenylhydrazone*, $C_{13}H_{12}O_3N_2$, from tannin, crystallises in needles, m. p. 172—176°; leucotannin does not yield a phenylhydrazine derivative.

W. R.

Furfuraldehydephloroglucide. EMIL VOTOČEK and C. KRAUZ (*Zeitsch. Zuckerind. Böhm.*, 1909, 34, 20).—The author has examined the dark green precipitate obtained when phloroglucinol is added to furfuraldehyde in the conditions obtaining in the well-known Tollens' method for estimating the pentosans. The precipitate has an indefinite composition, constant, however, with definite experimental conditions.

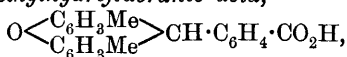
Zinc sulphate considerably retarded the condensation, and it was necessary to heat the mixture to boiling before the reaction was complete. The product was pure yellow in colour, and only took on the ordinary dark green tint after treatment with 12% hydrochloric acid. The yellow substance contained 61.55–62.38% C and 4.01–4.27% H, and the dark green 62.48% C and 4.03% H. Neither substance dissolved in any of the reagents tried.

Ammonium chloride and sodium chloride influence the condensation in the same way; intermediate products with lower carbon content are obtained, which are convertible into the ordinary dark green substance on treatment with acid. E. J. R.

Pyrone Derivatives. RUDOLF PUMMERER (*Ber.*, 1909, 42, 3554).—The conclusions drawn by Baly, Collie, and Watson (*Trans.*, 1909, 95, 144) from the absorption spectra of pyrone derivatives are at variance with those derived from the chemical evidence adduced by Willstätter and Pummerer (*Abstr.*, 1904, i, 1043; 1905, i, 457).

W. R.

Action of Phthalic Anhydride on *m*-Cresol. WALTHER LAMBRECHT (*Ber.*, 1909, 42, 3591–3595. Compare Bentley, Gardner, and Weizmann, *Trans.*, 1907, 91, 1636).—The chief product obtained by condensing phthalic anhydride with *m*-cresol in the presence of stannic chloride or concentrated sulphuric acid at 120–130° is 3:6-dimethylfluoran, which melts at 213–214° (not 204°). When the fluoran is reduced with potassium ethoxide and zinc dust, the chief product is *dimethylhydrofluoranic acid*,

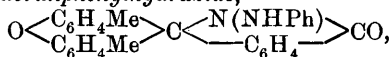


which crystallises from alcohol in small needles, m. p. 232°. When dimethylfluoran, dimethylhydrofluoranic acid, or its salts (silver and calcium) are subjected to destructive distillation, an orange-coloured product is obtained; this is probably O. Weber's 3:6-dimethyl-xanthone (*Abstr.*, 1892, 1093).

Dimethylfluoran does not form salts with hydrochloric, sulphuric, or picric acids, but yields a *stannichloride*, $\text{C}_{22}\text{H}_{16}\text{O}_3 \cdot \text{HCl} \cdot \text{SnCl}_4$, in the form of a yellow, crystalline mass.

3:6-Dimethyldibromofluoran, $\text{C}_{22}\text{H}_{14}\text{O}_3\text{Br}_2$, obtained by the action of bromine on a hot solution of dimethylfluoran in glacial acetic acid, crystallises from alcohol in colourless needles, m. p. 330°.

3:6-Dimethylfluoranphenylhydrazide,



crystallises from xylene in colourless, slender needles, m. p. 240°, and

3 : 6-dimethylfluorananilide, $C_{28}H_{21}O_2N$, crystallises from dilute alcohol in colourless prisms, m. p. 229° . J. J. S.

Preparation of 2:3-Diketodihydro-(1)-thionaphthen. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 212782). — 2:3-Diketodihydro-1-thionaphthen, m. p. 118° , separates in orange-yellow prisms when 2:2-dichloro- or 2:2-dibromo-3-ketodihydro-1-thionaphthen is boiled with water.

2:3-Diketo-5-methyldihydro-(1)-thionaphthen, m. p. $143-144^\circ$, brown plates, is prepared in a similar manner from 2:2-dichloro- or 2:2-dibromo-3-keto-5-methyldihydrothionaphthen.

5-Chloro-2:3-diketodihydro-(1)-thionaphthen, m. p. $148-149^\circ$, prepared from 5-chloro-2:2-dibromo-3-ketodihydro-(1)-thionaphthen, crystallises in red plates. When 2:2-dibromo-3-ketodihydrothionaphthen is boiled in alcoholic solution with aniline and sodium acetate, and subsequently acidified, a product is obtained which crystallises in brown, microcrystalline plates. F. M. G. M.

Preparation of Substituted Halogen Derivatives of 3-Oxy-(1)-thionaphthen. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 212942. Compare preceding abstract).—When 3-oxy-(1)-thionaphthen or its homologues are treated with halogens (in the presence or absence of solvents or diluting agents), either mono- or di-halogen substitution products of 3-ketodihydro-(1)-thionaphthen, probably of the general formula $C_6H_4 \begin{smallmatrix} S \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} CR_2$, are formed (R = halogen).

2-Bromo-3-ketodihydro-(1)-thionaphthen, m. p. 89° , crystallises in colourless prisms.

2-Chloro-3-ketodihydro-(1)-thionaphthen is a red oil with penetrating odour.

2:2-Dibromo-3-ketodihydro-(1)-thionaphthen crystallises in golden-yellow plates, m. p. 133° .

2:2-Dichloro-3-ketodihydro-(1)-thionaphthen, a heavy, red oil of characteristic odour resembling that of 2:3-diketodihydro-(1)-thionaphthen, is prepared from 3-oxy-(1)-thionaphthen and sulphuryl chloride.

2:2-Dibromo-3-keto-5-methyldihydro-(1)-thionaphthen, prepared from 3-keto-5-methyl-(1)-thionaphthen, crystallises in golden-yellow needles, m. p. 99° .

5-Chloro-2:2-dibromo-3-ketodihydro-(1)-thionaphthen, m. p. 93° , is obtained from 5-chloro-3-ketothionaphthen. F. M. G. M.

Constituents of Meat Extract. R. KRIMBERG (*Ber.*, 1909, 42, 3878—3880. Compare Engeland, this vol., i, 557; Krimberg, *Abstr.*, 1908, i, 842).—Polemical. A claim for priority in establishing the constitution of carnitine. It is agreed that the compound described as oblitine is in reality carnitine ethyl ester. E. F. A.

Nitrocodeinic Acid, an Oxidation Product of Nitrocodeine and Nitro- ψ -codeine. FRITZ ACH, LUDWIG KNORR, H. LINGENBRINK, and HEINRICH HÖRLEIN (*Ber.*, 1909, 42, 3503—3510. Compare *Abstr.*, 1903, i, 849).—When nitrocodeine is dissolved in cold

nitric acid (D 1.3) there is produced after a short time a vigorous evolution of gas, and the temperature rises to 40° . The mixture, after remaining at the ordinary temperature for four days and then heating for ten hours at 60° , is poured into water, when a weakly basic substance is precipitated. The filtrate is neutralised and lead acetate added, when a lead salt is precipitated. The lead is removed by dilute sulphuric acid, and the hot filtrate deposits a resinous mass on cooling; extraction with hydrochloric acid yields *nitrocodeinic acid hydrochloride*, which forms yellow needles. *Nitrocodeinic acid*, $C_{16}H_{18}O_9N_2$, purified through its ammonium or barium salt, crystallises in slender needles, decomp. 300° . This acid can also be obtained from nitro- ψ -codeine, but not from nitro-oxycodine. Its *potassium* and *barium*, $C_{16}H_{16}O_9N_2Ba \cdot 2H_2O$, salts have been prepared, and show it to be dibasic. Its salts with mineral acids are completely dissociated in water.

Aminocodeinic acid is obtained in the form of its *hydrochloride*, $C_{16}H_{20}O_7N_2 \cdot HCl$, by reduction with tin and hydrochloric acid. It forms leaflets.

When nitrocodeinic acid is heated at 140 — 150° with hydrochloric acid, *nitronorcodeinic acid*, $C_{15}H_{16}O_9N_2$, is obtained in needles. Heating nitrocodeinic acid with hydriodic acid results in the formation of *aminonorcodeinic acid*, $C_{15}H_{18}O_7N_2$, as a crystalline powder.

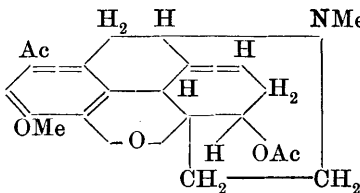
When nitrocodeinic acid is esterified with alcohol and hydrogen chloride, an ester is obtained, but a molecule of water has also been removed. The *methyl* ester, $C_{17}H_{18}O_8N_2 \cdot 2MeOH$, forms plates; its *hydrochloride*, $C_{17}H_{18}O_8N_2 \cdot HCl$, needles; the *ethyl* ester *hydrochloride*, $C_{18}H_{20}O_8N_2 \cdot HCl$, slender needles. Probably a lactone is formed of the nature of betaine.

Diazomethane and nitrocodeinic acid give a *compound*, $C_{18}H_{20}O_8N_2$ (or $C_{19}H_{22}O_8N_2$), containing three methoxyl groups, which forms yellow prisms, m. p. 180° . When this ester is heated with 20% hydrochloric acid, it yields the *hydrochloride*, $C_{18}H_{20}O_8N_2 \cdot HCl$, which contains only two methoxyl groups.

W. R.

Morphine. XX. Acetoxyacetylcodeine. LUDWIG KNORR, HEINRICH HÖRLEIN, and FRANZ STAUBACH (*Ber.*, 1909, 42, 3511—3521).—The preparation of a triacetylmorphine and diacetylcodeine has been given by Causse (*Abstr.*, 1899, i, 394) and by Knoll & Co. (*Abstr.*, 1907, i, 235).

As morphine contains two hydroxyl groups and codeine only one, this behaviour is surprising, and experiments were undertaken to ascertain the position of the acetyl groups. Causse's results could not be obtained, and are regarded as erroneous, but Knoll & Co.'s were corroborated. As (1) the diacetylcodeine is hydrolysed to a monoacetylcodeine and no further, (2) the latter compound is a ketone, and (3) the morphine alkaloids are derivatives of pyrogallol, the conclusion is drawn that the acetyl group is substituted in benzene nucleus (I) of the codeine, and that the acetoxyacetylcodeine (diacetylcodeine)



has the annexed constitution. This conclusion as to the position of the acetyl group is strengthened by the fact that this compound cannot be nitrated under conditions in which codeine itself is nitrated with ease. Acetoxyacetylcodeine has $[\alpha]_D^{17} - 207^\circ$ in chloroform solution; the *oxime*, $C_{22}H_{26}O_5N_2 \cdot \frac{1}{2}EtOH$, crystallises in needles, m. p. $176-178^\circ$.

Hydrolysis of the acetoxyacetylcodeine with sodium ethoxide gives *acetylcodeine*, $C_{20}H_{28}O_4N_4$, which crystallises in rectangular plates, m. p. 150° , $[\alpha]_D^{21} - 141^\circ$; the *oxime*, $C_{20}H_{24}O_4N_2$, has m. p. 100° (decomp.). *Acetylcodeine methiodide*, $C_{21}H_{26}H_4NI$, crystallises in rectangular leaflets, m. p. 235° , $[\alpha]_D^{18} - 64^\circ$. When decomposed by boiling sodium hydroxide solution, *acetylmethylmorphimethine* $C_{21}H_{25}O_4N$, is formed in 85% yield; it forms needles, m. p. 149° , $[\alpha]_D^{21} + 150^\circ$. This compound is not changed by alcoholic potassium hydroxide, and therefore behaves similarly to ϵ - and ζ -methylmorphimethine, and is distinguished from α - and γ -compounds, in which a wandering of the ethenoid linking occurs. That the diacetyl compound is a derivative of codeine, and not of ψ -codeine or *allo-ψ*-codeine, is shown by these compounds also forming isomeric diacetyl compounds with acetic anhydride and sulphuric acid. It is accordingly assumed that the migration of the ethenoid linking occurs during the decomposition of the methiodide, an assumption which is supported by the striking change in the rotation.

Acetoxyacetylmethylmorphimethine, prepared by digesting acetylmethylmorphimethine and acetic anhydride for half an hour, is an oily base, which, with methyl iodide, yields the *methiodide*, $C_{24}H_{30}O_5N$, separating in yellow crystals, m. p. $180-182^\circ$.

When acetylmethylmorphimethine is heated with an alcoholic solution of sodium ethoxide for six hours at 160° , a 75% yield of *acetylmethylmorphol*, $C_{17}H_{14}O_3$, is obtained in needles, m. p. $161-162^\circ$; its *semicarbazone*, $C_{18}H_{17}O_3N_3$, has m. p. 220° (decomp.). The basic product of the above hydrolysis is dimethylaminoethyl ether (compare Abstr., 1904, i, 916).

Morphine. XXI. Acetoxyacetyl Derivatives of *iso*Codeine, ψ -Codeine, and *allo-ψ*-Codeine. LUDWIG KNORR, HEINRICH HÖRLEIN, and FRANZ STAUBACH (*Ber.*, 1909, 42, 3521—3522. Compare preceding abstract).—*Acetoxyacetyl-ψ-codeine*, $C_{22}H_{25}O_5N$, crystallises in prisms, m. p. 170° , $[\alpha]_D^{18} - 126^\circ$. *Acetoxyacetylisocodeine*, $C_{22}H_{25}O_5N \cdot \frac{1}{2}EtOH$,

has m. p. $80-85^\circ$; the alcohol-free substance, m. p. 105° , $[\alpha]_D^{14} - 236^\circ$. The diacetyl derivative from *allo-ψ*-codeine is an oil. The above compounds are all prepared similarly to that obtained from codeine itself.

W. R.

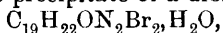
Constitution of Stachydrine. R. ENGELAND (*Arch. Pharm.*, 1909, 247, 463—466. Compare Planta and Schulze, Abstr., 1893, i, 447, 679; Jahns, *ibid.*, 1896, i, 712).—Stachydrine closely resembles betaine in its reactions, but differs in yielding dimethylamine by distillation with potassium hydroxide. In this respect it resembles Willstätter's *N*-methylhygric acid (Abstr., 1900, i, 405). The author

shows that the two substances are identical by a comparison of the chlorides, aurichlorides, and platinichlorides. C. S.

Bromination of Strychnine, Brucine, and other Alkaloids.

JÓZEF BURACZEWSKI and M. DZIURZYŃSKI (*Bull. Acad. sci. Cracow*, 1909, 333—343. Compare Abstr., 1908, i, 1007; this vol., ii, 472).—On adding a solution of bromine in carbon disulphide to a cold saturated alcoholic solution of cinchonine, a bright yellow precipitate is obtained, which readily dissolves in excess of bromine. If the addition of bromine is stopped when a maximum amount of precipitate has been formed, and the latter then collected, a bright yellow tetrabromocinchonine derivative, $C_{19}H_{22}ON_2Br_2Br_2$, which is apparently non-crystalline, is obtained, two of the bromine atoms being differently combined from the other two. It is not soluble without decomposition in most organic solvents. Towards acetone it shows a very characteristic behaviour; it first dissolves to a clear yellow solution, and then almost immediately a white, crystalline precipitate forms.

If bromine is added to the alcoholic solution of cinchonine until the precipitate first formed redissolves, and the solution left for some time, a heavy, crystalline precipitate of a dibromo-derivative,



m. p. 203° , is formed, but begins to turn brown above 190° . It is identical with Comstock and König's (Abstr., 1884, 1382; 1886, 281, 1122) α -cinchonine dibromide, although the melting point is different. When the alcoholic solution is treated with bromine (in carbon disulphide), the tetrabromocinchonine derivative is again produced.

When cinchonine is replaced by quinine and bromine added, a white precipitate of a monobromoquinine, $C_{20}H_{24}O_2N_2Br$, is produced, which with excess of bromine yields a yellow pentabromo-derivative, $C_{20}H_{24}O_2N_2Br_2Br_2Br_2$. If this yellow product is treated with cold water, in which it is quite insoluble, and then gently warmed (below 40°), it loses its yellow colour, and a small portion of it dissolves in water. If the liquid is now rapidly filtered and treated with concentrated ammonia, a white, flocculent precipitate is first produced, which almost immediately becomes emerald-green. This substance contains bromine, and is easily soluble in alcohol to a green solution; it is possibly the substance which gives the thalleoquinine reaction.

The authors have previously shown that monobromobrucine dissolves in mineral acids in the cold, forming a red solution. They have now isolated the compound to which the red colour is due, by adding concentrated sulphuric acid, drop by drop, to a mixture of monobromobrucine and water until the acid was in slight excess; on addition of alcohol, a cherry-red precipitate is produced. After purification it is readily soluble in water, and gives a precipitate of barium sulphate on addition of barium chloride; it contains bromine. It could not be further investigated, but was probably the sulphate of monobromobrucine.

If a solution of brucine in dilute nitric acid is added, drop by drop, to absolute alcohol, a cherry-red precipitate is produced of the

formula $C_{23}H_{26}O_2N,N_2O_4,HNO_3$. It dissolves readily in water, giving a red solution T. S. P.

Strychnos Alkaloids. VII. Fission of Brucinonic Acid and of Brucinolone. HERMANN LEUCHS and L. E. WEBER (*Ber.*, 1909, 42, 3703—3710).—The decomposition of brucinolic acid into glycollic acid and brucinolone by sodium hydroxide (this vol., i, 253) makes it probable that brucinonic acid contains a carbonyl group in the α -position. If this is so, the acid should lose carbon dioxide by treatment with aniline, and should yield glyoxylic or oxalic acid by fission with sodium hydroxide. Neither of these expectations is fulfilled, since brucinonic acid yields an *anilide*, $C_{29}H_{29}O_7N_3$, m. p. 239—240°, when heated with aniline in a current of hydrogen, and is decomposed by alkalis with the formation of glycollic acid. Thus the acid and 1.5 equivalents of *N*-sodium hydroxide at 0° yield glycollic acid and an uncrystallisable product, together with *brucinonic acid hydrate*,



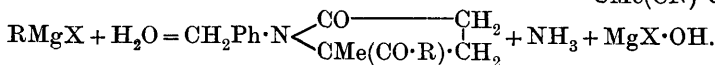
m. p. 245°, with previous darkening, which is also produced by the action of boiling 5*N*-hydrochloric acid on brucinonic acid, and is possibly formed by an addition of water, thus: $:N \cdot CO \rightarrow :NH \cdot CO_2H$.

The decomposition of brucinolic acid by sodium hydroxide yields a small amount of a *substance*, $C_{21}H_{24}O_6N_2$, m. p. 290° (decomp.), which gives the brucine reaction, dissolves in 20% hydrochloric acid and alkali hydroxides, but is insoluble in dilute hydrochloric acid and in sodium carbonate. An isomeric *substance*, $C_{21}H_{24}O_6N_2$, m. p. 267—268°, is obtained in the form of the *hydrochloride*, $C_{21}H_{24}O_6N_2 \cdot HCl \cdot \frac{1}{2}H_2O$, m. p. 245° (decomp.), by treating brucinolone with concentrated hydrochloric acid, at first in the cold and then at 100°.

When brucinolone is treated with 5*N*-nitric acid, carbon dioxide and nitric oxide are evolved, and a *quinone*, $C_{19}H_{16}O_5N_2$, m. p. 295° (decomp.), is obtained, which crystallises in large, light red prisms, is decomposed by alkali hydroxides, and is converted by aqueous sulphurous acid at 0° into *bis-desmethylbrucinolone*, $C_{19}H_{18}O_5N_2$, which crystallises in yellow prisms and has m. p. 300°, and a small amount of another crystalline substance having the same m. p. The quinol can be re-converted into the quinone by warm dilute or cold concentrated nitric acid. C. S.

Ketones of the Pyrrolidone Series. OTTO KÜHLING and L. FRANK (*Ber.*, 1909, 42, 3952—3958).—The interaction of ethyl lævulate, hydrocyanic acid, and benzylamine in absolute alcoholic solution under pressure yields 2-cyano-1-benzyl-2-methylpyrrolidone, which, when treated according to Blaise's modification (compare *Abstr.*, 1901 i, 133, 252; 1902, i, 164) of the Grignard synthesis,

reacts according to the equation: $CH_2Ph \cdot N \begin{matrix} \text{CO} \text{---} CH_2 \\ \diagdown \\ CMe(CN) \cdot CH_2 \end{matrix} +$

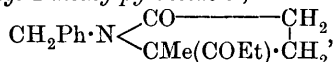


The acetyl, propionyl, and benzoyl derivatives thus obtained are extremely stable, and can be heated with concentrated alkali solutions in a reflux apparatus, or with dilute mineral acids in a sealed tube at

150° without decomposing. They exhibit the ordinary reactions for ketones only in a restricted degree, probably owing to the steric hindrance of the pyrrolidone nucleus and the methyl group. The phenylhydrazones and semicarbazones could not be obtained, and the oximes are only obtainable in quantity in presence of excess of potassium hydroxide.

2-Cyano-1-benzyl-2-methylpyrrolidone, $\text{CH}_2\text{Ph}\cdot\text{N} \begin{smallmatrix} \text{CO} \text{---} \text{CH}_2 \\ \text{CMe}(\text{CN}) \cdot \text{CH}_2 \end{smallmatrix}$, m. p. 76—77°, prepared from ethyl lævulate, hydrocyanic acid, and benzylamine, is accompanied by a basic derivative of glutaric acid, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CMe}(\text{CN})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (?), which was not obtained sufficiently pure for analysis.

2-Propionyl-1-benzyl-2-methylpyrrolidone,



prepared by the action of magnesium and ethyl iodide on 2-cyano-1-benzyl-2-methylpyrrolidone in ethereal solution, has m. p. 66—67°, and yields an *oxime*, $\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}_2$, m. p. 135—136°, which gives the original pyrrolidone derivative, m. p. 66—67°, when heated in a sealed tube with 12% sulphuric acid at 150°.

2-Acetyl-1-benzyl-2-methylpyrrolidone, $\text{CH}_2\text{Ph}\cdot\text{N} \begin{smallmatrix} \text{CO} \text{---} \text{CH}_2 \\ \text{CAcMe} \cdot \text{CH}_2 \end{smallmatrix}$, forms white, prismatic crystals, m. p. 67—68°; the corresponding *oxime*, $\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}_2$, has m. p. 141°.

2-Benzoyl-1-benzyl-2-methylpyrrolidone, $\text{CH}_2\text{Ph}\cdot\text{N} \begin{smallmatrix} \text{CO} \text{---} \text{CH}_2 \\ \text{CBzMe} \cdot \text{CH}_2 \end{smallmatrix}$, prepared by the action of magnesium and bromo- or iodo-benzene on 2-cyano-1-benzyl-2-methylpyrrolidine, is obtained as a pale yellow oil which does not solidify; its *oxime*, $\text{C}_{19}\text{H}_{20}\text{O}_2\text{N}_2$, has m. p. 218—219°. T. H. P.

New Cinchonic Acid Syntheses. WALTHER BORSCHKE (*Ber.*, 1909, 42, 4072—4088. Compare this vol., i, 52).—When mono-substituted pyruvic acids (for example, phenyl-, *o*-nitrophenyl-, benzoyl-, and benzyl-pyruvic acids) are condensed with an aldehyde and a primary arylamine according to Doebner's method, cinchonic acids are not formed as a rule. Benzylpyruvic acid, however, with aniline and benzaldehyde yields 13% of 2-phenyl-3-benzylcinchonic acid, and with *m*-toluidine and benzaldehyde it yields 18% of 2-phenyl-3-benzyl-7-methylcinchonic acid. The remaining three acids yield under similar conditions diketopyrrolidines. When β -naphthylamine is substituted for the amines of the benzene series, somewhat better yields of cinchonic acids are obtained, for example, phenylpyruvic acid, benzaldehyde, and β -naphthylamine give a 40% yield of 2:3-diphenyl- β -naphthylcinchonic acid and no pyrrolidine derivative.

It has also been found possible to condense β -naphthylamine and formaldehyde with the substituted pyruvic acids, yielding substituted naphthaquinoline-4-carboxylic acids.

4:5-Diketo-1:2:3-triphenylpyrrolidine, $\text{NPh} \begin{smallmatrix} \text{CHPh} \cdot \text{CHPh} \\ \text{CO} \text{---} \text{CO} \end{smallmatrix}$, ob-

tained by heating an alcoholic solution of aniline, benzaldehyde, and phenylpyruvic acid (Erlenmeyer, Abstr., 1893, i, 36) on the water-bath, crystallises in colourless needles, m. p. 250°. It is feebly acidic, and dissolves to a certain extent in warm sodium hydroxide solution. It does not react with phenylhydrazine, hydroxylamine, or semicarbazide, but yields an *acetyl* derivative, $C_{22}H_{16}O_2N \cdot Ac$, m. p. 185°, and a *benzoyl* derivative, $C_{29}H_{21}O_3N$, m. p. 174°. When boiled with zinc dust and acetic acid, it is reduced

to 4-hydroxy-1:2:3-triphenyl-5-pyrrolidone,
$$NPh \begin{array}{c} \text{CHPh} \cdot \text{CHPh} \\ | \\ \text{CO} - \text{CH} \cdot \text{OH} \end{array}$$
 colourless crystals, m. p. 238°, and when subjected to destructive distillation yields stilbene and a compound, $C_{21}H_{17}ON$, m. p. 338°.

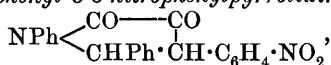
4:5-Diketo-2:3-diphenyl-1-o-tolylpyrrolidine, $C_{23}H_{19}O_2N$, forms a white, crystalline powder, m. p. 232—234°; the corresponding m-tolyl derivative forms an insoluble resin, and the p-tolyl compound, colourless crystals, m. p. 224°.

4:5-Diketo-2:3-diphenyl-1-m-nitrophenylpyrrolidine, $C_{22}H_{16}O_4N_2$, forms yellow needles, m. p. 226°; aniline, formaldehyde, and phenylpyruvic acid yield 4:5-diketo-1:3-diphenylpyrrolidine, m. p. 208°; aniline, p-nitrobenzaldehyde, and phenylpyruvic acid yield 4:5-diketo-1:3-diphenyl-2-p-nitrophenylpyrrolidine, $C_{22}H_{16}O_4N_2$, m. p. 192°; aniline, salicylaldehyde, and phenylpyruvic acid yield 4:5-diketo-1:3-diphenyl-2-o-hydroxyphenylpyrrolidine, $C_{22}H_{17}O_5N$, colourless needles, m. p. 252°, and the same acid with aniline and anisaldehyde yields 4:5-diketo-1:3-diphenyl-2-p-methoxyphenylpyrrolidine, $C_{23}H_{19}O_3N$, m. p. 195°.

Phenylpyruvic acid, benzaldehyde, and β -naphthylamine yield 2:3-diphenyl- β -naphthaquinoline-1-carboxylic acid, $C_{26}H_{17}O_2N$, in the form of a yellow, crystalline powder, sparingly soluble in the usual solvents. It has m. p. 275°, and is at the same time converted into 2:3-diphenyl- β -naphthaquinoline, $C_{25}H_{17}N$, which crystallises from aqueous acetone in colourless needles or from ethyl acetate and alcohol in plates, m. p. 179—180°. When acetaldehyde is substituted for benzaldehyde in the above condensation, 2-phenyl-3-methyl- β -naphthaquinoline-1-carboxylic acid is obtained in colourless needles, which lose carbon dioxide when heated, yielding 2-phenyl-3-methyl- β -naphthaquinoline, $C_{20}H_{15}N \cdot H_2O$, m. p. 101°. The nitrate is sparingly soluble, and crystallises in glistening plates. 2-Phenyl- β -naphthaquinoline-1-carboxylic acid, $C_{26}H_{13}O_2N$, obtained by using formaldehyde, forms colourless, crystalline flocks, and 2-phenyl- β -naphthaquinoline,

$C_{19}H_{13}N \cdot 2H_2O$,
colourless needles, m. p. 111°.

4:5-Diketo-1:2-diphenyl-3-o-nitrophenylpyrrolidine,



obtained from o-nitrophenylpyruvic acid and benzylideneaniline, crystallises in yellow plates, m. p. 207—208°. The same acid, with benzaldehyde and β -naphthylamine yields 3-phenyl-2-o-nitrophenyl- β -naphthaquinoline-1-carboxylic acid, $C_{26}H_{16}O_4N_2$, which crystallises in

small, yellow needles; the corresponding base, $C_{25}H_{16}O_4N_2 \cdot \frac{1}{2}H_2O$, forms yellow plates, m. p. 193—194°.

4:5-Diketo-3-benzoyl-1:2-diphenylpyrrolidine, $C_{23}H_{17}O_3N$, prepared from benzoylpyruvic acid, benzaldehyde, and aniline, crystallises from alcohol in colourless needles, m. p. 242—244° (decomp.). With anisaldehyde, 4:5-diketo-3-benzoyl-1-phenyl-2-p-methoxyphenylpyrrolidine, $C_{24}H_{19}O_4N$, m. p. 228°, is obtained. Benzoylpyruvic acid, benzaldehyde, and β -naphthylamine yield 2-benzoyl-3-phenyl- β -naphthaquinoline-1-carboxylic acid, $C_{27}H_{17}O_3N$, which crystallises in brilliant, colourless needles. When heated, the acid yields 2-benzoyl-3-phenyl- β -naphthaquinoline, $C_{26}H_{17}ON$, in slender needles, m. p. 185°. When formaldehyde is substituted for benzaldehyde, 2-benzoyl- β -naphthaquinoline-1-carboxylic acid is obtained, and this, when heated, yields 2-benzoylnaphthaquinoline, $C_{20}H_{13}ON$, as colourless needles, m. p. 108—109°.

4:5-Diketo-1:2-diphenyl-3-benzylpyrrolidine, $C_{23}H_{19}O_2N$, colourless needles, m. p. 196°, and 2-phenyl-3-benzylquinoline-4-carboxylic acid, $C_{23}H_{17}O_2N$, m. p. 290°, are formed by the action of benzylpyruvic acid on benzaldehyde and aniline, and are readily separated by means of sodium hydroxide solution. 2-Phenyl-3-benzylquinoline, $C_{22}H_{17}N$, crystallises in colourless needles, m. p. 96—97°. Benzylpyruvic acid, benzaldehyde, and *m*-toluidine yield 2-phenyl-3-benzyl-7-methylquinoline-4-carboxylic acid, $C_{24}H_{19}O_2N$, as colourless needles, which lose carbon dioxide when heated, and then form 2-phenyl-3-benzyl-7-methylquinoline, $C_{23}H_{19}N$, m. p. 99°.

Benzylpyruvic acid, benzaldehyde, and β -naphthylamine yield 3-phenyl-2-benzyl-naphthaquinoline-1-carboxylic acid, $C_{27}H_{19}O_2N$, which readily loses carbon dioxide, giving the base, $C_{26}H_{19}N$, m. p. 152°.

J. J. S.

Synthesis of γ -Coniceine. SIEGMUND GABRIEL (*Ber.*, 1909, 42, 4059—4062).—Previous investigations (*Abstr.*, 1908, i, 649; this vol., i, 491) have shown that when δ -phthaliminobutyl methyl ketone and δ -phthaliminovaleophenone are hydrolysed, the products are not δ -amino-ketones, but the cyclic compounds, 2-methyltetrahydropyridine and 2-phenyltetrahydropyridine, formed by the elimination of water from the δ -amino-ketones.

It is now shown that γ -bromopropylphthalimide and sodio-ethyl butyrylacetate react, yielding δ -phthaliminobutyl propyl ketone, $C_8H_4O_2 \cdot N \cdot [CH_2]_4 \cdot CO \cdot C_3H_7$, and that when this is hydrolysed, 2-propyltetrahydropyridine (γ -coniceine) is formed (compare V. Braun and Steindorff, *Abstr.*, 1905, i, 812).

J. J. S.

The System Water-Pyridine. ÉMILE BAUD (*Bull. Soc. chim.*, 1909, [iv], 5, 1022—1033).—The conclusions published in the preliminary note (this vol., i, 120) are somewhat modified.

Aqueous solutions of pyridine, on freezing, deposit a mixture of ice and pyridine hydrate until the concentration of pyridine reaches 70%, thence to 85% concentration, pyridine hydrate is deposited, and after that crystals of pyridine. Determinations of the heat of solution of a

mixture of pyridine and water in excess of water indicate the existence of a hydrate, $C_5H_5N \cdot 2H_2O$. On these new data, and those recorded formerly (*loc. cit.*), the conclusion is drawn that only one hydrate can be separated from mixtures of pyridine and water, and that this exists in solution and is not merely formed at the moment of crystallisation.

T. A. H.

Cyanodihydrocyclic Amines. II. Quinoline Series. ADOLF KAUFMANN and ALBERTO ALBERTINI (*Ber.*, 1909, 42, 3776—3789. Compare this vol., i, 606).—By the action of potassium cyanide on quinoline alkyl halides, cyanodihydroquinolines are obtained, but they differ from the acridine derivatives in being unstable and readily oxidisable, so that they cannot be recrystallised. Oxidation does not result in the loss of the cyano-group, but 4-cyano-1-alkyl-2-quinolones are formed.

For the preparation of 4-cyano-1-methyldihydroquinoline, the reaction between quinoline methiodide and potassium cyanide is carried out in aqueous solution in the presence of ether. The unstable product is dissolved in the ether as it is formed, and may be obtained by evaporation of the solution at the ordinary temperature in the form of rosettes of white needles, m. p. 80° . 4-Cyano-1-ethyldihydroquinoline is obtained similarly; it forms white needles, m. p. 26° . 4-Cyano-1:6-dimethyldihydroquinoline (from 6-methylquinoline) forms white needles, m. p. 54° . 4-Cyano-1:8-dimethyldihydroquinoline crystallises in cubes, m. p. $79-80^\circ$. When warmed with alcoholic potassium hydroxide, ammonia is evolved, and a yellow coloration is produced, which afterwards becomes violet. 4-Cyano-1-methyldihydroquinoline is the most stable of these derivatives. On treating the ethereal extract (not the crystallised substance) with an alcoholic solution of picric acid, a red coloration is produced, and quinoline methyl picrate, m. p. $164-165^\circ$, is precipitated. From the mother liquor a substance was isolated in small, bright yellow needles, m. p. $209-210^\circ$. The cyanodihydroquinolines oxidise spontaneously in the air to form black products, from which pure substances could not be isolated. Attempts to effect the oxidation in alcoholic solution in presence of alkali, or by means of hypobromic acid, hydrogen peroxide, or silver oxide, led to similar results. The cyanoquinolones are prepared by oxidising with air or oxygen in alcoholic solution in the presence of platinised asbestos. 4-Cyano-1-methyl-2-quinolone is a stable substance, forming white, silky needles, m. p. $165-166^\circ$. 4-Cyano-1-ethyl-2-quinolone forms pale orange, glistening needles, m. p. 152° . It can also be prepared directly from quinoline ethiodide by dissolving it in methyl alcohol, and treating the boiling solution with potassium cyanide solution while a current of air is driven through the liquid. 4-Cyano-1:6-dimethyl-2-quinolone crystallises in small needles, m. p. $197-198^\circ$. 4-Cyano-1:8-dimethyl-2-quinolone forms small laminae, m. p. 180° . Hydrolysis of the cyanoquinolones with alkalis, or, preferably, with acids, yields the 2-quinolone-4-carboxylic acids of Claus, Roser, and Decker. This proves the constitution of the cyanoquinolones. 1-Methyl-2-quinolone-4-carboxylic acid was found to have m. p.

242—243°. The *sodium* and *silver* salts were prepared. 1-Ethyl-2-quinolone-4-carboxylic acid was found to have m. p. 202°. The m. p. differ from those previously given for these two compounds. 1:6-Dimethyl-2-quinolone-4-carboxylic acid crystallises in small, bright yellow needles, and has m. p. 287—290°. The distillation of the alkylquinolonecarboxylic acids in a current of hydrogen or carbon dioxide yields the corresponding alkylquinolones. R. V. S.

Reactions of 2:3:3:5-Tetramethylindolenine. GIUSEPPE PLANCHER and ORESTE CARRASCO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 274—278).—This base prepared from methyl isopropyl ketone *p*-tolylhydrazine is, according to Kanschegg (Abstr., 1905, i, 924; 1906, i, 452), 3:3:5-trimethyl-2-methyleneindoline, and forms acetyl and benzoyl derivatives, whilst with nitrous acid it forms a product which gives the reactions of a nitrosoamine. The authors find, however, that the latter compound is, in reality, an oxime (compare Abstr., 1898, i, 536; 1899, i, 543).

The action of benzoyl chloride on 2:3:3:5-tetramethylindolenine in presence of sodium hydroxide yields: (1) a *benzoyl* derivative, $C_{19}H_{21}O_2N$, which forms colourless prisms, m. p. 107°, and (2) a small proportion of a *compound*, $C_{19}H_{19}ON$, which separates in needles, m. p. 158—160°, and is to be investigated later.

The *oxime*, $C_{12}H_{14}ON_2$, obtained by the action of nitrous acid on 2:3:3:5-tetramethylindolenine, forms yellow, acicular crystals, m. p. 214°, and gives no trace of Liebermann's nitrosoamine reaction when pure. The *acetyl* derivative of the oxime, $C_{14}H_{16}O_2N_2$, forms colourless prisms, m. p. 129—130°.

3:3:5-Trimethylindolenine-2-formonitrile, $C_{12}H_{12}N_2$, prepared by the vigorous action of acetic anhydride on either the oxime or its acetyl derivative, forms colourless, rhombic plates, m. p. 50—51°, b. p. 144—145°/13 mm. When hydrolysed with alcoholic potassium hydroxide, this nitrile yields two products: (1) a small proportion of the corresponding *indolinone* (?), $C_{11}H_{13}ON$, which crystallises in minute needles, m. p. 81—82°, having the odour of limonene, and (2) an isomeric *compound*, $C_{11}H_{13}ON$, which forms colourless and almost odourless prisms, m. p. 146—147°, and does not give Brunner's indolinone reaction with sulphuric acid and solid dichromate.

3:3:5-Trimethylindolenine-2-formamidoxime, $C_{12}H_{12}N_2 \cdot NH_2 \cdot OH$, prepared by the action of hydroxylamine on the formonitrile, forms colourless crystals, m. p. 172—173°. T. H. P.

Condensation of Esters of Acetonedicarboxylic Acid with Aldehydes by means of Ammonia and Amines. V. PAVEL PETRENKO-KRITSCHENKO (*Ber.*, 1909, 42, 3683—3694. Compare this vol., i, 605).—The product of the reaction between acetonedicarboxylic ester and an aldehyde in the presence of ammonia or an amine has been shown previously to be a substituted piperidone. The correctness of this constitution is proved by the fact that ethyl 2:6-diphenylpiperidone-3:5-dicarboxylate yields by oxidation an ester, m. p. 195° (Abstr., 1908, i, 564) which is identical with ethyl 2:6-diphenyl-

pyridone-3:5-dicarboxylate, obtained by the action of alcoholic ammonia on Pechmann's ethyl diphenylpyrinedicarboxylate (Abstr., 1891, 673).

[With A. LILIENBLÜM.]—Ethyl 2:6-diphenyl-1-methylpiperidone-3:5-dicarboxylate can form, in addition to the ordinary insoluble salts (Abstr., 1907, i, 708), abnormal soluble salts, which are obtained as follows. An alcoholic solution of the base is treated with a few drops of hydrochloric acid, filtered, diluted with water until a turbidity is produced, again filtered, and the filtrate is treated with a platinumchloride or a nitrate, whereby a sparingly soluble *platinichloride*, $(C_{24}H_{27}O_5N)_2 \cdot H_2PtCl_6$, or *nitrate*, $C_{24}H_{27}O_5N \cdot HNO_3$, m. p. 137—139°, is obtained.

The benzene mother liquor, from which the hydrochloride of the preceding base has been separated (*loc. cit.*), yields after a few days a second *hydrochloride*, m. p. 153°, from which ammonium hydroxide liberates a *base*, $C_{24}H_{27}O_5N$, m. p. 138°, which is stereoisomeric with ethyl 2:6-diphenyl-1-methylpiperidone-3:5-dicarboxylate. The new base, m. p. 138°, forms abnormal soluble salts and a sparingly soluble *nitrite*, $C_{24}H_{27}O_5N \cdot HNO_2$, m. p. 108° (decomp.), which responds to Liebermann's reaction and regenerates the unchanged base by treatment with ammonium hydroxide. The hydrochlorides of both bases are oxidised by chromic and acetic acids to ethyl 2:6-diphenyl-1-methylpyridone-3:5-dicarboxylate (this vol., i, 605). The acid obtained by the hydrolysis of this ester decomposes at its m. p., 270°, yielding 2:6-diphenyl-1-methylpyridone, $NMe \begin{smallmatrix} \text{CPh:CH} \\ \text{CPh:CH} \end{smallmatrix} CO$, m. p. 176°, which forms a *hydrochloride*, m. p. 245° (decomp.), and a *platinichloride*, m. p. 242—244° (decomp.).

[With Z. HIRSCHBERG.]—The product obtained by the condensation of ethyl acetonedicarboxylate, benzaldehyde, and ethylamine depends on the nature of the solvent. In alcoholic solution, using benzyldieneethylamine instead of its two components, the main product is a *substance*, $C_{25}H_{32}O_{10}$, m. p. 121—123°, which is apparently identical with Knoevenagel's ethyl benzyldienebisacetonedicarboxylate (Abstr., 1896, i, 210), *ethyl 2:6-diphenyl-1-ethylpiperidone-3:5-dicarboxylate*, $C_{25}H_{29}O_5N$, m. p. 92° (*hydrochloride*, m. p. 179—181°), being only a by-product. When, however, benzene is used as the solvent, an isomeric *ethyl 2:6-diphenyl-1-ethylpiperidone-3:5-dicarboxylate*, m. p. 137—140° (*hydrochloride*, m. p. 152—153°; *nitrite*, m. p. 118—120°; *platinichloride*), is the sole product. [With B. MALACHOFF.]—The stereoisomerism of the two compounds is proved by the oxidation of their hydrochlorides by chromic and acetic acids to *ethyl 2:6-diphenyl-1-ethylpyridone-3:5-dicarboxylate*, $C_{25}H_{25}O_5N$, m. p. 189—190°, which by hydrolysis with alcoholic potassium hydroxide and subsequent acidification yields the *acid*, $C_{21}H_{17}O_5N$, m. p. 248—250° (decomp.). The acid forms a *silver salt*, $C_{21}H_{15}O_5N \cdot Ag_2$, yields the preceding ethyl ester, and loses carbon dioxide at its m. p., forming 2:6-diphenyl-1-ethylpyridone, $C_{19}H_{17}ON$, m. p. 105—110°.

Mayer's ethyl 1:2:6-triphenylpiperidone-3:5-dicarboxylate is stable to hydrogen chloride in benzene solution, and yields the *hydrochloride*, $C_{29}H_{29}O_5N \cdot HCl$, m. p. 145° (decomp.), whereas 1:2:6-

triphenylpiperidone is decomposed under the same treatment, yielding aniline and distyryl ketone.

The mother liquor, from which Mayer's triphenylpiperidone is separated, contains a yellow *isomeride*, m. p. 132°, which also yields aniline and distyryl ketone by treatment with hydrogen chloride, and probably has the constitution: $\text{NHPh} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH} \cdot \text{CHPh}$.

C. S.

Carbazole Derivatives. PAUL ZIERSCH (*Ber.*, 1909, 42, 3797—3800).—Carbazole, in suspension in glacial acetic acid at 80°, is easily nitrated by nitric acid (D 1.38). The main product is the 3-nitrocarbazole, m. p. 205°, described by Mazzara and by Votocka, but 1-nitrocarbazole is also formed, crystallising in yellow needles, m. p. 164°. Either nitro-compound is reduced by warming with alcoholic potassium hydroxide and subsequent addition of sodium hyposulphite. 3-Aminocarbazole forms colourless needles, m. p. 240°; 1-aminocarbazole crystallises in snow-white needles, m. p. 230° (decomp.), which are very sensitive to light. The *hydrochloride* and *sulphate* are colourless; the *picrate* forms yellow needles, m. p. 180°; the *benzoate* has m. p. 225°. The *dibenzoate* of diaminocarbazole forms colourless plates, m. p. 270°, which are not sensitive to light.

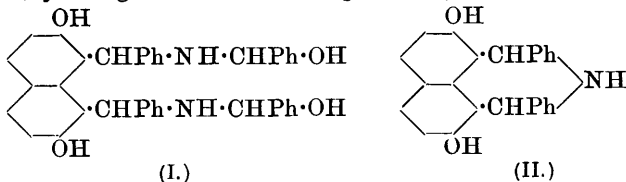
Dichlorodinitrocarbazole, produced by the action of chlorine gas on a suspension of dinitrocarbazole in acetic acid, forms yellow needles, m. p. 285°. When reduced in the manner above described, *dichlorodiaminocarbazole* is obtained in yellow flakes; the *sulphate* forms colourless needles, m. p. 320° (decomp.). By the action of fuming nitric acid on carbazole, a tetranitrocarbazole, m. p. 285°, crystallising in bright yellow, rhombic plates, is obtained. This is identical with one of the four products obtained by Ciamician and Silber by the action of fuming nitric acid on acetylcarbazole (*Abstr.*, 1882, 1103). *Tetra-aminocarbazole* was obtained in yellow flakes, which rapidly became black and decomposed. All these aminocarbazole derivatives when diazotised and coupled with naphtholsulphonic acids yield reddish-violet wool dyes.

E. F. A.

Condensation of 2:7-Dihydroxynaphthalene with Aromatic Aldehydes and Ammonia. Synthesis of Substituted Acenaphthylenes. ERICH BESCHKE [with H. RÖLLE and S. STRUM] (*Annalen*, 1909, 369, 157—183).—The condensation of 2:7-dihydroxynaphthalene with ammonia and aromatic aldehydes, particularly benzaldehyde, *p*-methoxybenzaldehyde, *o*-methoxybenzaldehyde, *o*-hydroxybenzaldehyde, *m*-hydroxybenzaldehyde, and furfuraldehyde, has been investigated with the object of obtaining information on the relative reactivity of the two nuclei in 2:7-dihydroxynaphthalene in a reaction characteristic of naphthols (compare Betti, *Abstr.*, 1903, i, 510; 1904, i, 581).

In this particular case it is found that the two nuclei of the naphthalene molecule react in the same manner; the hydrogen atoms in positions 1 and 8 are replaced by organic residues, with the formation of substances which decompose quite readily with ring formation in the peri-position (compare Sachs, this vol., i, 426). For

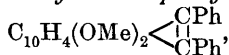
example, 2:7-dihydroxynaphthalene reacts with ammonia and benzaldehyde, yielding the condensation product (I), which, when boiled



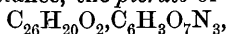
with alcohol, water, or aqueous alkali, yields 2:7-dihydroxynaphthylene-1:8-dibenzylideneimine (II) with elimination of 1 mol. of ammonia and 2 mols. of benzaldehyde. The cyclic base is converted by excess of methyl sulphate into the dimethylammonium compound, $C_{10}H_4(OMe)_2 \begin{smallmatrix} \text{CHPh} \\ \diagup \quad \diagdown \\ \text{CPh} \end{smallmatrix} NMe_2 \cdot SO_4Me$, which, when boiled with an aqueous solution of sodium hydroxide, yields 10-dimethylamino-2:7-dimethoxy-9:10-diphenylacenaphthene, $C_{10}H_4(OMe)_2 \begin{smallmatrix} \text{CHPh} \\ \diagup \quad \diagdown \\ \text{CPh} \cdot NMe_2 \end{smallmatrix}$ (compare Graebe, Abstr., 1903, i, 408).

Substituted acenaphthylenes are obtained from the aminoacenaphthenes with the greatest of ease; in order to eliminate, quantitatively, the nitrogen complex as dimethylamine, it is only necessary to heat the tertiary base at its m. p., or boil it for a short time with an acid, preferably glacial acetic acid.

The condensation product of 2:7-dihydroxynaphthalene with benzaldehyde and ammonia, $C_{38}H_{34}O_4N_2$, crystallises in colourless, transparent plates, m. p. 125°. 2:7-Dihydroxynaphthylene-1:8-dibenzylideneimine, $C_{24}H_{10}O_2N$, crystallises with $1\frac{1}{2}Et \cdot OH$ in stout, reddish-brown prisms, m. p. 126—127°, and from aqueous acetone in long, yellow needles, m. p. 102—104°, which contain water and acetone in unknown proportions; the base with $\frac{1}{2}H_2O$ or $\frac{1}{2}Et \cdot OH$ has m. p. 152—153°; the hydrobromide, $C_{24}H_{19}O_2N \cdot HBr$, with $1H_2O$ forms glistening, golden-yellow crystals, m. p. 228° (decomp.), and with $1Et \cdot OH$, pale yellow needles, m. p. 281°; the hydrochloride ($1H_2O$) crystallises in golden-yellow prisms, m. p. 227—228°; the sulphate, $(C_{24}H_{19}O_2N)_2 \cdot H_2SO_4 \cdot 2H_2O$, decomposes without melting; the triacetyl derivative, $C_{30}H_{25}O_5N$, crystallises in hexagonal plates, m. p. 241—242°; the tribenzoyl derivative, $C_{45}H_{31}O_5N$, crystallises in rectangular prisms, m. p. 213°. The substance, $C_{29}H_{31}O_6NS$, obtained by the action of methyl sulphate on 2:7-dihydroxynaphthylene-1:8-dibenzylideneimine, crystallises in colourless needles, m. p. 234—235°, and when boiled with a 40% aqueous solution of sodium hydroxide yields 10-dimethylamino-2:7-dimethoxy-9:10-diphenylacenaphthene, $C_{28}H_{27}O_2N$, which crystallises in colourless needles, m. p. 173° (decomp.). The latter substance is converted by hot glacial acetic acid into 2:7-dimethoxy-9:10-diphenylacenaphthylene,



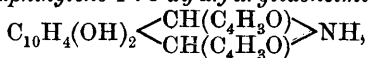
a yellow, crystalline substance, the picrate of which,



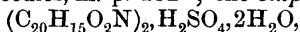
crystallises in reddish-brown, glistening needles with a metallic lustre, m. p. 166°.

The following compounds are prepared by methods similar to those already described.

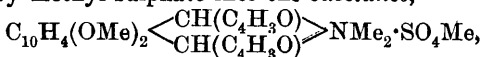
2 : 7-Dihydroxynaphthylene-1 : 8-difurfurylideneimine,



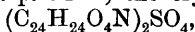
has m. p. 198°; it crystallises with 1Et·OH in colourless prisms, m. p. 198°; the *hydrochloride* (1H₂O) crystallises in golden-yellow prisms, and turns black at 220°, m. p. 228°; the *hydrobromide* (1H₂O) forms golden-yellow needles, m. p. 232°; the *sulphate*,



when heated turns black, m. p. 195—196°; the *triacetyl* derivative, C₂₆H₂₁O₇N, crystallises in needles, m. p. 228°; the *tribenzoyl* derivative, C₄₁H₂₇O₇N, crystallises in rectangular prisms, m. p. 211°. The base is converted by methyl sulphate into the *substance*,



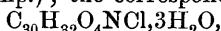
which crystallises in colourless needles, m. p. 215°; the corresponding *chloride*, C₂₄H₂₄O₄NCl, forms colourless needles, m. p. 205—206°; the *aurichloride* forms pale yellow crystals, m. p. 158—159°; the *platini-chloride* is red, and has m. p. 211°; the crystalline *sulphate*,



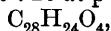
has m. p. 202—203°. 2 : 7-Dimethoxy-9 : 10-difurylacenaphthylene,

C₁₀H₄(OMe)₂ $\left\langle \begin{array}{c} \text{C}_4\text{H}_3\text{O} \\ \text{C}_4\text{H}_3\text{O} \end{array} \right\rangle$, crystallises in dark red leaflets, m. p. 131°; the *picrate*, C₂₂H₁₆O₄, C₆H₃O₇N₃, forms dark reddish-brown needles with a metallic lustre, m. p. 195°.

2 : 7-Dihydroxy-1 : 8-di-p-methoxybenzylideneimine, C₂₆H₂₃O₄N, crystallises in slender, white needles, m. p. 206—207°; the *hydrochloride* has m. p. 258°; the *hydrobromide* (1H₂O), golden-yellow prisms, has m. p. 265°; the *triacetyl* derivative, C₃₂H₂₉O₇N, crystallises with 1Et·OH, m. p. 213—214°. The *substance*, C₃₁H₃₅O₈NS, obtained by treating the base with methyl sulphate, crystallises in slender, colourless needles, m. p. 232° (decomp.); the corresponding *chloride*,



forms colourless rhombohedra, m. p. 214—215°; the *aurichloride*, C₃₀H₃₂O₄NAuCl₄, is a pale yellow powder, which decomposes at 120—125°. 2 : 7-Dimethoxy-9 : 10-di-p-anisylacenaphthylene,



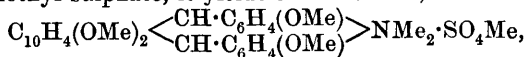
forms glistening, brick-red needles, m. p. 192°; the *picrate* crystallises in dark brown needles, m. p. 184°.

2 : 7-Dihydroxy-1 : 8-di-o-methoxybenzylideneimine, C₂₆H₂₃O₄N, crystallises with 1Et·OH, m. p. 266—267°; the *triacetyl* derivative has m. p. 167°. The *substance*, C₃₁H₃₅O₈NS, crystallises in small, colourless needles, m. p. 268—269°. 2 : 7-Dimethoxy-9 : 10-di-o-anisylacenaphthylene, C₂₈H₂₄O₄, crystallises in glistening, yellow prisms, m. p. 178—179°.

2 : 7-Dihydroxy-1 : 8-di-o-hydroxybenzylideneimine, C₂₄H₁₉O₄N, crystallises with 3Et·OH in colourless rhombohedra, m. p. 265—266°; the *hydrochloride* has m. p. 314—315°; the *hydrobromide* (1H₂O) forms

violet needles, m. p. 307—308°; the *penta-acetyl* derivative has m. p. 219—220°.

2 : 7-*Dihydroxy-1 : 8-di-m-hydroxybenzylideneimine*, $C_{24}H_{19}O_4N$, crystallises in greyish-white needles, m. p. 195—198°; when treated with excess of methyl sulphate, it yields the *substance*,



which is converted by aqueous sodium hydroxide into 10-*dimethyl-amino-2 : 7-dimethoxy-9 : 10-di-m-anisylacenaphthene*, $C_{30}H_{31}O_4N$, crystallising in stellate aggregates of colourless needles, m. p. 164—165°; at this temperature it decomposes into dimethylamine and 2 : 7-*dimethoxy-9 : 10-di-m-anisylacenaphthylene*, $C_{28}H_{24}O_4$, which crystallises in yellowish-brown, monoclinic prisms, m. p. 146—147°. W. H. G.

[Preparation of Benzoyl-*p*-phenylenediaminesulphonic Acid.] BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 210471).—*p*-Phenylenediaminesulphonic acid reacts readily with benzoyl or the isomeric nitrobenzoyl chlorides in alkaline solution. The products are sparingly soluble powders; they form insoluble diazonium compounds, which yield dyes when combined with naphtholsulphonic acids.

F. M. G. M.

[Preparation of Acyl-3-nitro-*p*-phenylenediamines.] FARBEN-FABRIKEN VORM. F. BAYER & Co. (D.R.P. 211966).—When mono- or di-acyl derivatives of *p*-phenylenediamine (such as formyl, benzoyl, or oxalyl derivatives) are nitrated, the hitherto unknown *acyl-3-nitro-p-phenylenediamines* are produced; these compounds are utilised in the preparation of azo-dyes.

F. M. G. M.

New Phototropic Substances. MAURICE PADOA and F. GRAZIANI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 269—273. Compare this vol., i, 676).—Further experiments have been made with the α - and β -naphthylhydrazones and the *p*-tolylhydrazones of a number of aldehydes, the only general result obtained being that all the β -naphthylhydrazones are phototropic, but none of the α -naphthylhydrazones. Of fifteen hydrazones examined, eight are more or less phototropic, decolorisation in the dark at the ordinary temperature requiring from a few hours to a few days; the more marked the phototropy, the more rapid is the decolorisation. On heating, decolorisation occurs at temperatures varying from 80° to 145°.

Benzaldehyde- α -naphthylhydrazone is non-phototropic.

Anisaldehyde- α -naphthylhydrazone, $OMe \cdot C_6H_4 \cdot CH : N_2H \cdot C_{10}H_7$, forms yellow needles, m. p. 176°, and is not phototropic.

Cuminaldehyde- α -naphthylhydrazone, $CHMe_2 \cdot C_6H_4 \cdot CH : N_2H \cdot C_{10}H_7$, forms aggregates of yellow needles, m. p. 159°, and is not phototropic.

Cinnamaldehyde- α -naphthylhydrazone separates as a yellow, crystalline powder, m. p. 165°, and is not phototropic.

Benzaldehyde- β -naphthylhydrazone, when exposed to sunlight, becomes pale rose-coloured in two to three minutes; decolorisation takes place either on heating at 120° or after four to five days in the dark.

Anisaldehyde- β -naphthylhydrazone, m. p. 176° (Rothenfusser, Abstr., 1908, i, 52, gave 187°), is distinctly phototropic.

Cuminaldehyde- β -naphthylhydrazone, $\text{CHMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N}_2\text{H} \cdot \text{C}_{10}\text{H}_7$, separates in white leaflets, m. p. 184° , and is phototropic.

Cinnamaldehyde- β -naphthylhydrazone separates as a yellow powder, m. p. 193° (Rothenfusser, *loc. cit.*, gave 188°), and is intensely phototropic.

Benzaldehyde- p -tolylhydrazone forms pale yellow, silky needles, m. p. 125° (Reutt and Pawlewski, Abstr., 1904, i, 99, gave 114° , but Schlenk, Abstr., 1908, i, 737, gave 125°), and is coloured red by exposure to sunlight for four to five minutes.

Anisaldehyde- p -tolylhydrazone, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4\text{Me}$, forms lemon-yellow, elongated scales, m. p. 136° , and is not phototropic.

Cinnamaldehyde- p -tolylhydrazone, $\text{CHPh} \cdot \text{CH} \cdot \text{CH} \cdot \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4\text{Me}$, forms voluminous, canary-yellow needles, m. p. 155° , and is intensely phototropic.

Cuminaldehyde- p -tolylhydrazone, $\text{CHMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4\text{Me}$, forms pale yellow, voluminous needles, m. p. 137° , and is strongly phototropic; decoloration occurs on heating to about 80° .

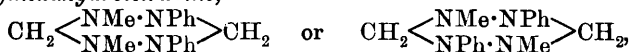
Piperonaldehyde- p -tolylhydrazone, $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} \cdot \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4\text{Me}$, forms white needles, m. p. 123° , and is intensely phototropic; the colour formed disappears at 110 — 115° .

p -Tolualdehyde- p -tolylhydrazone, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH} \cdot \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4\text{Me}$, forms white scales, m. p. 151° , and is not phototropic.

Vanillin- p -tolylhydrazone, $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CH} \cdot \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4\text{Me}$, crystallises in slender, white needles, m. p. 127° , and is non-phototropic.

T. H. P.

Hydrazophenylmethyl [*s*-Phenylmethylhydrazine] from Phenylpyrazole. LUDWIG KNORR and ARNO WEIDEL (*Ber.*, 1909, 42, 3523—3529. Compare Knorr and Köhler, Abstr., 1906, i, 817).—To avoid oxidation during the preparation of *s*-secondary aromatic hydrazines, the 50% potassium hydroxide solution is added slowly to the aqueous solution of 1-phenylpyrazole, through which a current of steam and nitrogen is passed. *s*-Phenylmethylhydrazine, purified from the oxalate, and distilled in a current of nitrogen, has b. p. 110 — $112^{\circ}/12$ — 15 mm., 229 — $230^{\circ}/738$ mm. (compare Abstr., 1906, i, 893), D_{15}^{15} 1.04, n_D^{15} 1.5755, and is very readily oxidised by air to benzeneazomethane. When shaken with formalin and water, diphenyl-dimethylhexahydrodrotetrazine,



is immediately precipitated as a quickly crystallising oil; it crystallises in pearly leaflets from alcohol, m. p. 148° , and this reaction can be used as a test for either the hydrazine or formaldehyde.

The following salts of *s*-phenylmethylhydrazine are described: hydrochloride, m. p. 160 — 161° ; sulphate; oxalate, m. p. 148° ; picrolonate.

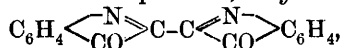
Diphenylmethylthiosemicarbazide, $\text{C}_{14}\text{H}_{15}\text{N}_3\text{S}$, obtained from the hydrazine and phenylthiocarbimide, has m. p. 175° . *s*-Phenylmethyl-

hydrazine picrazide, from picryl chloride and base in alcoholic solution, forms dark red needles, m. p. 172°.

s-Phenylethylhydrazine (compare Fischer and Ehrhardt, Abstr., 1880, 243) has b. p. 110°/14 mm., 235—236°/741 mm., n_D^{25} 1.004, n_D^{15} 1.55; the *hydrochloride* has m. p. 164°; the *oxalate*, 167—168°; the *benzoyl* derivative, $\text{COPh}\cdot\text{NEt}\cdot\text{NHPh}$, m. p. 100°. *Diphenylethylthiosemicarbazide*, $\text{C}_{15}\text{H}_{17}\text{N}_3\text{S}$, has m. p. 163—164°. *Diphenyldiethylhexahydrotetrazine*, $\text{C}_{18}\text{H}_{24}\text{N}_4$, has m. p. 123°. W. R.

Dehydroindigotin, a New Oxidation Product of Indigotin.

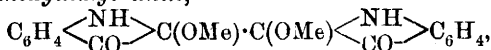
I. LUDWIG KALB (*Ber.*, 1909, 42, 3642—3652. Compare Marchlewski and Radcliffe, Abstr., 1899, i, 74).—When a suspension of very finely-powdered indigotin, lead peroxide, and anhydrous calcium chloride in gently boiling benzene is treated carefully with glacial acetic acid, and, after five minutes, the solution is filtered and concentrated under diminished pressure, *dehydroindigotin*,



is obtained in 60.6% yield. It crystallises in dark yellowish-red, hexagonal plates, dissolves more or less readily in indifferent solvents, and shows a great tendency to regenerate indigotin; this change occurring at 195° [the substance has m. p. 210—215° (decomp.)], or by heating in high-boiling solvents, or by treatment with acids, alkalis, boiling water, stannous chloride, acidified potassium iodide, quinol, phenylhydrazine, and indigo-white. The colour change produced by the reduction of yellow dehydroindigotin to dark blue indigotin is explained by the fact that the process of reduction converts a part of a chromophoric group into an auxochromic group, resulting in a deepening of the colour in accordance with Scholl's generalisation (Abstr., 1904, i, 109; 1908, i, 696). When dehydroindigotin, dissolved in an indifferent solvent, is treated with an anhydrous acid, "salts" are produced; in this way a pale yellow diacetate, a yellow *dibenzoate*, $\text{C}_{16}\text{H}_8\text{O}_2\text{N}_2\cdot 2\text{Ph}\cdot\text{CO}_2\text{H}$, and a yellowish-green *dihydrochloride*, $\text{C}_{16}\text{H}_8\text{O}_2\text{N}_2\cdot 2\text{HCl}$, have been obtained. The diacetate is identical with oxyacetoinidigotin, obtained by O'Neill and formulated as diacetoxindigotin by Marchlewski and Radcliffe (*loc. cit.*). The author inclines to the belief, however, that the acid is attached to the nitrogen atom in these "salts."

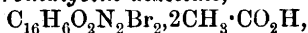
Dehydroindigotin can also be obtained by decomposing a hot mixture of benzene, pyridine, and the diacetate (conveniently obtained by O'Neill's method), or by treating a suspension of indigotin and finely-powdered calcium hydroxide in chloroform with bromine.

2:2'-Dimethoxyindigo-white,



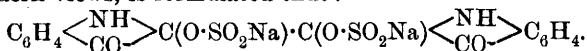
is obtained by the addition of a trace of sodium methoxide to a suspension of dehydroindigotin in methyl alcohol. It crystallises in canary-yellow, hexagonal plates, decomposes at 200°, is stable in hot water, and cannot be reconverted into dehydroindigotin.

5:5'-Dibromodehydroindigotin diacetate,



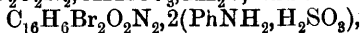
is obtained by the action of potassium permanganate on a suspension of 5:5'-dibromoindigotin in glacial acetic acid. It crystallises in insoluble, yellowish-green prisms, and is decomposed by a boiling mixture of benzene and pyridine, yielding 5:5'-dibromodehydroindigotin m. p. 270° (decomp.), which crystallises in dark reddish-brown leaflets and is stable in hot water. C. S.

Dehydroindigotin. II. The Hydrogen Sulphite Compounds of Dehydroindigotin and a New Process of Indigo-dyeing. LUDWIG KALB (*Ber.*, 1909, 42, 3653—3664. Compare preceding abstract).—The most pronounced property of dehydroindigotin is its capability of forming sulphites. The sodium hydrogen sulphite derivative, $C_{16}H_8O_2N_2 \cdot 2NaHSO_3 \cdot 2H_2O$, is obtained by shaking powdered dehydroindigotin with a solution of sodium hydrogen sulphite, 38—40° Bé., or by boiling an aqueous alcoholic solution of dehydroindigotin diacetate and sodium sulphite. It separates from water in canary-yellow crystals, has an intensely sweet taste, and, in accordance with modern views, is formulated thus:



From its concentrated aqueous solution, the corresponding potassium derivative, $C_{16}H_8O_2N_2 \cdot 2KHSO_3 \cdot 2H_2O$, is obtained by the addition of potassium chloride; it forms yellow crystals, and is less soluble than the sodium compound. The aniline hydrogen sulphite compound, $C_{16}H_8O_2N_2 \cdot 2(PhNH_2, H_2SO_3)$, is almost insoluble.

The aqueous solution of the sodium compound is decomposed even by sodium carbonate or hydrogen carbonate; sodium hydroxide precipitates indigotin, whilst the solution contains anthranilic acid. Sodium hyposulphite and sodium carbonate, with free access of air or boiling hydriodic acid, convert the sodium compound quantitatively into indigotin. The sodium hydrogen sulphite derivative of 5:5'-dibromodehydroindigotin, $C_{16}H_6Br_2O_2N_2 \cdot 2NaHSO_3 \cdot 2H_2O$, is prepared by boiling an aqueous alcoholic solution of sodium sulphite and 5:5'-dibromodehydroindigotin diacetate, or, better, by the addition of bromine, followed by sodium hydrogen carbonate, to a cold aqueous solution of the sodium hydrogen sulphite derivative of dehydroindigotin. In the latter case, the orientation of the halogen atoms is proved by oxidation by potassium dichromate and dilute sulphuric acid, whereby a 60—70% yield of 5-bromoisatin is obtained. The corresponding potassium derivative, $C_{16}H_6Br_2O_2N_2 \cdot 2KHSO_3 \cdot 2H_2O$, and aniline derivative,



are described. By using twice the quantity of bromine in the preceding preparation, the sodium hydrogen sulphite derivative of 5:7:5':7'-tetrabromodehydroindigotin is obtained; it is oxidised by potassium dichromate and sulphuric acid to 5:7-dibromoisatin. The corresponding potassium and aniline derivatives are mentioned. When a solution of the sodium hydrogen sulphite derivative of tetrabromodehydroindigotin is treated with fuming hydrochloric acid below 0°, the free acid, $C_{16}H_4Br_4O_2N_2 \cdot 2H_2SO_3 \cdot 14H_2O$, is obtained in yellow, crystalline plates. The sodium hydrogen sulphite derivative of 5:7:5':7'-tetrachlorodehydroindigotin and the corresponding potassium and aniline

derivatives are obtained by methods analogous to the preceding; the two former contain $5\text{H}_2\text{O}$; the last is anhydrous.

The alkali hydrogen sulphite compounds of dehydroindigotin and its halogenated derivatives are decomposed by boiling dilute hydrochloric acid. The derivatives of the tetrahalogenated compounds are converted almost quantitatively into the tetrahalogenated indigotins, whilst the alkali hydrogen sulphite compounds of dehydroindigotin and of dibromodehydroindigotin yield about 50% of indigotin and dibromoindigotin respectively, the remainder of the materials remaining in the solution as isatin and bromoisatin.

These alkali hydrogen sulphite compounds are sensitive to light. That of tetrabromodehydroindigotin, in particular, is so sensitive that it must be prepared in the dark; paper, soaked in its solution, dried, exposed to sunlight under a negative, and washed, reveals a positive picture.

Silk and cotton, but not wool, can be dyed by immersing the fabric in a solution of the sodium hydrogen sulphite derivative of dehydroindigotin, drying, and treating with dilute mineral acid, alkali hydroxide, or alkali carbonate at $80-100^\circ$, whereby indigotin is produced.

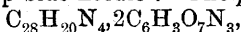
C. S.

Indigotin. I. Action of Primary Arylamines on Indigotin. EUGÈNE GRANDMOUGIN and ED. DESSOULAVY (*Ber.*, 1909, 42, 3636—3641).—When indigotin is boiled for some time with a primary arylamine in the presence of boric acid, crystalline products are formed. With aniline, the reaction proceeds according to the equation: $\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2 + 2\text{C}_6\text{H}_5\cdot\text{NH}_2 = \text{C}_{28}\text{H}_{20}\text{N}_4 + 2\text{H}_2\text{O}$, and the product is regarded as a dianilide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{C}(\text{:NPh}) \\ \diagdown \text{NH} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \diagup \text{C}(\text{:NPh}) \\ \diagdown \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$.

The compounds have a deep indigo-blue colour, and are stable towards alkalis. Acids transform them into isomeric, colourless bases, which yield salts of a deep yellow colour. The colourless bases appear to be quindoline derivatives, as they can be decomposed, yielding quindoline (Fichter and Boehringer, *Abstr.*, 1907, i, 92).

The original condensation products, when oxidised with chromic acid, yield isatin, but with nitric acid yield deep red, crystalline compounds.

Indigotin dianilide, $\text{C}_{28}\text{H}_{20}\text{N}_4$, is obtained by heating together indigotin (1 part), aniline (5 parts), and boric acid (1 part) until when a portion is extracted with alcohol, then dissolved in sulphuric acid, an orange-yellow solution is given. It is usually accompanied by a considerable amount of its leuco-derivative. Alcohol is added, and the solution boiled for half an hour, when the condensation product separates in a crystalline form; it may be recrystallised from pyridine or xylene, and forms deep blue needles. The *picrate*,



crystallises in green needles. *Leucoindigotin dianilide*, $\text{C}_{28}\text{H}_{22}\text{N}_4$, is less soluble in xylene, but more soluble in pyridine, than the anilide, and forms colourless needles.

Indigotin di-p-toluidide, $\text{C}_{30}\text{H}_{24}\text{N}_4$, crystallises from xylene in blue needles. Similar condensation products have been obtained with *o*- and *m*-toluidines, *m*-xylylidine, and *adj*-xylylidine.

7:7'-Dimethylindigotin also condenses with primary arylamines, and the products yield *o*-methylisatin (Bauer, Abstr., 1907, i, 603) when oxidised.

J. J. S.

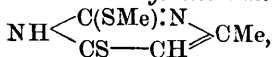
Action of Primary Amines on Indigotin. EUGÈNE GRAND-
MOUGIN (*Ber.*, 1909, 42, 4218).—7:7'-Dimethylindigotin (*o*-toluene-
indigotin) (preceding abstract) may be characterised by its spectro-
scopic behaviour. It dissolves in xylene, giving violet-blue solutions,
which, for suitable concentrations, exhibit a comparatively sharp
absorption line with a band drawn out towards the right; when the
solution is diluted with xylene, the line and band disappear. In
dilute solution, the absorption line has the wave-length $\lambda = 603.8$.
Indigotin is less soluble in xylene than 7:7'-dimethylindigotin, and
the solution exhibits an absorption band having $\lambda = 591.4$. In acetic
acid the absorption bands are less sharp and closer together, λ being
615.9 for indigotin and 617.7 for the 7:7'-dimethyl derivative.

T. H. P.

**Pyrimidines. XLVII. Action of Methyl Iodide and of
Benzyl Chloride on 6-Methylthiol-4-methyl-2-pyrimidone.**
HENRY L. WHEELER and DAVID F. McFARLAND (*Amer. Chem. J.*,
1909, 42, 431—440).—It has been shown in earlier papers that, in
general, 2-thiol-6-pyrimidones on alkylation yield both 1- and 3-alkyl
derivatives. Recently, however (this vol., i, 677), it has been found
that 2-methylthiol- and 2-ethylthiol-4-methyl-6-pyrimidones yield only
the 1-alkyl derivatives. It has therefore been considered of interest
to study the alkylation of the compound having the opposite con-
figuration, namely, 6-methylthiol-4-methyl-2-pyrimidone, and in this
case it has been found that both 1- and 3-derivatives are produced.
With methyl iodide, the 1- and 3-isomerides are formed in about
equal proportions, whilst with benzyl chloride a larger amount of the
3-derivative is obtained.

6-Chloro-2-methylthiol-4-methylpyrimidine, $\text{N} \begin{smallmatrix} \text{C(SMe):N} \\ \text{CCl—CH} \end{smallmatrix} \text{CMe,}$

m. p. 39—40°, obtained by the action of a mixture of phosphoryl
chloride and phosphorus pentachloride on 2-methylthiol-4-methyl-6-
pyrimidone, forms long needles, and is converted by potassium
hydrogen sulphide into 6-thio-2-methylthiol-4-methylpyrimidine,



m. p. 214°, which crystallises in needles, and when heated above its
m. p. undergoes decomposition with formation of 2:6-dithio-4-
methyluracil. 6-Thio-4-methyluracil, $\text{NH} \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CS}\cdot\text{CH} \end{smallmatrix} \text{CMe,}$ obtained

by boiling 6-thio-2-methylthiol-4-methylpyrimidine with concentrated
hydrochloric acid, forms irregular, yellow prisms, decomposes above
250°, and reacts with methyl iodide in presence of sodium hydroxide to

form 6-methylthiol-4-methyl-2-pyrimidone, $\text{N} \begin{smallmatrix} \text{CO—NH} \\ \text{C(SMe)\cdot CH} \end{smallmatrix} \text{CMe,}$ m. p.
174—175°, which crystallises in flat, pale yellow needles. When the

latter compound was treated with benzyl chloride, a product was obtained which could not be purified, but, when heated with concentrated hydrochloric acid, yielded a mixture of 4-methyluracil and its 1- and 3-benzyl derivatives, the last-mentioned compound being obtained in the larger amount; it is therefore inferred that the 3-benzyl compound of the pyrimidone is formed in the larger proportion. By the action of methyl iodide on 6-methylthiol-4-methyl-2-pyrimidone, a mixture of the 3:4- and 1:4-dimethyl derivatives is produced. 6-Methylthiol-3:4-dimethyl-2-pyrimidone, m. p. 170—171°, crystallises in prisms, and when boiled with hydrochloric acid is converted into 3:4-dimethyluracil. The corresponding 1:4-dimethyl compound was not isolated, but was identified by its conversion into 1:4-dimethyluracil.

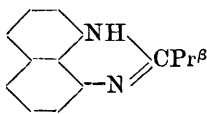
6-*o*-Nitrobenzylthiol-4-methyl-2-pyrimidone, m. p. 205°, obtained by the action of *o*-nitrobenzyl chloride on 6-thio-4-methyluracil, forms clusters of yellow, lancet-shaped crystals. 6-*m*-Dinitrophenylthiol-4-methyl-2-pyrimidone, m. p. 208°, prepared in a similar manner, crystallises in slender, yellow needles. E. G.

Cinnoline Compounds. OSCAR WIDMAN (*Ber.*, 1909, 42, 4216—4217).—A claim for priority (compare Abstr., 1884, 1022) to Stoermer and Fincke (this vol., i, 841) in the preparation of cinnoline derivatives by the diazotisation of an amino-group occupying the ortho-position to an olefinic side-chain. T. H. P.

Ring Formation in the Peri-Position in the Naphthalene Series. II. FRANZ SACHS and M. STEINER (*Ber.*, 1909, 42, 3674—3683. Compare this vol., i, 426).—2-iso-Propylperimidine (annexed formula), m. p. 87°, crystallises in yellowish-green needles, and is prepared by the interaction of 1:8-naphthylenediamine and isobutyric anhydride; the product is purified by means of the hydrochloride, $C_{14}H_{15}N_2Cl$, which decomposes above 260°; the nitrate decomposes at 240°. 2-Butylperimidine, $C_{15}H_{16}N_2$, m. p. 165°, is prepared from the diamine and valeric anhydride, and is purified by means of the hydrochloride, m. p. 252—253° (decomp. beginning at 245°). 2-Styrylperimidine, m. p. 136°, is prepared from the diamine and an alcoholic solution of cinnamoyl chloride, and 2-methylvinylperimidine, m. p. 140°, from the diamine and crotonyl chloride in benzene. The chromophoric influence of the ethylenic linking in these two compounds is manifested in the dark red colour of the former and the deep yellow colour of the latter.

2-*p*-Methoxyphenylperimidine, m. p. 205°, is prepared from 1:8-naphthylenediamine and anisoyl chloride in cold benzene, the resulting hydrochloride being treated with cold ammonium hydroxide. The yield is quantitative when 1:8-naphthylenediamine hydrochloride, suspended in benzene, is boiled with an equal molecular quantity of anisoyl chloride; the hydrochloride has m. p. 280° (decomp. beginning at 260°).

2-*o*-Nitrophenylperimidine, m. p. 177°, is obtained from *o*-nitrobenzoyl chloride in cold glacial acetic acid, and crystallises in pale red needles



Its reduction is difficult, but by means of zinc and 50% acetic acid, 2-*o*-aminophenylperimidine, m. p. 148—150°, can be obtained. 2-*m*-Nitrophenylperimidine, obtained in a similar manner, crystallises in dark red needles, decomposes at 184°, and is reduced by zinc and 50% acetic acid to 2-*m*-aminophenylperimidine, m. p. 175—180°, which crystallises in reddish-yellow prisms. 2-*p*-Nitrophenylperimidine forms copper-coloured needles, decomposes above 180°, and is reduced to 2-*p*-aminophenylperimidine, m. p. 205° (with previous decomp.), which forms an *acetyl* derivative, $C_{19}H_{15}ON_3$, decomposing above 200°. When 2-*o*-aminophenylperimidine is treated with acetic anhydride, an *anhydro*-compound, m. p. 139—141° (annexed constitution), is obtained, which separates from 30% alcohol in golden-yellow needles.

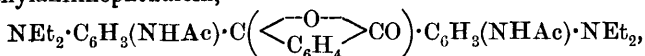
A similarly constituted azoimide, containing N in place of CMe, is obtained by diazotising 2-*o*-aminophenylperimidine in cold acetic acid; it is a dark red substance, which decomposes explosively at 140°. C. S.

Oxidation of Dimethylanilinoisatins. N. DANAILA (*Compt. rend.*, 1909, 149, 793—795. Compare Abstr., 1907, i, 976).—It has already been shown from a study of their oxidation products that phenolisatin and its derivatives are derivatives of *o*-aminobenzaurin and not of an *o*-aurin. The malachite-greens produced by the oxidation of Baeyer's dimethylanilinisatin (Abstr., 1886, 155) and of its nitro-, chloro-, bromo-, dichloro-, and dibromo-derivatives have now been studied in the same way, and the results found to confirm the theory previously advanced.

The *acetyl* derivative of dimethylanilinisatin has m. p. 179—180°. The compounds obtained by oxidising the substituted dimethylanilinisatins with lead peroxide are green, crystalline substances analogous to the malachite-greens. The results of analyses agree more closely with the formulæ of *p*-hydroxy-*o*-aminomalachite-greens, $C_{23}H_{25}ON_3$, $C_{23}H_{24}ON_3X$, $C_{23}H_{23}ON_3X_2$, than with those of the corresponding *o*-amino-compounds.

The constitution of the unsubstituted green base is considered to be best represented by the annexed formula. W. O. W.

Flaveosines. EUGÈNE GRANDMOUGIN and ARNOLD LANG (*Ber.*, 1909, 42, 4014—4019. Compare D.R.-P. 49850).—*Acetyldiethyl-m-phenylenediamine*, $NHAc \cdot C_6H_4 \cdot NEt_2$, separates from aqueous alcohol in colourless crystals, m. p. 73°, and when heated with phthalic and acetic anhydrides for five hours at 150° yields diacetyldiamino-diethylanilinephthalein,



which forms colourless, stable crystals, m. p. 246°. The condensation product, when boiled for some time with 20% hydrochloric acid, yields 2:7-tetraethyldiamino-9-phenylacridine-2'-carboxylic acid (tetra-

ethylflaveosine), $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \text{---} \text{N} \text{---} \text{C}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}) \text{---} \text{N} \text{---} \text{C}_6\text{H}_3 \cdot \text{NMe}_2$, which crystallises from alcohol in orange-yellow needles, m. p. 333°. When freshly precipitated, the dye is soluble in dilute sodium hydroxide solution, but is precipitated on the addition of acetic acid. Its solution in concentrated sulphuric acid has a pale yellow colour with a bluish-green fluorescence, and, when diluted, has a deep red colour with a pale brown fluorescence. It forms well-defined salts; the following have been prepared and analysed: *picrate*, $\text{C}_{28}\text{H}_{31}\text{O}_2\text{N}_3 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, m. p. 268°; *hydrochloride*, $\text{C}_{28}\text{H}_{31}\text{O}_2\text{N}_3 \cdot 2\text{HCl}$; *zincchloride*, $2\text{C}_{28}\text{H}_{31}\text{O}_2\text{N}_3 \cdot 2\text{HCl} \cdot \text{ZnCl}_2$;

mercurichloride, $\text{C}_{28}\text{H}_{31}\text{O}_2\text{N}_3 \cdot 2\text{HCl} \cdot 2\text{HgCl}_2$, and *platinichloride*.

The *ethyl* ester, $\text{C}_{30}\text{H}_{35}\text{O}_2\text{N}_3$, prepared with the aid of alcoholic hydrogen chloride, crystallises from a mixture of alcohol and benzene in orange-yellow needles, m. p. 248°. The *hydrochloride* forms brilliant red needles, and the *picrate*, orange-red crystals, m. p. 227°. The ester when brominated in alcoholic solution yields a *tetrabromo-derivative* which crystallises in red needles, m. p. 167°.

Tetramethylflaveosine, obtained from *acetyltrimethyl-m-phenylenediamine*, m. p. 87°, crystallises from glacial acetic acid in orange-coloured prisms, which are not molten at 360°. Its acetic acid solution imparts to silk a yellow colour with a green fluorescence. Its *tetrabromo-derivative*, $\text{C}_{24}\text{H}_{19}\text{O}_2\text{N}_3\text{Br}_4$, separates from alcohol in reddish-brown crystals, m. p. above 360°.

The *ethyl* ester of tetramethylflaveosine forms reddish-brown needles, m. p. 350°, and reacts with a nitrobenzene solution of methyl sulphate, yielding the *acridinium methyl sulphate* derivative of the ester, $\text{C}_{28}\text{H}_{33}\text{O}_6\text{N}_3\text{S}$, which crystallises from alcohol and benzene in brownish-violet needles, m. p. 268°. Most of the flaveosines and their derivatives give well-defined absorption spectra.

Phthalanil derivatives are formed in the preparation of the flaveosines, and can be used for characterising *as*-dialkylphenylenediamines.

Dimethyl-m-aminophthalanil, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \text{---} \text{C}(\text{CO})_2 \text{---} \text{C}_6\text{H}_4$, is best prepared by heating an alcoholic solution of dimethyl-*m*-phenylenediamine and phthalic anhydride with sodium acetate. It crystallises from alcohol in colourless needles, m. p. 144°. The corresponding *diethyl* compound, $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_2$, forms pale yellow needles, m. p. 120°.

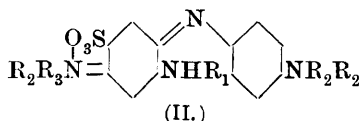
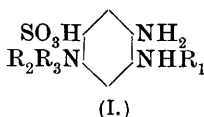
Dimethyl-p-aminophthalanil, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \text{---} \text{C}(\text{C}_6\text{H}_4\text{O}) \text{---} \text{CO}$, forms yellow needles, m. p. 255°, and the corresponding *diethyl* compound, deep yellow needles, m. p. 217°.

Diacetyltrimethyl-m-phenylenediamine, $\text{C}_{12}\text{H}_{16}\text{O}_2\text{N}_2$, separates from alcohol in colourless crystals, m. p. 69°, and does not yield a flaveosine with phthalic anhydride.

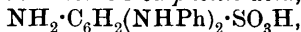
J. J. S.

Preparation of Safraninesulphonic Acids. BADISCHE ANILIN- & SODA - FABRIK (D.R.-P. 212472).—1 : 2 : 4 - Triaminobenzene-5-sulphonic acids of the type (I), where R_1 is an alkyl, arylalkyl, or

aryl group; R_2 and R_3 , hydrogen, similar or different alkyl, arylalkyl, or aryl groups, are condensed with aromatic amines, and the resulting indamines (II) oxidised to safranines.



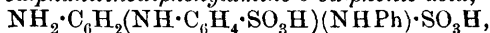
1-Amino-2:4-dianilinobenzene-5-sulphonic acid,



is prepared by heating sodium 2:4-dichloro-1-nitrobenzene-5-sulphonate with aniline at 120—150°, and subsequent reduction of the resulting nitrodianilinobenzenesulphonic acid.

Sodium 5-chloro-2-nitrodiphenylamine-4-sulphonate, yellow crystals, is formed when sodium 2:4-dichloro-1-nitrobenzene-5-sulphonate is heated with aniline in the presence of sodium acetate. This substance, after heating with 20% ammonium hydroxide, at 150°, during five hours, yields sodium 2-nitro-5-aminodiphenylamine-4-sulphonate, crystallising in glistening leaflets; on subsequent reduction, it gives 2:5-diaminodiphenylamine-4-sulphonic acid, colourless, glistening leaflets; the alkaline solution becomes violet on exposure to air, whilst the acid solution oxidises to a blue liquid.

4-Amino-3-sulphanilinodiphenylamine-6-sulphonic acid,



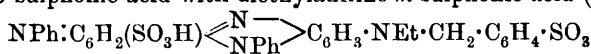
is prepared as follows: sodium *m*-dichloronitrobenzenesulphonate, sodium aniline-*p*-sulphonate, and sodium carbonate are heated together in aqueous solution during fifteen hours. The yellow, crystalline condensation product separates on cooling, and, after heating at 140—150° with aniline, yields 4-nitro-3-sulphanilinodiphenylamine-6-sulphonic acid, yellow crystals; the sparingly soluble potassium salt crystallises in slender needles; on reduction, this acid yields the amino-acid mentioned previously.

When the condensation product from *m*-dichloronitrobenzenesulphonic acid and aniline-*p*-sulphonic acid is boiled in aqueous solution with *p*-phenylenediamine and potassium carbonate, potassium 1-nitro-2-sulphanilino-4-aminoanilinobenzene-5-sulphonate (reddish-brown crystals) is produced; this yields an acetyl derivative, the potassium salt of which crystallises in red needles, and on reduction yields 1-amino-2-sulphanilino-4-acetylanilinoanilinobenzene-5-sulphonic acid, $\text{NH}_2 \cdot \text{C}_6\text{H}_2(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H})(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}) \cdot \text{SO}_3\text{H}$, colourless needles from water.

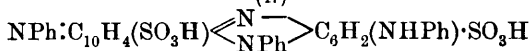
Details of preparation and properties of the dyes prepared from the following compounds are given in the patent. 1-Amino-2:4-dianilinobenzene-5-sulphonic acid condenses with ethylbenzylaniline-sulphonic acid (I) and with phenyl- α -naphthylamine-6(or 7)-sulphonic acid (II).

1-Amino-2-sulphanilino-4-acetylanilinobenzene-5-sulphonic acid with ethylbenzylanilinesulphonic acid (III) with diethylaniline-*m*-sulphonic acid (IV). 2:5-Diaminodiphenylamine-4-sulphonic acid with ethyl-

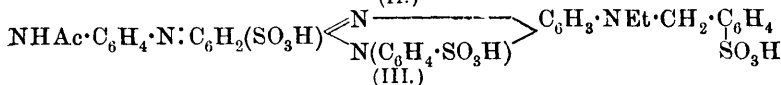
benzylanilinesulphonic acid (V). 4-Amino-3-sulphanilinodiphenylamine-6-sulphonic acid with diethylaniline-*m*-sulphonic acid (VI) :



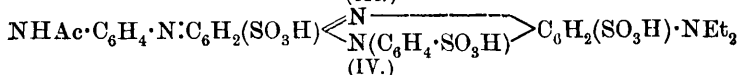
(I.)



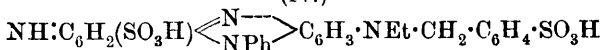
(II.)



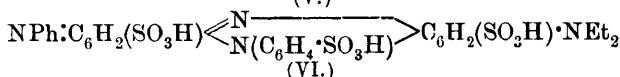
(III.)



(IV.)



(V.)



(VI.)

F. M. G. M.

Amino-derivatives of Phenylauramines and of Rheonine. EUGÈNE GRANDMOUGIN and ARNOLD LANG (*Ber.*, 1909, 42, 3631—3635).—A number of *m*-aminoauramines have been prepared in order to determine their relationship to the *rheonines* (D.R.-P. 82989).

m-Aminophenylauramine, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, obtained by heating auramine base with *m*-phenylenediamine at 140° in a current of hydrogen until ammonia ceases to be evolved, crystallises from alcohol in pale yellow prisms, m. p. 198° . Salts cannot be obtained in aqueous solution, as the addition of acids brings about hydrolysis. The *picrate*, $\text{C}_{25}\text{H}_{26}\text{N}_4\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, has m. p. 198° .

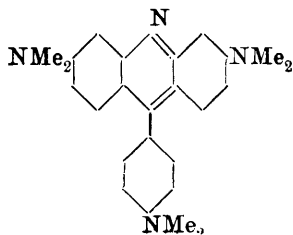
m-Dimethylaminophenylauramine, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, forms pale yellow crystals, m. p. 180° ; the orange-red *picrate* has m. p. 151° . The corresponding *diethyl* compound, $\text{C}_{27}\text{H}_{34}\text{N}_4$, has m. p. 157° .

2-Amino-*p*-tolylauramine, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}:\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, obtained from auramine and *m*-tolylenediamine, separates from a mixture of benzene and alcohol in pale yellow prisms, m. p. 229° . Dimethyl-*p*-aminophenylauramine, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, forms deep

yellow crystals, m. p. 179° , and the corresponding *diethyl* compound, $\text{C}_{27}\text{H}_{34}\text{N}_4$, has m. p. 142° , and its *picrate*, m. p. 217° .

m-Aminoauramines, when heated with zinc chloride, yield acridine derivatives, whereas phenylauramine and its *p*-amino-compounds do not.

2:8:4'-Hexamethyltriamino-5-phenyl-acridine (hexamethylrheonine) (annexed formula) is obtained from *m*-dimethyl-



aminophenylauramine and zinc chloride at 200—210° in the form of the zinc chloride, $C_{25}H_{28}N_4 \cdot 2HCl \cdot ZnCl_2 \cdot 3H_2O$. The base, $C_{25}H_{28}N_4$, forms brown crystals, m. p. 285°, and dissolves in acids, yielding deep red solutions.

J. J. S.

Aniline-black. III. RICHARD WILLSTÄTTER and STEFAN DOROGI (*Ber.*, 1909, 42, 4118—4135. Compare Abstr., 1907, i, 641; this vol., i, 535).—The aniline-black richest in hydrogen is a trebly quinonoid derivative of the leuco-base of the formula $C_{48}H_{36}N_8$. It is possible to prepare aniline-blacks containing less hydrogen, and even those containing oxygen. The base of the least oxidised dye is blue, forms green salts, and is turned light green by sulphurous acid. The most oxidised product is deep black, and not affected by sulphurous acid. The trebly quinonoid aniline-black previously described (this vol., i, 535) can also be prepared by oxidation with chlorate or persulphate in the cold, less than the calculated quantity of oxidising agent being used. This can be further oxidised by hydrogen peroxide to the *quadruply quinonoid aniline-black*, $C_{48}H_{34}N_8$:

$NPh \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot NH$.
The new compound is a darker blue-black, and the salts are dark green; sulphurous acid has relatively little influence. The trebly quinonoid substance unites with 4HCl, all of which are displaced by ammonia. The quadruply quinonoid, however, only adds about $2\frac{1}{2}$ HCl, one of which enters the nucleus, forming a chlorinated aniline-black base. The quadruply quinonoid compound is formed from aniline when an excess of the oxidising agent is employed; thus it is formed in Green's process of oxidation in presence of copper sulphate and *p*-phenylenediamine. It is most conveniently obtained by oxidation with chlorate in the cold. The "copper sulphate chlorate black" of Müller and Nietzki, and the "vanadium chlorate black" of Keyser, represent the same substance containing some chlorine.

Preparations obtained by these various methods agree in that (1) they are almost quantitatively oxidised to quinone, (2) one-eighth of the nitrogen is eliminated as ammonia, (3) they form a chlorine compound with 4.5% chlorine.

The trebly quinonoid black is hydrolysed by heating in sealed tubes at 200° to $C_{48}H_{35}ON_7$; the base is dull black with a blue shade; the salts are greenish-black. Sulphurous acid turns the base greenish-black. Both when these compounds are further oxidised, or when the quadruply quinonoid aniline-black is hydrolysed, the aniline-black, $C_{44}H_{33}ON_7$:

$NPh \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot O$, is formed. Both base and salts are of the same dull black colour, which is unchanged by sulphurous acid. It is possible to produce this hydrolysed quadruply quinonoid black from aniline salts in one operation when an excess of strong oxidising agents is employed.

The historic emeraldine described by Crace Calvert, Lowe, and Clift is in reality the trebly quinonoid aniline-black. The name emeraldine was also assigned by Caro to the phenylquinonedi-imine subsequently prepared by Willstätter and Moore, which has the

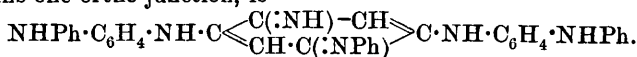
formula $\text{NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}$, and differs from aniline-black in being easily soluble in chloroform, forming reddish-violet solutions, and in being decolorised by ammonium sulphate. It is proposed to abandon the name emeraldine for the trebly quinonoid aniline-black, and restrict its use to the polymeride of phenylquinone-di-imine. These results afford a complete explanation of the processes in the technical preparation of aniline-black.

E. F. A.

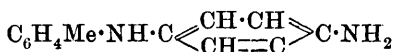
Polymerisation of Quinonedi-imines. RICHARD WILLSTÄTTER and HEINRICH KUBLI (*Ber.*, 1909, 42, 4135—4151).—Benzoquinone-phenyldi-imine is easily condensed to a blue bimolecular product, the emeraldine of Willstätter and Moore (*Abstr.*, 1907, i, 641, and preceding abstract), which may either possess an indamine or anilinoquinone constitution. To settle this structure the condensation of benzoquinonephenyldi-imines, substituted in the para-position, benzoquinonetolyldi-imine, and benzoquinoneanisylldi-imine has been studied. These substituted imines are deeper in colour than benzoquinonephenyldi-imine; the salts of the tolyl derivative give red, of the anisyl derivative violet, solutions. These imines are unable to polymerise to emeraldine, but they are polymerised in quite another manner by the action of hydrogen chloride on their solution in methyl alcohol, when much of the corresponding aminodiphenylamine is present. Red-coloured termolecular imines are formed, which do not alter in colour on mild oxidation, are not hydrolysed to benzoquinone, and are not further condensed to aniline-black. A similar termolecular amine is yielded by benzoquinonephenyldi-imine.

In reality the reaction consists in a condensation of imine with amine to form a leuco-compound, which has a reducing action on a further molecule of imine.

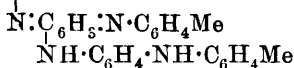
Emeraldine, when oxidised with chromic acid, gives only three-fourths of the theoretical quantity of benzoquinone; when lead peroxide is used, 94% of the theoretical quantity is obtained. The new termolecular compound when oxidised only yields benzoquinone from five of the six aryl groups. Accordingly, emeraldine only contains para-junctions, and the constitution of the new compound, which contains one ortho-junction, is



The tolyl derivative contains only one benzene nucleus, which forms a

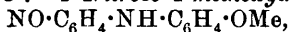


quinone (annexed formula).



4-Methoxydiphenylamine, prepared by methylation of *p*-hydr-

oxydiphenylamine with methyl sulphate, forms thin, glistening prisms, m. p. 105° (corr.), b. p. 195°/12 mm. The nitrosoamine forms bright yellow prisms, m. p. 83°. 4'-Nitroso-4-methoxydiphenylamine,



formed by the internal rearrangement of the nitrosoamine, separates

in prisms with a steel-blue lustre, but appearing olive-green or brown by transmitted light; m. p. 165° (corr.). It forms the 4'-amino-4-methoxydiphenylamine, m. p. 102° , b. p. $238^{\circ}/12$ mm., described by Jacobson, Jaenicke, and Meyer (Abstr., 1897, i, 148) on reduction.

p-Benzoquinone-*p*-anisyl-di-imine, $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, forms rosettes of glistening, flat prisms of golden-yellow colour, which becomes ochre-yellow when they are powdered, m. p. 71 — 72° . It forms a dark blue solution in concentrated sulphuric acid. The *monohydrate* is lighter in colour, m. p. 49° .

p-Benzoquinone-*p*-anisylmonoimine, $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, obtained on keeping the di-imine in aqueous solution, forms rhombic plates, m. p. 84° , with a green shimmer and a bluish-brown red powder.

p-Benzoquinone-*p*-tolyl-di-imine, $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$, prepared by oxidation of *p*-aminophenyl-*p*-tolylamine by means of silver oxide in ethereal solution, forms brownish-yellow prisms, m. p. 114° . *p*-Benzoquinone-*p*-tolylmonoimine, $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_7\text{H}_7$, forms bright, reddish-brown, four-sided prisms, m. p. 83 — 83.5° . The *mono*- and *di*-hydrochlorides form reddish-brown powders, and, after drying, dissolve in water, alcohol, or acetone, giving red solutions. *p*-Benzoquinonetolyl-di-imine, when reduced with stannous chloride, changes from red to blue, and then becomes decolorised. On the other hand, the salts of amino-methoxydiphenylamine, when oxidised with successive small quantities of bromine, become at first blue and finally violet; the corresponding tolyl compounds become first blue and then red on oxidation.

The termolecular *p*-benzoquinonephenyl-di-imine, $\text{C}_{36}\text{H}_{30}\text{N}_6$, crystallises in rhombic plates, m. p. 217 — 218° (corr.); the *monohydrochloride* is a blue powder, giving blue solutions; the *dihydrochloride*, a green powder, forming bluish-green solutions in acetone and alcohol.

The termolecular *p*-benzoquinonetolyl-di-imine, $\text{C}_{39}\text{H}_{36}\text{N}_6$, crystallises in lustrous, copper-like, light reddish-brown prisms, which soften at 180° , m. p. 187° (corr.). It forms carmine-red solutions, but dissolves in acetic acid with a blue coloration. The *monohydrochloride* is blue; the *dihydrochloride*, dark green.

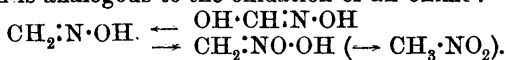
Termolecular *p*-benzoquinoneanisyl-di-imine, $\text{C}_{39}\text{H}_{36}\text{O}_3\text{N}_6$, forms chocolate-brown prisms, which darken at 150° , and soften at 170° , m. p. 176° .

On oxidation of equimolecular proportions of *p*-hydroxydiphenylamine and *p*-aminophenyl-*p*-tolylamine with hydrogen peroxide, the *leuco-base*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, is obtained, crystallising in colourless plates, m. p. 211 — 212° . This, when further oxidised, yields the homologue of the red imine described by Willstätter and Moore (*loc. cit.*), namely, $\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{O}$; it crystallises in red aggregates of pointed crystals, m. p. 205 — 206° .

The corresponding *leuco-base* from 4'-amino-4-methoxydiphenylamine forms colourless plates, m. p. 189 — 190° ; the red *imine* crystallises in pointed prisms, m. p. 229 — 230° . E. F. A.

Oxidation of Normal Diazohydroxides with Hydrogen Peroxide. EUGEN BAMBERGER and OSCAR BAUDISCH (*Ber.*, 1909, 42, 3568—3582. Compare Abstr., 1893, i, 326—327; 1894, i, 412).—When a strongly alkaline solution of a normal diazohydroxide is

oxidised with hydrogen peroxide at low temperatures (-6°), the products obtained are the alkali salts of a benzenediazoic acid and of a nitrosophenylhydroxylamine: $\text{ArN:N}\cdot\text{ONa} \begin{cases} \text{ArN:NO}\cdot\text{ONa} \\ \text{O:NAr:N}\cdot\text{ONa} \end{cases}$, a reaction which is analogous to the oxidation of an oxime:



In the case of sodium *p*-chlorodiazobenzene oxide, it has been found possible to isolate both oxidation products together with *p*-dichloroazobenzene and a compound, m. p. $135\cdot5$ — 136° , which is probably dichloroazoxybenzene, but with diazobenzene hydroxide the amount of nitrosohydroxylamine is so small that its formation has been merely confirmed; it was not found possible to isolate the pure compound.

Previous experiments on the oxidation of diazobenzene hydroxide have shown that nitrosobenzene is sometimes formed. This compound is now regarded as a secondary product formed by the decomposition of the nitrosohydroxylamine, $\text{O:NPh:N}\cdot\text{ONa}$, since this latter is readily transformed by alkaline oxidising agents (Abstr., 1898, i, 367) into nitrosobenzene and an alkali nitrite. This reaction does not occur when alkaline hydrogen peroxide is used; the oxidation then stops at the formation of the aryl nitrosohydroxylamine.

It is shown that nitrosobenzene cannot be obtained by the oxidation of benzenediazoic acid, and also that the diazoic acid and nitrosohydroxylamine cannot be transformed into each other.

The diazo-compounds are not oxidised by hydrogen peroxide in the presence of a very large excess of alkali, and *isodiazohydroxides* appear to be stable towards alkaline hydrogen peroxide.

The author is of opinion that free benzenediazoic acid has the nitroamine constitution, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NO}_2$, but that it reacts as a tautomeric substance and can give rise to *O*- and *N*-derivatives: $\text{C}_6\text{H}_5\cdot\text{NX}\cdot\text{NO}_2$ and $\text{C}_6\text{H}_5\cdot\text{N:N}\cdot\text{OX}$.

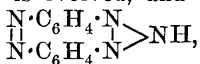
The ammonium salt of nitrosophenylhydroxylamine crystallises from alcohol in broad, silver-white needles, m. p. 163 — 164° , and sublimes on the water-bath in glistening plates. The iron salt separates from its light petroleum solution in the form of reddish-brown crystals, or from its ethereal solution in garnet-red needles with a blue, metallic lustre. The physical and chemical properties of the compound indicate that it is a complex metallic salt.

p-Chlorophenylnitrosohydroxylamine, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}(\text{NO})\cdot\text{OH}$, is best separated from *p*-chlorobenzenediazoic acid (Abstr., 1897, i, 467) by conversion into its *barium* salt, which is insoluble in boiling water, and is then purified by conversion into the ferric compound. It crystallises from light petroleum, has m. p. $73\cdot5$ — $74\cdot5^{\circ}$, and may also be prepared by the action of nitrous acid on *p*-chlorophenylhydroxylamine. The *ammonium* salt, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}(\text{NO})\cdot\text{ONH}_4$, forms reddish-brown, glistening plates, m. p. 164 — 165° ; the *phenylhydrazine* salt forms colourless, glistening plates, m. p. $115\cdot5$ — $116\cdot5^{\circ}$, and the *hydroxylamine* salt has m. p. 93 — 96° (decomp.). The *iron* compound forms dark red, glistening prisms.

p-Chlorophenylhydroxylamine, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{OH}$, obtained from

p-chloronitrobenzene, crystallises from water in colourless, glistening plates, *m. p.* 86° J. J. S.

Tri-imides of *m*- and *p*-Azo- and Azoxy-benzenes. FRITZ BUCHNER (*J. pr. Chem.*, 1909, [ii], 80, 355—368.)—The author has prepared tri-imides of *m*- and *p*-azobenzene or azoxybenzene, analogous to the tri-imides or azoimides of the diphenyl series (Vaubel and Scheuer, *Abstr.*, 1906, i, 323), as follows. *m*:*m'*-Diaminoazobenzene is dissolved in glacial acetic acid, and treated with the requisite amount of hydrochloric acid and sodium nitrite; the resulting diazotised base is treated with ammonium hydroxide and heated, whereby nitrogen is evolved, and the *tri-imide*,



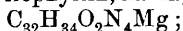
is produced. The *tri-imides* of *m*:*m'*-diaminoazoxybenzene and of *p*:*p'*-diaminoazobenzene have been prepared in the same way. None of the compounds are described. C. S.

Protein-Cleavage by Dilute Mineral Acids. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1909, 62, 492—495).—By boiling the iodo-protein prepared from egg-white with 10% sulphuric acid, the undissolved residue exhibits in different cases a widely varying percentage of iodine, whereas that of nitrogen varies within much narrower limits. The groups which combine with iodine are amongst others tyrosine and, perhaps, histidine. Similar results were obtained with iodothyreoglobulin. W. D. H.

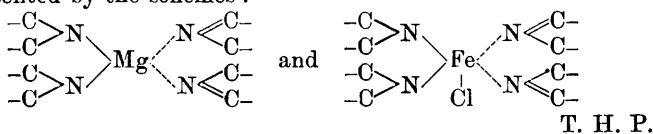
Chemistry of the Bacterial Cellular Proteins. SYBIL MAY WHEELER (*J. Biol. Chem.*, 1909, 6, 509—552).—These proteins were obtained in large quantities freed from non-toxic extractives soluble in alcohol and ether. They are highly poisonous whether prepared from pathogenic or non-pathogenic organisms. They give all the protein colour tests; they are scarcely affected by physical solvents, but are partly digested by pepsin and trypsin with a lessening of their toxicity. Hydrolysis with mineral acids effects the usual cleavage, but does not separate the poisonous group in a free form. Hydrolysis with dilute alkali leaves the non-toxic portion undissolved; this is accompanied by loss of ammonia. The insoluble residue shows most of the protein colour tests, contains all the carbohydrate and most of the phosphorus of the original, and is the specific part which immunises and sensitises. The poisonous portion is soluble in alcohol, and shows all the protein tests except those due to carbohydrate. It is very lethal, and the symptoms are the same whatever protein is employed as its source. W. D. H.

Linking of the Iron in the Colouring Matter of the Blood. RICHARD WILLSTÄTTER (*Ber.*, 1909, 42, 3985—3986).—In a forthcoming paper it will be shown that chlorophyll is derived from a tricarboxylic acid, and that on heating with concentrated alkali

solution it yields, firstly, two dicarboxylic acids, glaucophyllin and rhodophyllin, containing magnesium, and then two monocarboxylic acids, pyrrophyllin and phyllophyllin, having the composition



these mono- and di-basic acids form salts and esters, their carboxyl groups not being related to the metal present in the complexes (compare Willstätter and Pfannenstiel, *Abstr.*, 1908, i, 198). The magnesium in chlorophyll and the group FeCl in hæmoglobin are similarly combined, rhodophyllin and hæmin being analogous dicarboxylic acids (compare Nencki and Zaleski, *Abstr.*, 1900, i, 709; Zaleski, *Abstr.*, 1903, i, 217). Piloty and Merzbacher's conclusion (this vol., i, 857) that the iron atom in hæmin and in hæmatin is united with the two carboxyl groups is inadmissible, since hæmin is not the iron salt of a carboxylic acid, but a free acid. The conclusion must be drawn that the metal in chlorophyll and in hæmin is united only to nitrogen, and in accord with Ley and Werner's views concerning the constitution of complex metallic salts of acid imides, biuret and dicyanodiamidine (*Abstr.*, 1907, i, 302; see also Tschugaeff, *ibid.*, 595), the author regards the condition in which the magnesium atom exists in the chlorophyll molecule and the group FeCl in the hæmin molecule as represented by the schemes:



The Destructive Effects of Shaking on Proteolytic Enzymes. A. O. SHAKLEE and SAMUEL J. MELTZER (*Amer. J. Physiol.*, 1909, 25, 81—112. Compare this vol., i, 277; Harlow and Stiles, this vol., i, 861). Shaking in time destroys pepsin, rennin, and trypsin, especially readily at high temperatures; trypsin is more readily destroyed than pepsin. The assumption is made that what occurs is similar to the destruction of living cells, both these and enzymes having to some extent a similar structure.

W. D. H.

m-Nitro-p-aminophenylarsinic Acid. EFISIO MAMELI (*Boll. Chim. Farm.*, 1909, 48, 682—683).—*m-Nitro-p-aminophenylarsinic acid*, $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{AsO}(\text{OH})_2$, obtained by the interaction of arsenic acid and *o*-nitroaniline, separates from water as a microcrystalline powder, behaves as a dibasic acid towards phenolphthalein, and yields 4-iodo-2-nitroaniline when its sodium salt is treated with potassium iodide and sulphuric acid. The sodium, ammonium, silver, barium, calcium, and copper salts are all stable.

m-Nitro-p-aminophenylarsenic iodide, $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{AsI}_2$, prepared by the action of concentrated hydriodic acid on the preceding compound, has m. p. 96°.

T. H. P.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

General Relationship between Volume Contraction and the Three Usual Forms of the Refraction Formula in the Case of Mixtures of Liquids. V. F. HESS (*Ann. Physik*, 1908, [iv], 27, 589–625).—When a volume v_1 of a liquid of density D_1 is mixed with a volume v_2 of a liquid of density D_2 , the contraction, c , is given by the formula $c = (D - D_v)/D$, where $D_v = (v_1 D_1 + v_2 D_2)/(v_1 + v_2)$ is the density which the mixture would have if no contraction took place, and D is the observed density. It is now shown, from the available experimental data, that the relation holds:

$$(R - R_v)/R = q.(D - D_v)/D = qc,$$

where R_v denotes the refraction which the mixture would have if no contraction took place on mixing, R is the actual refractive power of the mixture, and q is a constant for any one binary mixture. The relation holds when the refraction is expressed in any of the three usual forms: $n^2 - 1$ (Newton), $n - 1$ (Beer, Gladstone), or $(n^2 - 1)/(n^2 + 2)$ (Lorenz and Lorentz).

From this relationship, the refraction or the refractive index of mixtures of the components in any proportion can be calculated when the composition of the mixture, the refractive indices of the pure components, as well as q and c , are known, and, similarly, the composition of a mixture can be calculated when all the other factors are known.

The relationship holds, also, almost independently of the temperature and of the wave-length of light used in measuring the refractive indices. G. S.

The So-called Asymmetry Product. EMIL BOSE (*Physikal. Zeitsch.*, 1908, 9, 860—863).—A theoretical discussion of the significance of the asymmetry product as determining the optical rotatory power. The fact that Guye's theory, according to which the masses of the groups attached to the asymmetric carbon atom are the determining group factors, is inconsistent with experimental observations, does not preclude the possibility that the optical rotatory power may be determined by an asymmetric product. The fact that the rotatory power varies with the temperature and with the wave-length indicates that these factors must be taken into account in any satisfactory explanation of the observed facts. Each atom or group will be characterised by a specific variation of the determining factor with the temperature and the wave-length of the light, and a possible method of ascertaining the values of the group factors from experimental observations is outlined. H. M. D.

Spectroscopic Experiments with Small Quantities of Liquids. JULIUS DONAU (*Monatsh.*, 1908, 29, 959—963).—Data are recorded which show that measurements of the wave-lengths of the bands of the absorption spectra of solutions can be made with very small quantities of liquid contained in capillary tubes. Aqueous solutions of potassium permanganate, neodymium and praseodymium nitrate, and erbium chloride were examined. The arrangement described is suitable for the detection of very small quantities of these substances. H. M. D.

Production of Line Spectra. EUGEN GOLDSTEIN (*Ann. Physik*, 1908, [iv], 27, 773—796).—A method for the production of well-developed line spectra of certain metals and of all chemically reactive non-metals is described. Finely-powdered salts are introduced into a cylindrical discharge tube until the anode at the lower end of the tube is completely covered, and the electrodes connected with an induction coil. Under these circumstances, the discharge does not take place along the shortest path, but between the column of salt and the walls of the discharge tube; an emission spectrum is thereby obtained which can be maintained in many cases for several hours.

The spectra of the alkali metals, which are obtained by introducing alkali halides into the discharge tube, are remarkably well-developed. Whereas, for instance, the Bunsen flame-spectrum only shows the double red and violet lines of potassium, it is possible to recognise seventeen other lines in the spectrum produced in the above way.

By placing suitable condensers in parallel with the discharge tubes containing the alkali metal halides, well-developed spectra of the halogens are obtained. By using calcium sulphide or potassium sulphate, the line spectrum of sulphur is produced. In a similar way, omission spectra of tellurium, selenium, phosphorus, arsenic, and

antimony can be obtained by introducing the sodium salts of the corresponding highest oxygen acids into the discharge tubes.

The halogen salts of the alkaline earth metals give rise, in general, both with and without condenser, to the spectra of the halogens. If, however, the discharge tubes are made very narrow at the anode end, the spectra of the metals are obtained.

Various modifications of discharge tubes are described, by means of which the spectra can be most conveniently obtained. H. M. D.

Infra-red Line Spectra. I. (Normal Wave-lengths up to 27,000 Ångstrom Units.) FRIEDRICH PASCHEN (*Ann. Physik*, 1908, [iv], 27, 537—570).—The measurements were made with a special form of grating spectro-bolometer. The methods of measurement are fully described. The main object of the investigation was to determine standard wave-lengths in the infra-red, and, except for the measurements with the alkali metals, the results are accurate to within one or two Ångstrom units.

Measurements have been made in Geissler tubes with helium, argon, hydrogen, and oxygen; with lithium, sodium, and potassium in the electric arc with carbon poles, and also with mercury. In the case of helium, new lines of wave-lengths 12,784.6, 12,792.8, 18,684.2, and 18,694.2 were discovered, which belong to two new series. Similarly, lines belonging to a new series were discovered in the case of hydrogen. The existence of this new series, as well as the series to which the new lines of helium belong, had been foreseen by Ritz from the data referring to series previously known. Satisfactory results were obtained for some mercury lines, and these are particularly suitable as standards. The results with the alkali metals are much less accurate than the others; they were determined in order to test some of the formulæ employed in calculating the wave-lengths of the different members of a series. G. S.

Spectral Analysis of the Glow Light in Different Gases. FRANS HIMSTEDT and H. VON DECHEND (*Physikal. Zeitsch.*, 1908, 9, 852—853).—The authors have made a spectroscopic examination of the luminous glow which accompanies point discharge in gases at atmospheric pressure, and have compared the spectra with those obtained in the action of radium on the same gases. In the case of air and nitrogen, the two spectra are identical, but with hydrogen, carbon monoxide, and carbon dioxide, considerable differences are found.

The point discharge spectra of oxygen, chlorine, and nitrogen are similar to those obtained in spark or Geissler tube discharge.

In the immediate neighbourhood of the discharging points, hydrogen exhibits the secondary hydrogen spectrum. Corresponding with the radiation of negatively-charged particles from the cathode, a second region of emission is found, which gives lines which do not correspond with any known spectrum. The authors attribute this new spectrum to the presence of traces of impurities in the hydrogen.

Hydrogen chloride yields the stronger chlorine lines, and some of the hydrogen lines on a continuous background. Methane gives

hydrogen lines and the Swan spectrum; nitric oxide and air, the first banded spectrum of nitrogen. Carbon monoxide and dioxide do not give the same spectrum; the monoxide shows the Swan spectrum and the sharp bands found at the red end of the Geissler tube spectrum, whilst the dioxide yields the sharp lines at the violet end of this spectrum.

H. M. D.

Emission Spectra of Certain Elements at High Temperatures. EMANUALE PATERNÒ and ARRIGO MAZZUCHELLI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 428—432).—In the spectrum of sulphur vapour (compare Abstr., 1907, ii, 451) no luminous bands or discontinuity is observable, but photographic reproduction of the spectrum indicates the presence of somewhat broad, but indistinct, bands. The complete or almost complete continuity of the emission spectrum of sulphur is doubtless related to the high density of its vapour, and it cannot be affirmed that distinct bands may not be obtained under reduced pressures.

In the authors' experiments, the heating of the sulphur was effected in quartz test-tubes, under which conditions certain other elements were examined, with the following results. Selenium vapour, which is yellow just above the boiling point, acquires at higher temperatures a red luminosity, increasing in intensity until, just before the quartz softens, it becomes a faint yellow, dazzling white light; the spectrum exhibits numerous, well-defined bands, which shade off towards the red end of the spectrum. The yellow vapour of tellurium, as the temperature is raised, assumes a green appearance, owing to a blue light, which increases in intensity and becomes dazzling at the temperature at which quartz softens; the spectrum exhibits, in greater number than that of selenium, bands which shade off more towards the red, and are not very marked on the luminous background. With phosphorus and arsenic, even at the highest temperature reached, the vapours are almost dark, and the feeble spectra which they yield exhibit no discontinuity or bands; the same is the case with mercury vapour. The emission spectrum of antimony at 1400° is almost continuous, but exhibits several bands.

In no case was a line spectrum observed, such a spectrum probably corresponding with a temperature higher than that at which bands appear. Band spectra are obtained more easily with elements of high atomic weight, which also give greater luminosity.

According to Fredenhagen (Abstr., 1907, ii, 146), discontinuous spectra of vapours are due to polymerisation and depolymerisation occurring during changes of temperature, whilst with an absolutely uniform temperature only continuous spectra are obtained. The phenomena of variable dissociation are not, however, sufficient to determine discontinuous radiation, since, in the quartz tubes employed by the authors, considerable variations of temperature occur, whilst sulphur, phosphorus, and arsenic, the molecules of which are polyatomic and liable to dissociate, seem to give spectra which are either continuous or give only feeble indications of more luminous bands.

T. H. P.

Spectrum of Scandium, and its Relation to Solar Spectra.

A. FOWLER (*Phil. Trans.*, 1908, 209, A, 47—70; *Proc. Roy. Soc.*, 1908, 81, A, 335—336).—Most of the results were obtained with a specimen of pure scandium oxide prepared by Sir William Crookes. Only the spectrum obtained with the electric arc was examined, but the conditions were varied so as to give in some cases an approach to the spark spectrum, and in others to the flame spectrum.

The arc spectrum consists of two distinct sets of lines, including both strong and faint lines, which behave very differently in solar spectra. One set are feeble or missing from the arc-flame spectrum, and are strengthened in passing to the arc, the arc in hydrogen, or the spark. They occur as relatively strong lines in the Fraunhofer spectrum, are weakened in the sun-spot spectrum, and occur as high-level lines in the chromosphere. The other set are relatively strong in the arc-flame, are feebly represented in the Fraunhofer spectrum, and do not appear to be present in the spectrum of the chromosphere, but the stronger lines are prominent in sun-spots. There is evidence that the greater part of the scandium absorption in the solar spectrum originates at a higher level than that at which the greater part of the iron absorption is produced.

The flutings in the arc and arc-flame spectra are absent when the arc is passed in hydrogen, and are probably due to scandium oxide.

G. S.

Absorption Spectra of Some Compounds of Pyridine. JOHN

E. PURVIS (*Proc. Camb. Phil. Soc.*, 1908, 14, 568—577. Compare Abstr., 1908, ii, 745; Baker and Baly, *Trans.*, 1907, 91, 1122).—The absorption curves of 2:3:5-trichloro- and 3:4:5-trichloro-pyridine are very similar in form, but the absorption band of the former compound is nearer the red end of the spectrum than that of the isomeride, and is of greater persistency. The positions of the bands expressed in oscillation frequencies are 3580 for the 2:3:5-compound and 3650 for the 3:4:5-isomeride.

Tetrachloro-2-aminopyridine, tetrachloro-4-aminopyridine, and pentachloropyridine give similar absorption curves, but the absorption band of the first compound is displaced more, and that of its isomeride less, towards the red end of the spectrum than that of pentachloropyridine; the positions of the bands expressed in oscillation frequencies, are: tetrachloro-2-aminopyridine, 3050; tetrachloro-4-aminopyridine, 3550, and pentachloropyridine, 3400. The persistency of the band of pentachloropyridine is greater than that of the 2-amino-compound, and considerably greater than that of the 4-amino-compound; in fact, the band of the latter compound has almost disappeared.

The absorption curves indicate that the relative positions and persistencies of the bands are influenced by the nature and spacial positions of the atoms or groups introduced into the nucleus.

W. H. G.

Luminescence Phenomena of Blue Fluorspar. EDGAR MEYER

(*Ber. deut. physikal. Ges.*, 1908, 6, 643—657; *Physikal. Zeitsch.*, 1908, 9, 810—816).—Experiments are described the object of which was to

determine the nature of the luminescence phenomena exhibited by certain blue fluorspars after exposure to light. During the decay of the thermo-luminescence, and for a considerable time after the disappearance of the visible effect, the emission of ultra-violet photochemically active rays can be detected. The intensity of this radiation diminishes gradually, but in the case of fluorspar from Wölsendorf, in Bavaria, the ultra-violet radiation could still be detected by the photographic action after the substance had been kept in the dark for one hundred and fifty days.

If the fluorspars are heated at 230—260°, the luminescent properties are not developed by exposure to diffused daylight or to an arc light; on the other hand, they respond to the light from electric sparks or a mercury lamp even when heated to a bright red heat.

The experiments also show that the intensity of the luminescent radiation increases with the length of the period of exposure to the primary radiation when this period is small. Above a certain limit, the period of exposure has, however, no influence on the emitted radiation. There appears to be no connexion between the effect examined by the author and the photo-electric activity. H. M. D.

Actinic Electrolysis. CARL GEORGE SCHLUEDEBERG (*J. Physical Chem.*, 1908, 12, 574—631).—A number of chemical changes have been investigated from the point of view of Grotthuss' theory of photochemical action.

The rate of dissolution of copper in ferric sulphate solution is not altered by light, but, as the action is practically instantaneous at the surface of the copper and its velocity is entirely governed by the rate of stirring, it may be of a photochemical nature.

Nascent chlorine produced by electrolysis is without action on acetic acid, and does not resemble chlorine under the influence of sunlight. Similarly, in its substituting action on aromatic hydrocarbons, nascent chlorine resembles chlorine in presence of a halogen carrier rather than chlorine in sunlight, since the latter gives additive products (compare, however, Cohen, Dawson, and Crosland, *Trans.*, 1905, 87, 1034). When electrolytic chlorine acts on toluene without a halogen carrier, the proportion substituted in the nucleus and in the side-chain depends on current density and temperature, but not on light. In presence of dilute acids or alkalis, electrolytic chlorine also gives additive products with toluene. These facts are held to disprove Lothar Meyer's additive compound theory of the action of halogen carriers, particularly as lead tetrachloride or ferric chloride alone is found to chlorinate benzene under suitable conditions.

The development of a blue colour by ferrocyanide paper in light can be simulated electrolytically. Sulphur obtained by the electrolysis of sulphuric acid is partly insoluble, and in this resembles the sulphur precipitated from solution by the action of light (compare Rankin, *Abstr.*, 1907, ii, 254). With sulphuric acid, using lead electrodes, an alternating current produces luminescence at each electrode. The oxidation of quinine sulphate by solid sodium peroxide is also attended with luminescence.

Not only can oxidation and reduction processes give rise to light,

but the converse is also true. It is shown that photographic sensitisers, such as erythrosin, are reduced by light, halogen being in most cases liberated.

R. J. C.

Balloon Observations of Atmospheric Radioactivity. FLEMMING (*Physikal. Zeitsch.*, 1908, 9, 801—803).—The observations were made by suspending weighted copper wires from the balloon, the wires being connected with the two poles of a small dry battery of about 2000 volts. After an exposure of one to two hours, the negative wire was wound up on a wire gauze cylinder, and introduced into an Elster and Geitel apparatus for measuring the ionisation. The observed activities vary very considerably, but show that radium emanation is present in the atmosphere even at a height of 3000 metres above the earth's surface. The highest indications were obtained during a journey in which the meteorological conditions were described as "stormy."

H. M. D.

Radioactivity of Rocks and other Materials from the Island of Ischia. RAFFAELLO NASINI and MARIO G. LEVI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 432—434).—The authors give the radioactivities of a number of specimens of pumice, tufa, spring deposits, etc., from the island of Ischia.

T. H. P.

Appearance of Radioactivity in Inactive Volcanic Materials of the Last Great Eruption of Vesuvius (April, 1906). RAFFAELLO NASINI and MARIO G. LEVI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 435—437).—Most of the Vesuvian materials, which in June, 1906, were found to exhibit no radioactivity, that is, exhibited a dispersion of less than 1 volt per hour (compare Abstr., 1907, ii, 3), are now found to be distinctly radioactive. The authors suggest that their previous inactivity was due to the fact that they had only recently passed from the liquid to the solid condition (*loc. cit.*).

T. H. P.

Radioactivity of Soil. FRÉD. BORDAS (*Compt. rend.*, 1908, 147, 924—925).—Glass containing manganese when buried in the soil of certain nitrate districts in Chili develops a violet hue similar to that produced in it by radium. Although samples of the soil examined in Paris were not radioactive, photographic tests made in Chili revealed considerable activity in those districts in which glass was acted on. The author supposes that some relation may exist between terrestrial radioactivity and the formation of nitrate deposits.

R. J. C.

Instability of Radium Bromide. SIR WILLIAM RAMSAY (*Monatsh.*, 1908, 29, 1013—1016).—The radium salt, weighing 0.388 gram, which the author obtained from the Vienna Academy of Sciences, was examined by converting a small portion into the anhydrous bromide and comparing its activity with that of a small quantity of pure anhydrous radium chloride. The data indicate that the 0.388 gram of material corresponds with 0.4547 gram of anhydrous radium bromide.

The substance was only partly soluble in water, and on treatment with hydrobromic acid, carbon dioxide was evolved. The gases pumped off from the aqueous solution before the hydrobromic acid was added, consisted of hydrogen and oxygen; after the addition of the acid, large quantities of bromine were evolved, together with a little oxygen. After some months, the evolution of bromine ceased, and hydrogen and oxygen were obtained. When the substance was first dissolved in water, 1.312 c.c. of gas were pumped off; this consisted of 0.015 c.c. of carbon dioxide, 0.047 c.c. of hydrogen, 1.125 c.c. of oxygen, and 0.125 c.c. of nitrogen and helium.

The author records that the sealing up of the substance in a small flask in November caused blistering of the fingers in the following June.

H. M. D.

Radioactivity of Potassium, with Special Reference to Solutions of its Salts. NORMAN CAMPBELL (*Proc. Camb. Phil. Soc.*, 1908, 14, 557—567. Compare Abstr., 1907, ii, 597).—The results recorded previously (Campbell and Wood, Abstr., 1907, ii, 217) have been confirmed. All attempts to observe or to produce any difference in the activity of different samples of the same potassium salt in the same physical state were unsuccessful. The activity of a potassium salt is unchanged on heating, and attempts to separate an active component by electrolysis, recrystallisation, and precipitation were unsuccessful.

The activity of a thick layer of a potassium salt is not strictly proportional to the potassium content, possibly because in different compounds the ratio of the density of the substance to the absorption coefficient of the rays emitted by it differs. In the case of solutions, the variations in the value of this ratio are large and irregular. The ratio is not necessarily proportional to the density or concentration of the solution.

In conclusion, it is stated that the method employed by McLennan and Kennedy (Abstr., 1908, ii, 750) for measuring the activity of a salt gives untrustworthy results.

W. H. G.

Sodium Emanation. G. COSTANZO (*Ber. deut. physikal. Ges.*, 1908, 6, 854—857).—It has been stated by Phillips (*Nature*, 1908, 78, 79) that metallic sodium gives off an emanation and accelerates the discharge of a negatively-electrified electroscope. The author finds that the rate of discharge in an atmosphere of dry nitrogen is not influenced by the presence of sodium. In a second series of experiments, in which dry air was passed over sodium into the chamber of the electroscope, the same rate of discharge was found for both positive and negative electricity as in blank experiments in which the sodium was omitted from the apparatus.

H. M. D.

So-called Metallic Radiation. SEM SAELAND (*Ann. Physik*, 1908, [iv], 27, 903—904).—It is pointed out that the author's observations relating to the photographic activity of metals and hydrogen peroxide (Abstr., 1908, ii, 789) are in satisfactory agreement with the results obtained by O. and A. Dony-Hénault (Abstr., 1908,

ii, 647) in an investigation of the supposed radioactivity of hydrogen peroxide. By combining the two series of observations, the possibility that the photographic action is due to an emission of rays or an emanation is completely precluded.

H. M. D.

Influence of Temperature on the Transformation of Radioactive Substances. HEINRICH W. SCHMIDT and PAUL CERMAK (*Ber., deut. physikal. Ges.*, 1908, 6, 675—687; *Physikal. Zeitsch.*, 1908, 9, 816—821).—Reference is made to the apparently contradictory results obtained by different observers of the influence of temperature on the properties of radioactive substances. The changes which would result if a rise of temperature exerted an influence on the intensity of the radiation, on the rate of decay of the radioactive substance, or on both these factors are considered.

Experiments are described in which a small quantity of radium bromide was heated electrically in a quartz tube, the β - and γ -radiation being measured separately before, during, and after heating. When the temperature was raised to 1000—1400°, the intensity of the β -radiation diminished considerably; on cooling, a further diminution took place, but after some hours the normal value was again attained. No variation of the intensity of the γ -radiation with the temperature could be detected. When the same sample of radium bromide was enclosed in a second quartz tube and the experiment repeated, the β -radiation was found to remain constant. After repeated heating and cooling, evidence of variation was obtained, and the authors conclude that the observations indicate that quartz undergoes a change of structure under certain conditions and that in the transformed condition it is permeable to the volatile active substances.

It is pointed out that similar observations have already been recorded by Engler (*Abstr.*, 1908, ii, 650). The conclusion is drawn that the radiation and the rate of transformation of the disintegration products of radium as far as radium C are independent of the temperature up to 1500°.

H. M. D.

Chemically Active Electrical Radiation. A. REMELÉ (*Ber., deut. physikal. Ges.*, 1908, 6, 804—807).—The author has observed that a silver bromide plate is darkened slowly on exposure to boron nitride. The photo-chemical action takes place much more rapidly if the nitride is heated in a Bunsen flame. The active rays pass through paper, leather, and caoutchouc, but not through metals; they do not give rise to ionisation effects. Magnesium and lithium nitride have also been found to exert photochemical action at the ordinary temperature, and uranium nitride is much more active than other uranium salts or minerals.

H. M. D.

Reaction Radiation. H. W. WOUDESTRA (*Chem. Weekblad*, 1908, 5, 835—836).—When a photographic plate covered with an aluminium stencil V was exposed for five minutes close to a vessel containing 10% calcium chloride into which 10% sulphuric acid was allowed to flow, the letter could be distinctly seen on developing the plate. Neither calcium chloride nor sulphuric acid alone produced any result. With ferric chloride and potassium hydroxide, and with

stannous chloride and mercuric chloride or mercurous chloride respectively, the letter appeared light on a dark ground. Mercuric chloride and ferric chloride alone produce the same effect (compare Kof and Haehn, Abstr., 1907, ii, 732).

WILLEM P. JORISSEN (*Chem. Weekblad*, 1908, 5, 836—839.—A summary of other work on the foregoing subject. A. J. W.

Use of the Electroscope in Measuring Activity. J. OLIE, jun. (*Chem. Weekblad*, 1908, 5, 823—828. Compare Jorissen and Ringer, Abstr., 1907, ii, 422).—The sources of error incidental to the electroscopic method of measuring activity have been investigated, uranium oxide being employed. Neither the presence of moisture nor the position of the substance on the condenser plate influences the time of discharge, but an uneven distribution of the active substance prolongs the time. The distance between the condenser plates for distances between 3 and 5 cms. has no effect. The total quantity of active substance present is only of importance when the layer is very thin, the discharging action with thick layers taking place at the surface. Diminution in the surface area of the active substance considerably prolongs the time of discharge, which depends, not only on the quantity of material present, but also on its surface area.

WILLEM P. JORISSEN (*Chem. Weekblad*, 1908, 5, 828—830. Compare Rutherford and Grier, Abstr., 1902, ii, 637; Jorissen and Ringer, Abstr., 1907, ii, 731; Cameron and Ramsay, Trans., 1907, 1266 and 1593; Curie and Gleditsch, Abstr., 1908, ii, 793).—A comment on Olie's paper, and a summary of similar work. A. J. W.

Electromotive Force of the Hydrogen-Oxygen Cell. J. N. BRÖNSTED (*Zeitsch. physikal. Chem.*, 1908, 65, 84—92).—From observations on the dissociation of water vapour at high temperatures, Nernst (Abstr., 1906, ii, 17) has obtained the value 1.232 volts at 17° for the *E.M.F.* of the hydrogen-oxygen cell, and this result has been confirmed by Lewis (Abstr., 1906, ii, 262) by measurements of *E.M.F.* and thermal dissociation of silver oxide. The author has re-determined the *E.M.F.* of the cell in question indirectly by a method somewhat similar to that of Lewis, mercuric oxide being used instead of silver oxide.

The *E.M.F.* of the cell

hydrogen | sodium hydroxide | mercuric oxide | mercury
was determined at different temperatures with different concentrations of alkali. From the temperature-coefficient of the *E.M.F.* and the *E.M.F.* of the cell, the heat of oxidation of mercury has been calculated as 22.290 cal., in moderate agreement with the result obtained directly. It is shown that the *E.M.F.* of the hydrogen-oxygen cell can be calculated from the formula $E = 0.9290 + RT/4 \cdot \log_e 760/p$, where 0.9290 is the potential of the cell above-mentioned when dilute alkali is used as electrolyte, and p is the dissociation pressure of mercuric oxide in contact with mercury, as in the cell. The value of p at 70° has been calculated from the value of the heat of oxidation of mercury obtained as above, and the dissociation pressure of mercuric oxide at high temperatures, determined by

Pélabon. On substituting the value of p thus obtained, in the above formula, the value obtained for the *E.M.F.* of the hydrogen-oxygen cell is 1.238 ± 0.01 volt, in excellent agreement with the values obtained by Nernst and by Lewis.

G. S.

Reduction of Cadmium by Mercury and the *E.M.F.* of Cadmium Amalgams. GEORGE A. HULETT and RALPH E. DELURY (*J. Amer. Chem. Soc.*, 1908, 30, 1805—1827).—The work described in this paper was undertaken in order to gain a knowledge of the equilibrium conditions in the system mercury, cadmium sulphate, and water. From the behaviour of standard cells, it seemed probable that mercury reduced cadmium sulphate solution and formed a very dilute amalgam, an equivalent amount of mercury passing into solution.

A study of the *E.M.F.* of very dilute cadmium amalgams has been carried out. A difficulty was experienced at the outset, owing to the ease with which the cadmium in an amalgam undergoes oxidation, and a method was worked out for efficiently preventing oxidation in the preparation and manipulation of amalgams.

All cadmium amalgams containing between 6% and 13% of cadmium have the same potential against an electrolyte, since at the ordinary temperature any amalgam in this range is made up of two phases, and the composition of the liquid depends only on the temperature. When the temperature is fixed, there results a constant reproducible electrode, which renders it possible to detect at once the loss of cadmium from the amalgams and to estimate its amount.

Richards and Forbes (Abstr., 1907, ii, 693) have found that the density is a function of the composition of cadmium amalgams from the pure metal to 3% of cadmium, and it has now been ascertained that this is true up to the saturated amalgam, which contains 5.57% of cadmium.

From a study of the composition and density of the liquid phase of a cadmium amalgam, saturated at 25°, the following relation has been established: $D = 13.540 - 0.0606 \times p$, with a temperature-coefficient of $-(0.0024 + 0.0003 p)$, where p is the percentage of cadmium in the amalgam.

A method is described for removing oxygen from a solution and saturating the latter with hydrogen, and for effectively removing the residual oxygen from a cell and its contents.

Measurements have been made of the *E.M.F.* of cadmium amalgams at 25°, extending from the saturated amalgam to a dilution of 1 part of cadmium in 10^8 parts of mercury, and the results are tabulated. The most trustworthy value seems to be 0.052940 for the 1:1000 amalgam.

It has been found that any two amalgams from 1:100 to 1:10⁶ show an *E.M.F.* which is in agreement with the requirements of the gas laws, but a deviation from these requirements has been found for amalgams of greater dilution than 1:10⁶. This deviation is regarded as evidence that the reduction of mercury by cadmium is a reversible reaction which does not go to completion, but that a definite equilibrium is established.

E. G.

A New Method of Calculating the Ratio of the [Electric] Charge to the Mass of the Molecule of Mercury Vapour. ROBERT FÜRSTENAU (*Physikal. Zeitsch.*, 1908, 9, 849—851).—On the assumption that the equations of Drude and Lorentz for the thermal and electrical conductivities of metallic conductors can be applied to mercury vapour, the author shows that it is possible to obtain the ratio e/m of the electrical charge to the mass of the mercury molecule. According to Drude's equation, $e/m = 9.38 \times 10^3$, whilst Lorentz's equation gives 7.62×10^3 . The former value agrees very well with the value of the ratio, 9.53×10^3 , obtained by Wien for the canal rays in an atmosphere of pure hydrogen. H. M. D.

Electrical Conductivity of Magnesium-Lead Alloys. N. J. STEPANOFF (*Zeitsch. anorg. Chem.*, 1908, 60, 209—229 *).—The alloys were fused under a layer of potassium and lithium chlorides, and drawn by a pump into previously heated hard glass tubes, coated internally with lamp-black. After slow cooling, the glass tube was carefully broken away, leaving rods 3—4 mm. in diameter. This method is suitable for brittle and oxidisable metals.

The conductivity of each alloy was measured at 25° and at 100°. The results are in accordance with the indications of the freezing-point curve (Kurnakoff and Schemtschuschny, *Abstr.*, 1908, ii, 932), but the formation of a solid solution, containing up to 4 atomic % of lead, is indicated. The compound Mg_2Pb has a conductivity 8.55 times less than that of lead. C. H. D.

Conductivity of Acid Solutions in Presence of Salts. M. POUCHON (*Chem. Zentr.*, 1908, ii, 1005; from *Le Radium*, 1908, 5, 167—170. Compare *Abstr.*, 1908, ii, 346).—Similar results to those recorded by Boizard (*loc. cit.*) have been found with phosphoric acid and its salts, namely, that the conductivity of the acid is lowered by the addition of its salts. Employing Kohlrausch's method, slightly modified, a decrease in conductivity was observed at the first additions of mono-, di-, or tri-potassium phosphate, but on further additions of salt the conductivity increased. This may be explained by the formation in solution of the complex substance $H_3PO_4.KH_2PO_4$, obtained in the crystalline form by Staudenmeyer (*Abstr.*, 1904, ii, 137).

J. V. E.

Electrical Conductivity of Salts and Mixtures of Salts. ALFRED BENRATH (*Zeitsch. physikal. Chem.*, 1908, 64, 693—706).—The electrical conductivity of the solid nitrates of potassium, sodium, and silver has been determined at a series of temperatures up to the respective melting points, and the conductivity of the solid binary systems KNO_3-NaNO_3 and $NaNO_3-AgNO_3$ has also been measured at different temperatures. The solid salts were strongly compressed into small cylinders, the ends of the cylinders covered with a thin layer of graphite, and connexion made with the circuit by means of platinum disks pressed firmly against the ends. The resistances were measured by Kohlrausch's method. Special precautions were taken to exclude the effect of adsorbed moisture.

* and *J. Russ. Phys. Chem. Soc.*, 1908 40 1448—1467.

There is an enormous diminution in the resistance of all three salts when the melting point is reached, the resistance of the crystalline salt being more than 10,000 times as great as that of the fused salt in each case. The sudden change in conductivity may therefore be made use of for determining melting points. The relation between the specific conductivity, κ , of the solid salt and the temperature, t , is given by the equation $\log \kappa = a + bt$, where a and b are constants.

The melting-point curves for the binary systems $\text{KNO}_3\text{--NaNO}_3$ and $\text{AgNO}_3\text{--NaNO}_3$, determined by the above method, are in fair agreement with those determined in the usual way. Further, the isothermals for the binary systems, obtained by plotting the composition as abscissæ against the conductivity as ordinates, have been determined at 180° , 190° , and, for the system $\text{NaNO}_3\text{--KNO}_3$, also at 200° and 210° . For the latter system, the isothermals rise rapidly from the points representing the conductivity of the pure salts, but there is an intermediate part which alters in a linear manner with concentration. It may be anticipated that the rising parts of the curve correspond with mixed crystals, and the linear part with the presence of two non-miscible components, which do not enter into chemical combination. The above observations may therefore be used to determine the limits within which mixed crystals are formed, and the results agree fairly well with those obtained by the usual methods. The results for the system $\text{AgNO}_3\text{--NaNO}_3$ are similar, but less regular. The results therefore indicate that the conductivity of mixed crystals of salts is greater than that of the components, the converse of the behaviour of metals.

G. S.

Abnormal Course of Curves, showing the Change of Molecular Conductivity with the Concentration. WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1243—1247).—According to Steele, McIntosh, and Archibald (*Abstr.*, 1905, ii, 222; 1907, ii, 526), abnormal diminution of electrical conductivity of non-aqueous solutions on dilution may be explained by assuming that the electrolyte consists of a complex formed of n (2 or 3) mols. of the solute with m mols. of the solvent. On the basis of this hypothesis, they show that $\kappa V^n = aK$, where κ represents the specific conductivity, V the dilution, a the degree of the dissociation of the electrolyte, and K a constant. From the numbers given by these authors for the conductivities of solutions of potassium iodide in amylamine, the author shows that κV^n only ceases to exhibit a maximum when $n = 6$. The above hypothesis is rendered improbable by the large number of hydrates known, and by the fact, generally accepted, that ionisation in aqueous solution is always accompanied by hydration. This hypothesis is also quite incapable of explaining the results of Franklin and Gibbs (*Abstr.*, 1907, ii, 840), who found that, for solutions of silver nitrate in methylamine, the molecular conductivity at first increases with the dilution, then decreases, and afterwards increases again.

T. H. P.

Limiting Conductivity and Degree of Ionisation of Alcoholic Solutions. BENJAMIN B. TURNER (*Amer. Chem. J.*, 1908, 40, 558—574).—Determinations have been made of the conductivity

of alcoholic solutions up to dilutions of 20,000 to 50,000 litres. The precautions to be observed in such work have been carefully studied. It has been found that when alcohol of very low conductivity is placed in new glass vessels which have been cleaned and dried in the usual way, an error is introduced which leads to inconsistent results at high dilutions. It appears that in drying, either the surface of the glass becomes loosened or the solvent action of the drops of water on the glass at the high temperature used is sufficient to increase greatly the conductivity of the alcohol which is afterwards put into the vessel.

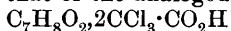
The conductivity of alcoholic solutions of potassium iodide between 0° and 78° has been measured, and it has been found that the molecular conductivity reaches a maximum of 48.5 ± 0.5 reciprocal ohms at 25° at about 20,000 litres dilution. A similar maximum appears to exist at all temperatures. The ionisation constants have been calculated for all the concentrations and temperatures. The temperature-coefficients increase with the temperature, and most markedly in the case of very dilute solutions. At any given temperature, the temperature-coefficient increases with the dilution. The ionisation decreases as the temperature rises. A $0.1N$ solution is dissociated to the extent of 49% at 0° , 46% at 25° , and about 35% at the b. p. The temperature-coefficient for pure alcohol is much less than for alcohol of conductivity 0.3×10^{-6} , and may even be negative.

Measurements have also been made with lithium chloride and bromide, but the results are regarded as less accurate than those obtained with potassium iodide.

The values for the conductivity of alcoholic solutions of potassium iodide agree fairly closely with those obtained by Dutoit and Rappeport (Abstr., 1908, ii, 924). E. G.

Electrical Conductivity of Solutions of Compounds of Dimethylpyrone with Tribromoacetic Acid in Ethyl Bromide. WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1238—1243. Compare Abstr., 1908, i, 281).—The electrical conductivity of a solution of a mixture of dimethylpyrone and tribromoacetic acid in ethyl bromide gradually diminishes, owing to the decomposition of the compound formed by the two solutes. This decomposition, which is rendered evident by the solution becoming brownish-green, is, however, sufficiently slow to allow of comparable numbers being obtained by measurements made immediately the solutions are prepared.

The molecular proportions of dimethylpyrone and tribromoacetic acid in the solutions examined were 1:1, 1:2, 2:1, and 1:3. The conductivity of the compound $C_7H_8O_2 \cdot 2CBr_3 \cdot CO_2H$ in ethyl bromide is considerably less than that of the analogous compound



(compare Abstr., 1905, ii, 433), but the curves connecting conductivity and concentration are perfectly similar in the two cases. The conductivity of the compound $C_7H_8O_2 \cdot 2CBr_3 \cdot CO_2H$ is considerably greater than that of the compound $C_7H_8O_2 \cdot CBr_3 \cdot CO_2H$, whilst that of the compound $2C_7H_8O_2 \cdot CBr_3 \cdot CO_2H$ is extremely small. Addition

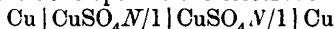
of a greater proportion of tribromoacetic acid than corresponds with the compound $C_7H_8O_2 \cdot 2CBr_3 \cdot CO_2H$ causes a diminution of the conductivity, which, for $C_7H_8O_2 \cdot 3CBr_3 \cdot CO_2H$, lies between the conductivities of $C_7H_8O_2 \cdot CBr_3 \cdot CO_2H$ and $C_7H_8O_2 \cdot 2CBr_3 \cdot CO_2H$.

T. H. P.

Oxide Theory of the Oxygen Electrode. RICHARD LORENZ (*Zeitsch. Elektrochem.*, 1908, 14, 781—783).—After referring to his previous work (Abstr., 1906, ii, 825), the author states that he has been observing the discharge curves of polarised electrodes, using a galvanometer in series with a very large resistance, so as to obtain a slow discharge. The *E.M.F.* at which the discharge occurs corresponds with some change at the electrode, and it is not complicated by *E.M.F.*'s due to changes of concentration in the electrolyte.

T. E.

Calorimetric Determination of Heat Development at Electrodes. P. BRÄUER (*Zeitsch. physikal. Chem.*, 1908, 65, 111—120).—The heat developed at the electrodes of the cell



when a current is sent through it has been determined directly, and the same factor has also been calculated indirectly from the magnitude of the temperature-coefficient of the same cell, which has been carefully re-determined.

The direct determination of the heat set free at the electrodes was made as follows. A small glass calorimeter, the bottom of which was a porous plate, and filled with *N/1* copper sulphate solution, was immersed nearly to the rim in a wider vessel, also containing *N/1* copper sulphate. Both compartments were provided with stirrers and thermometers, and in each a copper electrode was placed. The contents of the inner vessel were then cooled slightly, and a current of 0.5 ampere passed through the cell for sixteen minutes, the thermometers being read at intervals. The heat developed in the calorimeter, referred to $F = 96,540$ coulombs, is represented for the anode compartment by the expression $Q + F\pi - j$, and for the cathode compartment by the expression $Q - F\pi + j$, where Q is the Joule heat developed, π is the *E.M.F.* at the junction electrode/solution, and j the heat of ionisation of copper; hence, from the observed data, the value of $F\pi + j$ for 1 gram-equivalent of copper is 4464 cal., or for a gram-atom of copper, 8930 cal.

The temperature-coefficient of the same cell was also determined by measuring by the compensation method the *E.M.F.* between two similar cells differing in temperature by a few degrees; the value obtained was 0.00069 volt per degree, about 10% higher than Bouty's value (*J. Phys.*, [i], 9, 229; [ii], 1, 267). From this result, the heat developed, W , at the electrodes was calculated by the usual formula: $W = nFT \cdot d\pi/dT$; the value obtained was 9320 cal., in fair agreement with the above value. From the last-mentioned result, it is calculated that the heat of ionisation of copper is 18,800 cal., as compared with 17,500 cal. calculated by Ostwald.

G. S.

Thermo-electric Forces in Electrolytes. EMIL PODSZUS (*Ann. Physik*, 1908, [iv], 27, 859—889).—The thermo-electric differences of potential resulting from the juxtaposition of a cold and a hot pair of dilution solutions of different electrolytes have been measured. It is found that the thermo-electric potential is proportional to the difference of temperature, and for a given pair of electrolytes is almost independent of the concentration of the solutions. When different salts are combined with the corresponding acid to form a pair, it is found that the order in which the cations succeed one another, when arranged in the order of the thermo-electric difference of potential, is independent of the anion with which they are associated. For the electrolytes examined, the order is lithium, ammonium, sodium, potassium, magnesium, copper, barium, and iron (ferric). A similar relationship is found in the case of the anions, the order being sulphate, chloride, iodide.

In general, the direction of the current due to the thermo-electric force is from the cold to the hot pair of solutions. H. M. D.

Magnetic [Susceptibilities] of the Rare Earths. STEFAN MEYER (*Monatsh.*, 1908, 29, 1017—1022).—The author has compared the magnetic susceptibilities of the oxides of the two elements into which von Welsbach claims to have resolved ytterbium. Referred to one gram-atom, the magnetic susceptibility of aldebaranium is 9.15, and that of cassiopeium, 1.9. The difference between the two values corresponds with the much greater number of lines in the spectrum of the former element.

The spectra of holmium and dysprosium and the magnetic susceptibilities of the corresponding oxides are compared, and the conclusion is drawn that a strongly magnetic element having a large number of lines in its spectrum is present with dysprosium in holmium.

H. M. D.

Magnetic Properties of the Alloys of Ferromagnetic Metals. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1908, 65, 73—83).—Some general rules are given for the magnetic behaviour of alloys containing iron, cobalt, and nickel. The experimental data are mainly taken from papers by the author and his co-workers published during the last three years.

Apparently without exception, mixed crystals in which a ferromagnetic metal acts as solvent are magnetic, but similar crystals in which the non-magnetic metal acts as solvent, that is, is present in much the greater proportion, are non-magnetic. Chemical compounds containing iron, cobalt, and nickel are practically non-magnetic.

The temperatures at which the magnetic properties disappear on heating are only altered by the addition of other substances when the latter are soluble in the non-magnetic form. The effect of other substances on the transition temperature is usually to lower it. Van't Hoff has shown that (1) when the metal separates in the pure state at the transition temperature, and (2) when the work done in separating the pure metal from the mixed crystal can be calculated from the laws of osmotic pressure, the influence of foreign metals on the transition temperature of the ferromagnetic metal can be calculated by the formula

(the same as that for the freezing-point depression) $dT = 0.02T^2/W$, where W is the latent heat of fusion of the latter metal. The author shows from the available data that the experimental values of dT and those calculated from the above formula are very seldom in agreement, from which the conclusion is drawn that neither of the assumptions on which van't Hoff's formula are based are necessarily valid.

G. S.

Hydration of Ions Calculated from Transference Numbers and Electromotive Forces. B. REINHOLD (*Zeitsch. Elektrochem.*, 1908, 14, 765—766).—If the anion and cation of an electrolyte carry different numbers of molecules of water with them, the changes of concentration at the electrodes are partly due to this and partly to the different mobilities of the ions. If the real mobilities are known, it is possible to calculate the difference in the degree of hydration of the ions either from direct determinations of the transference numbers or from the *E.M.F.* of a concentration element.

T. E.

Decomposition of Complex Ions. WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1247—1257).—The mutual action of the components of complex ions serves to explain syntheses in presence of aluminium chloride or bromide, the catalytic properties and tendency to react of this salt standing in close relation to the propensity of the aluminium atom to form complex ions. In the majority of instances, the products of the reaction are electrolytes, and the whole course of the reaction can be explained by the formation of these complex ions. This view is supported by the electrochemical properties of the compounds of aluminium bromide with ether (Abstr., 1907, i, 580), and explains the decomposition of this complex compound on dry distillation. The electrochemical properties of the compounds formed by aluminium bromide, bromine, and carbon disulphide, and of the compounds of dimethylpyrone with trichloroacetic acid (compare Abstr., 1905, ii, 433) and tribromoacetic acid (compare this vol., ii, 14), are discussed in relation to the views of Hantzsch (Abstr., 1908, ii, 14).

The mechanism of the decomposition of the compounds of aluminium bromide with toluene and benzene by electrolysis (compare Abstr., 1908, i, 407) is discussed.

T. H. P.

Ratio of the Specific Heats of Gases and its Dependence on the Temperature. ROBERT FÜRSTENAU (*Ann Physik*, 1908, [iv], 27, 735—772*).—The author has investigated the variation of the ratio of the specific heats with the temperature for several gases by measurements of the wave-lengths of sound according to the resonance method. Two exactly similar pieces of apparatus were used in the experiments, one of these being used for the examination of the gases at higher temperatures, the other for a comparative measurement at the ordinary temperature. By this means it was possible to eliminate errors which would result from a gradual alteration in the pitch of the source of sound.

The experimental results indicate that between 0° and 500° the

* and *Ber. Deut. physikal. Ges.*, 1908, 6, 968—979.

ratio of the specific heats of air is constant within 1%. For carbon dioxide and sulphur dioxide, the values of the ratio are respectively 3.5% and 4.8% less at 500° than at 0°. For a rise of temperature from 0° to 300°, the ratio in the case of ethyl chloride diminishes to the extent of 3.4%.

From Regnault's determinations of the specific heat of carbon dioxide at constant pressure between 0° and 200°, and the corresponding values obtained by the author for the ratio of the specific heats, the following values are obtained for the specific heat at constant volume: 0°, 0.1436; 100°, 0.1654; 200°, 0.1856. For this range of temperature, the value of c_v increases to the extent of 29%.

H. M. D.

Condition of Substances in Absolute Sulphuric Acid. III. ARTHUR HANTZSCH (*Zeitsch. physikal. Chem.*, 1908, 65, 41—60. Compare Abstr., 1908, ii, 14, 462).—The statement in the previous paper, that substances which dissolve in absolute sulphuric acid as hydrogen sulphates give values for the molecular weight rather less than two-thirds, but always more than half, the theoretical value, and that the apparent molecular weights are practically independent of the dilution, is confirmed by further experiments. In some cases, however, such as acridine, the values in the most dilute solutions are much higher. Acetonitrile and certain other acid nitriles, as well as benzil and benzophenone, also give about two-thirds of the theoretical depression, and are dissolved as hydrogen sulphate; the alcohols, however, only give about one-third of the theoretical depression, being changed by the solvent to alkylsulphuric acids and water.

As regards nitro-compounds, di- and tri-nitrobenzene and nitromethane give the theoretical depression, but *p*-nitrotoluene causes considerably less than the theoretical depression.

Weak acids, the affinity constants of which can be readily determined, behave cryoscopically like water or ammonia, and are therefore present in solution as acylhydronium salts, formed according to the equation: $\text{AcOH} + \text{HSO}_4\text{H} = \text{AcOH}_2\cdot\text{SO}_4\text{H}$. Moderately strong acids, such as trichloroacetic, oxalic, and picric acids, give the theoretical depression, and are probably present as such in solution. The strongest acids, on the other hand, give less than the theoretical depression, and form conducting solutions with sulphuric acid; the ions are probably produced by dissociation of complex compounds of solute and solvent. The dissociation of the sulphonic acids increases in the order: benzenesulphonic acid, *p*-toluenesulphonic acid, azobenzenesulphonic acid; the latter is apparently about one-third ionised. Phosphorous and metaphosphoric acids behave as if split up into two ions, whilst nitric acid gives about four times the theoretical depression, and the solution probably contains a highly ionised complex acid.

G. S.

Fused Salt Hydrates as Solvents for Freezing-point Determinations. G. COCK (*Zeitsch. anorg. Chem.*, 1908, 60, 191—192).—Morgan and Benson (Abstr., 1907, ii, 747) have determined the lowering of freezing point produced by the addition of

water to fused salts, and hence calculated the molecular weight of water; in the case of calcium chloride hexahydrate as solvent, the results approximated to the theoretical value, 18. The present author's experimental results are in approximate agreement with those of Morgan and Benson, but the calculations of the latter observers are erroneous; the value for the molecular weight of water in fused calcium chloride hexahydrate is over 200 in 4% solution. Fused salt hydrates are therefore not suitable solvents for determining the molecular weight of other hydrates by the freezing-point method.

G. S.

cycloHexane as a Cryoscopic Solvent. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 494—498. Compare Abstr., 1907, ii, 602).—The author has investigated the cryoscopic behaviour of a number of compounds of various types dissolved in *cyclohexane*, with the following results.

Normal behaviour is exhibited by methylacetanilide in low concentrations, and also by *p*-dichlorobenzene and *s*-tribromophenol, the last-named being the only hydroxy-compound of those examined which does not show an abnormally high molecular weight in *cyclohexane*.

The following compounds all produce abnormally low depressions of the freezing point of *cyclohexane*: *tert*.- and active amyl alcohols, *sec*- and *iso*-butyl alcohols, menthol, and borneol; camphoroxime, carvonoxime, and acetophenoneoxime; *o*-, *m*- and *p*-cresols, thymol, and phenol; acetone, methyl ethyl ketone, acetylacetone, ethyl acetoacetate, acetophenone, benzophenone, 2-methyl*cyclohexanone*, and 4-methyl*cyclohexanone*; acetic and benzoic acids; nitrobenzene, *o*-, *m*- and *p*-nitrotoluenes, nitromethane, and nitroethane.

The author regards the abnormal behaviour of ketones as due to association, partly of the enolic form and partly of the ketonic form, $R \cdot CO \cdot R$, to the complex, $CR_2 \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix} CR_2$, which is similar to the associated molecules, $O \begin{smallmatrix} \diagup CR(OH) \\ \diagdown CR(OH) \end{smallmatrix} O$, formed by the carboxylic acids, $R \cdot CO_2H$.

Ebullioscopic measurements of solutions of naphthalene, benzil, diphenyl, and phenyl benzoate in *cyclohexane* give the mean value 27.53 for the molecular elevation of this solvent.

T. H. P.

Dependence of the Melting Point of a Solid Substance on its Surface Energy. P. PAWLOFF (*Zeitsch. physikal. Chem.*, 1908, 65, 1—35).—It has been shown by Ostwald and others that the solubility of a solid is the greater the more finely divided it is, and the author now shows, mainly from experiments with salol, that the more finely divided a solid is, the lower is its melting point.

The statement in question was proved by three different methods: (1) Salol, powdered to different degrees of fineness, was spread out on a thin glass plate, heated at definite, gradually increasing temperatures for short periods, and then examined under the microscope. The size of the largest drops was determined with a micrometer eyepiece, and this was taken as a measure of the fusibility of the particles.

Particles of commercial (impure) salol of diameter $8\ \mu$ ($\mu = 0.001\text{ mm.}$) fuse at a temperature 3.5° lower than those of diameter $32\ \mu$. When recrystallised once from methyl alcohol, however, particles of $6\text{--}40\ \mu$ in diameter melt within limits of temperature of 1.5° . (2) Salol was heated at definite intervals of temperature, as in the previous experiments, and observations made of the size of the smallest particles, the edges of which were not altered in appearance by this process. It was found that for a fairly pure (high melting) specimen of commercial salol, particles of size $7\ \mu$ fused 1.1° lower than those of $40\ \mu$. Particles of twice recrystallised salol, however, of diameters $2\text{--}40\ \mu$ fused within 1.1° . (3) When a finely-powdered solid in a thin-walled test-tube is placed in a thermostat, the temperature of which is gradually raised, a mist ultimately appears on the wall of the tube, and the appearance of this mist coincides with the melting point of the smallest particles of the substance. In this way it has been shown that a powder composed of particles less than $2\ \mu$ melts in the case of salol 7° , in the case of antipyrine $5\text{--}7^\circ$, and in the case of phenacetin 4° , lower than particles of diameter $0.5\text{--}2.0\text{ mm.}$

The lowest attainable temperature in the region of fusion is determined by the melting point of the crystalline germ of maximum surface, and larger solid particles above this temperature may be regarded as superheated. Similarly, the supercooling of liquids is a general phenomenon; a liquid supercooled to a definite extent is in equilibrium with solid particles of a definite size, larger particles cause crystallisation, smaller particles dissolve. The limit of supercooling is that temperature below which the crystalline germ can arise of itself in the interior of the liquid. G. S.

Measurement of Very Low Temperatures. XXI. Standardisation of Temperatures by means of Boiling Points of Pure Substances. Determination of the Vapour Pressure of Oxygen at Three Temperatures. H. KAMERLINGH ONNES and C. BRAAK (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 333—341).—The points of a temperature scale fixed by means of the b. p.'s of pure substances have the advantage over those fixed with resistance thermometers and thermo-elements in that they facilitate comparison of thermometers in different laboratories, and do not depend on the durability of special apparatus. The b. p. of oxygen under a pressure of 760 mm., 516.19 mm., and 366.24 mm. at sea-level, and 45° northern latitude, was found to be respectively -182.986° , -186.542° , and 189.442° on the absolute scale (compare Travers, Senter, and Jaquerod, *Abstr.*, 1903, ii, 9; Grunmach, *Abstr.*, 1906, ii, 655). W. H. G.

Determination of Boiling Points of Very Small Quantities of Liquids. L. O'DOWD and F. MOLLWO PERKIN (*Trans. Faraday Soc.*, 1908, 4, 95—98).—The liquid is heated in a small test-tube in a sulphuric acid bath. A small capillary tube, sealed at one end, is placed in the liquid with the open end downward. The whole is heated until bubbles are given off freely from the capillary, and the outer liquid is then slowly cooled. The temperature at which bubbles just cease to be given off is the boiling point. C. H. D.

New Method for Determining Vapour Densities. IV. PHILIP BLACKMAN (*Ber.*, 1908, 41, 4141—4144. Compare Abstr., 1908, ii, 564).—The author describes three forms of an apparatus which is practically a modification of the well-known Hofmann apparatus. A formula for the calculation of the vapour density and a table of results are given. C. S.

Influence of Dissociation on the Vapour Pressure of Solids. ANDREAS SMITS and F. E. C. SCHEFFER (*Zeitsch. physikal. Chem.*, 1908, 65, 70—72).—It has been found by Ramsay and Young (*Phil. Trans.*, 1886, 177, 71) that the vapour pressure of acetaldehyde-ammonia is different when determined by a static and by a dynamic method. If, as seems probable, this is due to the slow attainment of equilibrium, there is here an example of a different pressure-temperature curve for a dissociated and a practically undissociated vapour. On the other hand, the pressure-temperature curves for dissociated and undissociated ammonium chloride coincide, and the authors intend to investigate cases of the first type in order to throw light on the nature of the latter phenomenon. G. S.

Vapourisation. III. HANNS VON JÜPTNER (*Zeitsch. physikal. Chem.*, 1908, 64, 709—726. Compare Abstr., 1908, ii, 810).—Starting with the well-known expressions for the values of the critical constants, p_k , v_k , and T_k , in terms of a , b , R , and T , derived from van der Waals' equation (with certain modifications), a number of other relationships between these factors are deduced, and are employed more particularly to calculate the molecular association and the internal pressure at the critical point for a large number of substances.

If there is molecular association at the critical point, there will not simply be 1 mol. in the volume v_k (as there is in the gaseous volume v under ideal conditions), but n mols., where $1/n$ is the degree of association; hence the general equation $(p + \pi)(v - b) = RT$, where π is the internal pressure, becomes: $(p + \pi)(v - b) = nRT$. The value of n has been calculated for a large number of substances by different methods based on the relationships referred to above, but the agreement is only moderate, partly owing to the uncertainty in the critical data. As a mean of the results, $n = 0.6918$; in other words, the molecular complexity of gases under critical conditions is, in general, about 1.5 times the value under ideal conditions.

Further, the value of π_k , the internal pressure at the critical point, is calculated for a number of monatomic, diatomic, triatomic, and also more complicated substances. As a rule, a_k and b_k increase regularly with the molecular weight, a_k for water being an exception, but for simple compounds containing the same number of atoms, p_k and π_k do not, as a rule, alter greatly with the molecular weight. In complex molecules, however (as shown in homologous series), p_k and π_k diminish with increasing molecular weight. It is also shown that π_0 , the internal pressure at the absolute zero, $= 48p_k$, and the limiting value of π_0 in atmospheres for a number of substances is given.

Finally, certain relations between the latent heat of vaporisation and the internal pressure are deduced. G. S.

Binary Mixtures and Concentrated Solutions. FRIEDRICH DOLEZALEK (*Zeitsch. physikal. Chem.*, 1908, 64, 727—747).—As is well known, the total vapour-pressure curve of binary mixtures belongs to one of three types: it may be a straight line, or may be concave or convex with regard to the axis of composition. It is now shown that the regular form of the curve is a straight line, and that the apparent exceptions occur (1) when one or both of the components is complex, the curve being then concave to the axis of composition, (2) when the components enter into chemical combination, the curve being then convex towards the axis of composition.

The composition of the mixture is expressed as the relative number of mols. of each component present, and not as the relative concentrations by volume. Then, from Nernst's law of partition, the following law is deduced. The partial pressure of each form of substance in the vapour phase is proportional to the molar proportion of it present in the mixture. Hence, if for 1 mol. of one component, n mols. of the other component are present, the respective partial pressures p and π of the components are given by the equations $p = p_0 \cdot 1/(1 + n)$ and $\pi = \pi_0 \cdot n/(1 + n)$, where p_0 and π_0 represent the saturation pressures of the liquefied simple molecules of the two components.

On this basis, comparatively simple formulæ have been derived which give the relationship between the partial and total pressures and the constant for the equilibrium between simple and complex molecules, or between a chemical compound and its components. As an illustration of a system consisting almost entirely of simple molecules which enter into chemical combination, the system acetone-chloroform is considered, and it is shown that a compound is formed containing 1 mol. of each of the components. Further, the formulæ are applied to mixtures of benzene and carbon tetrachloride, the latter substance being partly polymerised, and it is shown that at 50° carbon tetrachloride contains about 15% of double molecules. Similarly, from partial pressure observations of mixtures of ether (simple) and methyl salicylate (complex), it is calculated that at 14° the latter, mixed with 34% by weight of ether, consists to the extent of 70% of double molecules.

The equations in question therefore allow of the determination of the constitution of mixtures and also of pure liquids, and the method is the only one for determining the molecular complexity of liquids which has a satisfactory theoretical basis. However, aqueous solutions, on account of their complexity, cannot readily be dealt with in this way.

The experimental data as to total and partial vapour pressures of binary mixtures, on which the above considerations are based, are mainly due to Zawidski (*Abstr.*, 1901, ii, 6). G. S.

Determination of the Vapour Density of Mixed Liquids. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1335—1337).—The methods of Dumas, Victor Meyer, and Hofmann for determining vapour densities are applicable only to individual liquids, since, with mixtures of liquids with widely varying boiling

points, the high temperature necessary for complete vaporisation is liable to cause decomposition of the constituents with low boiling points. In such a case, the liquid must be fractionated, and the vapour density of the mixture calculated from the proportions and vapour densities of the various fractions. The author has applied this method to several high and low boiling portions of Grosny naphtha, the molecular weights of the fractions being determined by physico-chemical methods, and the heat of vaporisation calculated by means of Trouton's formula. For the naphtha boiling at 100—200°, the vapour density rises, and the heat of vaporisation falls regularly as the boiling point rises. But with the portion boiling below 100°, the fraction b. p. 40—50° exhibits a maximum heat of vaporisation and a minimum vapour density. In this way, it is possible to draw conclusions concerning the presence of individual hydrocarbons in the complex mixtures representing naphthas.

T. H. P.

Catalytic Displacement of Equilibrium in the Vaporisation of Ammonium Chloride, from the Point of View of Thermodynamics. RUDOLF WEGSCHIEDER (*Zeitsch. physikal. Chem.*, 1908, 65, 97—110).—The fact that ammonium chloride has the same vapour pressure in the perfectly dry and in the moist state, (compare Abegg, Abstr., 1908, ii, 157) is only reconcilable with thermodynamics if the solid salt is in different conditions in the two cases. The two states may be polymorphous forms, one being changed into the other under the influence of water vapour. Another possibility is that one form has a greater internal pressure than the other, this being brought about by an alteration of the surface condition of one of the forms under the influence of water vapour. A mathematical discussion of these possibilities is given.

G. S.

Vapour Pressure of the Ammonium Halogen Compounds. FREDERICK M. G. JOHNSON (*Zeitsch. physikal. Chem.*, 1908, 65, 36—40).—The vapour pressures of ammonium bromide and iodide have been determined through a wide range of temperature by the method previously used for the chloride (Abstr., 1908, ii, 157). In the case of the iodide, the results are somewhat complicated by the secondary dissociation of the hydrogen iodide, but as the latter reaction is slow at relatively low temperatures, the error is slight when the measurements are made rapidly.

On the assumption that dissociation in all three cases is complete, the heats of vaporisation have been calculated from the pressure-temperature curve by means of the equation $d(\log p)/dt = Q/2RT^2$. The results are: for ammonium chloride, 37·8 Cal. per mol. between 245° and 345°; ammonium bromide, 45·4 Cal. per mol. between 296° and 394°; ammonium iodide, 44·5 Cal. per mol. between 286° and 392°.

G. S.

Thermochemical Investigations of Organic Compounds: Aliphatic Series. W. SVENTOSLAVSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1257—1323).—The author discusses the theories of Clarke (Abstr., 1903, ii, 8), Lemoult (Abstr., 1904, ii, 310), and Thomsen

(Abstr., 1904, ii, 605) concerning the heats of formation of organic compounds, Thomsen's theory being considered in connexion with the following classes of compounds: paraffins; hydrocarbons containing one or more double linkings; hydrocarbons containing triple linkings; ethers; alcohols; esters; acids; aldehydes, and ketones.

The following are the general conclusions drawn from a consideration of the results obtained for the heats of formation of organic compounds by Thomsen and other investigators, mainly of the French school. The law of the constancy of the heat of formation of atomic linkings formulated by Thomsen does not hold, or, at the most, only applies in the case of molecules containing completely saturated atomic linkings. All the conclusions, such as the equality of the heats of formation of double and single linkings, drawn by Thomsen on the basis of his expression for the heat of formation (which the author considers to be incomplete) must also be regarded as invalid. All hypotheses based on expressions, such as $x + \omega - z - v = A$ and $y + \omega - 2z = B$, given by Thomsen for his constants, must hence be excluded.

Unsaturated linkings are functions of the mass or molecular weights of the compounds. Increase of the molecule always raises the heat effect of the formation of unsaturated linkings or favours their saturation. This influence depends, not only on the molecular weight, but also on the structure of the compound; with all substances in which heavy atoms or radicles are heaped up near the double linking, the heat of formation is influenced very considerably. The heats of formation of atomic linkings retain their special characters quite independently of the chemical characteristics of the compound in which they occur. Thus the heat of formation of the linking C-O in an ether differs from that of the same linking in an alcohol only to the extent to which it is influenced by the presence of heavy radicles.

The author also discusses the mutual influence of several unsaturated linkings, of similar or different structure, in 1 molecule; the deviations from general regularities in the series of aldehydes and ketones, and also in formic and acetic acids; deviations caused by the presence of an amyl group in the various classes of compounds considered; and many other points influencing the heat of formation. T. H. P.

Temperature-coefficient of the Molecular Surface Energy of Equimolecular Mixtures of Aniline and the Three Isomeric Nitrophenols. ROBERT KREMANN and E. PHILIPPI (*Monatsh.*, 1908, 29, 891—894).—From measurements of the density and the capillary rise of the three isomeric nitrophenols, and of equimolecular mixtures of these with aniline at a series of temperatures, the temperature-coefficients of the molecular surface energy have been calculated. The values indicate that the three nitrophenols, and, in particular, the meta-compound, are to some extent associated. The values for the equimolecular mixtures are normal, and from this the conclusion is drawn that the three nitrophenols do not form compounds with aniline in the liquid condition. The normal values indicate, further, that the tendency to association which the nitrophenols exhibit in the free condition is inhibited in presence of aniline. H. M. D.

Tate's Law. THEODOR LOHNSTEIN (*Zeitsch. physikal. Chem.*, 1908, 64, 686—692).—Morgan and his co-workers (Abstr., 1908, ii, 356, 668) have brought forward evidence in favour of the validity of the empirical law proposed by Tate, according to which $G = K2\pi\alpha$, where G represents the weight of a drop falling from a tube of the external diameter $2r$, α is the capillary constant of the liquid, and K is a constant which is the same for all liquids. On the other hand, the author has previously pointed out (*Ann. Physik*, 1906, [iv], 20, 237; 1907, 22, 767) that the weight of a falling drop is not in general proportional to the capillary constant of the liquid; the true relation between these factors is given by the equation $G = 2\pi\alpha f(r/a)$, where $\alpha = \frac{1}{2}a^2\sigma$, σ representing the density of the liquid. It is shown that the experimental data of Morgan and his co-workers are more in accordance with the above formula than with Tate's "law." When r/a varies between 0.3 and 2.0 (the usual limits in practice), the value of $f(r/a)$ only varies from 0.6 to 0.7, so that within these limits Tate's law holds approximately. G. S.

Jones and Allen's "Colour Demonstration of the Dissociating Action of Water." JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1908, 30, 1914—1916).—Jones and Allen (Abstr., 1896, ii, 467) have described an experiment to demonstrate the dissociating action of water. To a few drops of phenolphthalein diluted with alcohol, a little aqueous ammonia is added. On diluting the solution with water, a red coloration is produced, which disappears on adding a further quantity of alcohol. It is now shown that other indicators, namely, litmus, *p*-nitrophenol, and rosolic acid, do not behave in this manner with alcohol, and it is suggested that the decolorisation of phenolphthalein by alcohol is not due to a decrease in the dissociation of the ammonia, but results from a combination of the alcohol with the colourless form of the phenolphthalein. E. G.

Diffusion in Colloidal Media. A. V. DUMANSKI (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 210—212*).—The diminution of area of the cross-section of a solution which results from the presence of a colloidal substance causes a diminution in the rate of diffusion of dissolved substances. The effect is similar to that already found for the diminution of the electrical conductivity of electrolytes in presence of gelatin (compare Abstr., 1907, ii, 841).

If the dissolved substances are soluble in the colloid, this plays a positive part in the diffusion process. An equation is deduced for the general case in which diffusion takes place through the liquid medium and also through the colloidal particles. The experimental data for the diffusion of sodium chloride, sodium sulphide, and methylene-blue through solutions of gelatin and agar-agar indicate that the diffusion of these substances through the colloids takes place very slowly.

H. M. D.

Studies on Capillarity and Adsorption. Method for Determining the Concentration of Dilute Solutions of Mineral Acids. I. HOLMGREN (*Biochem. Zeitsch.*, 1908, 14, 181—208).—When a drop of an aqueous solution of hydrogen chloride (less than

* and *J. Russ. Phys. Chem. Soc.*, 1908, 40, 1579—1583.

1%) is placed on filter or blotting-paper, the acid spreads itself out in the form of a circle, but is always surrounded by a wider circle of water, and the more dilute the original acid solution the greater is the difference in the diameters of the two circles. It is found that for two given solutions the percentages of acid present are in the same ratio as the quotient $\frac{\text{area of paper moistened by acid}}{\text{area of periphery moistened by water}}$.

On this relationship, the author has based a method for determining the concentrations of very dilute solutions of hydrogen chloride when only a very small volume (0.05 c.c.) of the solution is available.

Nitric, sulphuric, and phosphoric acids react in much the same manner, but they are not adsorbed by the paper so readily as hydrochloric acid.

The method of carrying out the determination is to select a blotting-paper of suitable quality, to draw on this a fine line with a 1% solution of Congo-red, and to mark off on this, by fine cross-lines, millimetres. When the drop of acid solution is added, the diameters of the two circles can be read off easily after a short time. The constant K for the paper can be first determined by using solutions of acid of known concentration, and afterwards the concentration of any solution can be calculated by means of the formula: $P = r^2k/R^2 - r^2$, where P = the percentage concentration of the acid, K is the constant for the paper, r is the radius of the acid drop, and R is the radius of the larger drop (acid and water).

The solution should be added slowly from a pipette, so that it does not simply flow over the surface of the paper, but distributes itself by means of capillary attraction.

The actual amounts of liquid used can be varied within limits without affecting the results; as a rule, drops from 6—24 mm. radius were used, but the best results were obtained with a radius of 10—12 mm.

Similar results are obtained when the lower end of a strip of paper is immersed in the solution, and the heights to which the acid and the water rise are measured. The results calculated from the equation $P = h.k/H - h$, where h is the height of the acid and H is the total height to which the water and acid rise, are, however, not so concordant.

Preliminary experiments indicate that in the latter type of experiment the solution of acid in the paper above the solution is more concentrated than the solution in the vessel below. It is shown that the concentration of the solution in the paper is equal to the original concentration of the solution + the constant for the paper: $P_1 = P + K$.
J. J. S.

Nature of Adsorption. HERBERT FREUNDLICH (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 212—220).—A critical consideration of the theories which have been brought forward to account for the phenomena of adsorption. The characteristic phenomena are tabulated, and it is shown that the curves which express the dependence of the quantities of adsorbed substances on the concentration of these in the medium with which the adsorbent is brought into contact, cannot be reconciled with the assumption that the phenomena are regulated

simply by the law of chemical mass action. The fact that the adsorption of chemically very different substances is regulated by the same numerical constants is also unexplainable on any simple chemical theory. On the other hand, the observed facts can be reconciled without difficulty with the view that adsorption is a surface condensation phenomenon. The cause of such surface condensation is supposed to be the differentiation of the layers at the surface of contact of two media in consequence of a modification in the resultant action of the intermolecular forces. The recent measurements by Lewis (Abstr., 1908, ii, 357) of the change of surface tension with the concentration at the surface of contact of an aqueous solution of sodium glycocholate and a hydrocarbon oil, and of the corresponding adsorption, are considered to lend support to the surface condensation theory. The fact that the adsorbed quantities of sodium glycocholate are very much greater than those required by the thermodynamic formula, is attributed to the invalidity of certain assumptions which are involved in the deduction of the formula.

H. M. D.

Robertson's Theory of Adsorption. KARL LANDSTEINER (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 221—224).—In reference to Robertson's paper (Abstr., 1908, ii, 818), the author discusses the applicability of the theory of adsorption to explain the observed facts of immunochemistry.

H. M. D.

Adsorption and its Connexion with Enzyme Action. WILLIAM M. BAYLISS (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 224—226).—A correction of certain statements attributed to the author by Robertson (Abstr., 1908, ii, 818), and a criticism of the latter's attempt to explain adsorption phenomena on the basis of the law of mass action.

H. M. D.

Adsorptive Power of the Hydroxides of Silicon, Aluminium, and Iron. PAUL ROHLAND (*Zeitsch. anorg. Chem.*, 1908, 60 366—368. Compare Abstr., 1907, ii, 957).—Dry, finely-powdered clay, after agitating with solutions of alkali carbonates, removes all carbonate ions from the solution. Other ions are not removed in the same way. The disappearance is attributed to the colloidal dissolution and subsequent coagulation of metallic hydroxides from the clay, followed by adsorption.

C. H. D.

Freezing of Hydrosols. ALFRED LOTTERMOSER (*Ber.*, 1908, 41, 3976—3979. Compare Abstr., 1907, ii, 851).—Recently prepared hydrosols of silicic acid or of ferric hydroxide which contain an appreciable quantity of ions do not become flocculent by freezing and subsequent thawing, and their specific conductivity remains unchanged. If submitted to dialysis before freezing, gelatinisation does occur, and the more readily the smaller the ionic concentration becomes; the specific conductivity diminishes, *pari passu*, with the elimination of the electrolyte, becomes nil, and finally begins to increase again. These results serve to explain the behaviour of liquor ferri dialysati,

aluminium acetate, and sodium silicate (compare Bobertag, Feist, and Fischer, Abstr., 1908, ii, 1024).

In the author's opinion the precipitation of a colloid by the freezing of its hydrosol is conditioned by the complete solidification of the solution to a crystalline mass. This is true, not only with sols, but also with certain (apparently) dry gels. For example, the gel of silicic acid, dried as completely as possible between filter paper, is cooled for a long time in ice and salt, and then brought to the ordinary temperature, when a large quantity of water separates, and small, apparently crystalline, glistening leaflets form on the walls of the vessel. The author conceives, and intends to test, the theory that the enormous pressure exerted by the water in solidifying causes the particles of the colloid to arrange themselves between the faces of the ice crystals, whereby they assume a leaf-like structure. C. S.

Freezing of Hydrosols. ALEXANDER GUTBIER and FERDINAND FLURY (*Ber.*, 1908, 41, 4259—4260. Compare Abstr., 1902, ii, 653; 1904, ii, 613; Bobertag, Feist, and Fischer, Abstr., 1908, ii, 1024; Lottermoser, preceding abstract).—The authors do not agree with Lottermoser's conclusion that the formation of gel from a hydrosol by the process of freezing depends on the complete solidification of the mass. J. J. S.

Solubility in Mixed Solvents. VII. WALTER HERZ and F. KUHN (*Zeitsch. anorg. Chem.*, 1908, 60, 152—162. Compare Abstr., 1908, ii, 569).—The solubility of mercuric chloride, bromide, iodide, and cyanide, of potassium iodide, of sodium bromide and iodide, and of ammonium chloride and bromide, has been determined in mixtures in varying proportions of methyl and propyl alcohols, of ethyl and propyl alcohols, and (when not previously measured) of methyl and ethyl alcohols, as well as in the pure solvents, at 25°, and the results are given in tabular form. The density and viscosity of the solutions have also been determined.

The solubility in the pure solvents diminishes as the molecular weight of the alcohol increases.

For mixtures of ethyl and propyl alcohols, the observed values are in all cases within 10% of those calculated on the assumption that the components exert their effect independently. For the mixtures of which methyl alcohol is a component, however, the difference between the observed and calculated values is greater than 10% in ten cases out of eighteen. The deviations are greatest for potassium iodide, ammonium chloride, mercuric chloride, and mercuric cyanide, and may be positive or negative. It is known that mercuric chloride enters into chemical combination with methyl alcohol, but the cause of the deviation from additive behaviour in the other cases is not known. G. S.

Influence of Substitution in the Components on the Equilibrium of Binary Solutions. III. ROBERT KREMANN [with ERWIN BENESCH, WILLY DECOLLE, P. DOLCH, K. KAAS, F. PILCH, and F. SCHERENZISS] (*Monatsh.*, 1908, 29, 863—890. Compare Abstr., 1906, ii, 268).—The freezing-point curves for mixtures of benzene and phenanthrene

with isomeric di- and tri-nitrobenzenes and di- and tri-nitrotoluenes have been determined.

According to these, benzene does not form compounds with any of the isomeric dinitrobenzenes, nor with 1:2:4-, 1:2:6-, and 1:3:4-dinitrotoluene.

No compounds are formed by phenanthrene with *o*- and *m*-dinitrobenzene, but with *p*-dinitrobenzene the freezing-point curve indicates the formation of a compound containing 3 mols. of phenanthrene and 1 mol. of *p*-dinitrobenzene. The curve corresponding with the compound extends from 70 to 77 mols. % phenanthrene, and is limited by eutectics at 79.5° and 79° respectively.

With the above trinitrotoluenes, phenanthrene yields no compounds, but with trinitrobenzene and trinitrotoluene, compounds containing equimolar quantities of the components are indicated by the curves. The compounds melt respectively at 125° and 87.5°. In the case of trinitrobenzene, the curve for the compound extends from 17 to 84.5 mols. % phenanthrene, the corresponding eutectic temperatures being 104° and 85.5°.

In the case of trinitrotoluene, the curve for the compound extends from 18 to 70 mols. % phenanthrene, the eutectic temperatures being 69° and 70°.

A comparison of the results with those previously obtained for naphthalene leads to the conclusion that of the hydrocarbons with one, two, and three benzene rings, naphthalene most readily yields compounds with the dinitro-benzenes and -toluenes. H. M. D.

Chemical Affinity. III. Solution-affinity of Binary Systems.

I. Theoretical. J. N. BRÖNSTED (*Zeitsch. physikal. Chem.*, 1908, **64**, 641—656. Compare Abstr., 1906, ii, 339, 834).—A mathematical paper. The phenomena of miscibility, like those of chemical combination, are very closely related to the thermal constants of the system.

In the first place, equations representing the relations between the solution-affinity, A , and the concentration, and between the heat given out on mixing, U , and the concentration for binary mixtures, are deduced, and the relative positions of the A and U curves are shown. Equations are then obtained showing the variation of the heat of admixture and the solution-affinity respectively with the temperature.

The solution-affinity may be represented by the equation:

$$A = a + bT - bT \log_e T - cT^2 - \frac{1}{2}dT^3 - \dots + kT,$$

where k is the affinity-constant of admixture. For "ideal" solutions (in which $U=0$), both dilute and concentrated, the differential affinity constants k_1 and k_2 , for the two components are given by the equations $k_1 = -R \log_e x$ and $k_2 = -R \log_e (1-x)$ respectively, where x represents the concentration of one of the components in unit quantity of the mixture. The case of non-ideal solutions, when U is not zero, is then considered, and it is shown that the separation of a homogeneous solution into two layers with increase of temperature is to be expected when the heat-capacity increases when solution takes place. Finally, formulæ are given showing how the solution-affinity

may be deduced from measurements of the partial vapour pressure of the components, from measurements with galvanic cells, and also from the freezing-point curves with the help of thermal data.

The application of these results to concrete cases will be made in a subsequent paper. G. S.

Determination of the Rate of Chemical Change by Measurement of the Gases Evolved. F. E. EVERARD LAMPLOUGH (*Proc. Camb. Phil. Soc.*, 1908, 14, 580—608).—A more detailed account of work which has already been published (*Proc.*, 1906, 22, 280; 1908, 24, 29). W. H. G.

Formation and Decomposition of Ammonia by the Silent Electric Discharge in a Siemens Tube, with Particular Reference to the Validity of the Law of Mass Action. JOHN H. DAVIES (*Zeitsch. physikal. Chem.*, 1908, 64, 657—685).—The greater part of the work described in this paper has already been published (*Le Blanc and Davies, Abstr.*, 1908, ii, 653. Compare Pohl, *ibid.*, 819). The velocity constant for the decomposition of ammonia is approximately a linear function of the current strength. The velocity of decomposition is practically independent of the frequency of the alternating current.

Starting with a mixture of nitrogen and hydrogen in the ratio 1 : 3 by volume, the equilibrium mixture contains 3% of ammonia, that is, 6% of the possible amount of ammonia is formed, and the same equilibrium point is reached on starting with pure ammonia. The maximum amount of ammonia at equilibrium is obtained when the gases are taken in the above ratio. The rate of formation falls off very rapidly, in other words, the greater part of the ammonia is formed during the first period of passing the current. The velocity of formation increases somewhat with increase in the current-strength. G. S.

The System Water, Ammonium, Barium, and Cupric Chlorides. FRANS A. H. SCHREINEMAKERS (*Chem. Weekblad*, 1908, 5, 847—852. Compare *Abstr.*, 1908, ii, 1020).—The author has employed his method of representing a quaternary system by means of a regular tetrahedron to represent the system water, ammonium, barium, and cupric chlorides. He finds that double salts sometimes behave as though they contained a single component, and sometimes as though they were composite. A. J. W.

Induction by Ferrous Salts of Interaction of Chromic and Hydriodic Acids. ROSS A. GORTNER (*J. Physical Chem.*, 1908, 12, 632—646).—A continuation of the work of Benson (*Abstr.*, 1904, ii, 316).

The rate of liberation of iodine is reduced by the presence of an alkali chloride, bromide, or fluoride, but the ferrous iron is more rapidly oxidised in presence of the halogen salt. Alkali sulphates, and also agar-agar, have no effect on the velocity; egg-albumin and

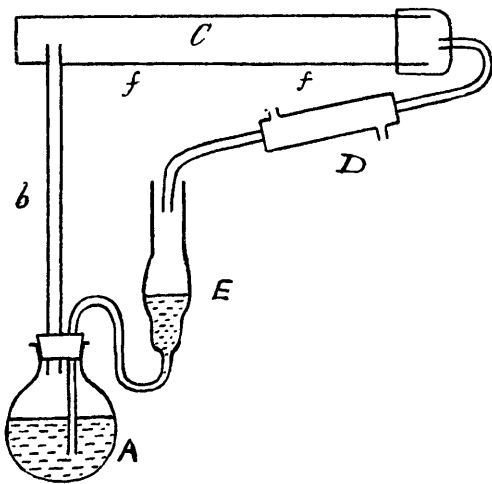
colloidal ferric hydroxide somewhat reduce it, and ferric salts have a marked retarding effect.

The liberation of iodine at 0° is more rapid than at 30° , because the ferrous salt is more rapidly oxidised at the latter temperature: The influence of concentration of various reagents is held to support the view that both Fe^{++} and FeI^{++} are undergoing oxidation in the solution.

R. J. C.

An Improved Method of Esterification. G. E. GIBSON (*Proc. Roy. Soc. Edin.*, 1908, 28, 703—704. Compare *Abstr.*, 1905, i, 852).—The author describes an apparatus whereby the method of preparing esters described by Taylor (*loc. cit.*) is rendered a continuous process.

C is a wrought iron tube 50 cm. long and of 5 cm. internal diameter; it is closed at one end, and fitted at the other end with a screw cap, which carries a tube connexion to the condenser, *D*. The condenser tube fits loosely into a glass syphon, *E*, of capacity about 150 c.c., the lower end of which passes through a cork and terminates well under the liquid contained in flask *A*. *C* and *A* are connected by the tube *b*, which projects about 1 cm. into *C*. All the joints, with the exception of *D* to *E*, are air-tight. The tube *C* is loosely packed with lumps of quicklime, and *A* is charged with the acid to be esterified, mixed with excess of alcohol, about 100 c.c. of benzene, and a few drops of concentrated hydrochloric acid. Two small gas flames are placed at *f, f*, and when the tube *C* is heated sufficiently to prevent condensation of alcohol or benzene, the flask *A* is heated on a steam-bath. As the liquid in *A* boils, the vapour of the ternary mixture, alcohol, benzene, and water (b. p. 68°), passes into *C* where it is deprived of the water, whilst the mixed vapour of alcohol and benzene pass on, are condensed by *D* and returned to the flask by the syphon *E*.



It is claimed that this method is applicable to all cases where Taylor's method may be used, and, as an indication of the efficiency of this process, figures are given showing that pure ethyl tartrate may be prepared in quantities which are more than 90% of the theoretical yield.

J. V. E.

Kinetics of the Formation and Saponification of the Esters of Nitrous Acid. WALDEMAR M. FISCHER (*Zeit. ch. physikal. Chem.*, 1908, **65**, 61—69).—Ethyl nitrite reacts so rapidly with water that the rate of reaction cannot be measured. In very dilute aqueous solution, when hydrolysis is complete (1 mol. in 500 litres), the nitrous acid in the ester can therefore be titrated like the free acid. The equilibrium mixture of acid, alcohol, ester, and water contains very little ester; $K = [\text{alcohol}][\text{acid}]/[\text{ester}][\text{water}]$ is about 0.012 at 0°. The rapid formation of ethyl nitrite in aqueous solution is partly conditioned by the relative insolubility of the ester in water, and its consequent removal from the system.

The velocity of saponification of ethyl nitrite by alkalis, both in aqueous and absolute alcoholic solution, is of the same order as that of other esters. It is hydrolysed by sodium hydroxide in aqueous solution about three times as rapidly as ethyl acetate under corresponding conditions, and about one-tenth as rapidly as the latter by sodium ethoxide in absolute alcohol.

The mechanism of ester formation in this case is discussed. Although the reaction is very rapid, it is probably not an ionic reaction, but proceeds through the formation of an unstable intermediate compound of acid and ester (Baeyer and Villiger).

G. S.

Esterification. I. Victor Meyer's Esterification Law. MARTIN A. ROSANOFF and W. L. PRAGER (*J. Amer. Chem. Soc.*, 1908, **30**, 1895—1907).—In accordance with Victor Meyer's law (*Abstr.*, 1894, i, 463), aromatic acids, in which both positions next to the carboxyl group are occupied by substituting groups, cannot be esterified by means of alcohol and acid. It has been found, however, that such acids can be readily esterified by simply heating them at high temperatures with ethyl alcohol, or even by prolonged warming at the temperature of the water-bath. The esterification law must therefore be modified as follows: "Aromatic acids with one or both positions next to the carboxyl occupied by substituting groups combine with alcohols more slowly, although to no less extent, than acids otherwise constituted."

A form of the mass law is presented in which the volumes of the reacting substances are taken into account, and is recommended for employment in kinetic studies generally.

The equilibrium and velocity constants of the esterification of several acids by ethyl alcohol have been determined, with the following results. Acetic acid, at the ordinary temperature, $K=4$, $k=0.00061$; 2:4:6-trichlorobenzoic acid, at 183°, $K=0.105$, $k=0.031$; 2:4:6-tribromobenzoic acid, at 183°, $K=0.42$, $k=0.088$; 2:3:5-tribromobenzoic acid, at 183°, $K=0.12$, $k=0.37$; 3:4:5-tribromobenzoic acid, at 183°, $K=0.30$, $k=0.90$; benzoic acid, at 183°, $K=0.40$, $k=0.63$. From these results, it is seen that the velocity constant of 2:4:6-tribromobenzoic acid is about one-fourth of that of the 2:3:5-tribromo-acid, and one-tenth of that of the 3:4:5-tribromo-acid. The steric hindrance hypothesis is shown to be untenable by the fact that the velocity constant of the di-ortho-substituted

trichlorobenzoic acid, instead of being greater, is much smaller than that of the corresponding tribromo-acid.

2 : 3 : 5-Tribromobenzoic acid, m. p. 193.5°, forms yellow crystals.

E. G.

Esterification. II. W. L. PRAGER (*J. Amer. Chem. Soc.*, 1908, 30, 1908—1914).—Rosanoff and Prager (preceding abstract) have shown that Victor Meyer's steric hindrance hypothesis and esterification law are untenable.

This conclusion is now confirmed by a study of the esterification of α -nitrophthalic acid with ethyl alcohol at 183°, which has given $K=1.58$ and $k=0.20$.

The investigation has been extended to aliphatic acids, and the following values have been obtained at 183°. Acetic acid, $K=4.0$, $k=1.48$; propionic acid, $K=2.24$, $k=0.95$; isobutyric acid, $K=2.10$, $k=10.7$; α -dimethylpropionic acid, $K=2.0$, $k=0.18$. The following values of k are derived from an application of the mass laws to Lichty's results (*Abstr.*, 1896, ii, 557) on the esterification of the chloroacetic acids at 80°. Chloroacetic acid, 2.46; dichloroacetic acid, 6.38, and trichloroacetic acid, 12.0. These results do not accord with the steric hindrance hypothesis. *iso*Butyric acid undergoes esterification more rapidly than propionic acid, whereas the reverse should be the case. Moreover, the velocity constants of the chloroacetic acids, even at 80°, are greater than that of acetic acid at 183°, and increase with the number of chlorine atoms near the carboxyl group, which is in direct opposition to the requirements of the steric hindrance hypothesis.

The electric dissociation constants of these acids are quoted, and it is shown that an increase in the esterification constants is accompanied by an increase in the dissociation constants.

It is shown that the large differences between the esterification constants of mono-ortho-substituted aromatic acids and those of acids with the two ortho-positions free, enable a separation of acids of the former class from other acids to be effected by a process of esterification.

E. G.

Esterification, Hydrolysis of Esters, and Formation of Salts with Arylacetic Acids and Some of their Derivatives. JOSEPH GYR (*Ber.*, 1908, 41, 4308—4322. Compare Sudborough and Feilmann, *Proc.*, 1897, 241; Sudborough and Lloyd, *Trans.*, 1898, 73, 81; 1899, 75, 467; Menshutkin, *Abstr.*, 1881, 883).—The work of Bistrzycki and his pupils has resulted in the convenient preparation of tertiary aromatic acids. The introduction of phenyl groups into acetic acid decreases the strength of the acid, unlike the introduction of chlorine, which increases the strength. Further, these substituted acetic acids are more difficult to esterify, and the inquiry was instituted in the hope that a systematic comparison of the different arylacetic acids would throw some light on these properties. Methyl alcohol was chosen, as Menshutkin has already shown that the velocity of esterification at the start of the reaction is greater than with the others (this *Journ.*, 1877, ii, 865; *Abstr.*, 1879, 36). The alcohol was

carefully dehydrated over calcium (this vol., i, 2), as traces of water depress the constant. The solution was $N/10$ both as regards organic acid and the catalytic hydrochloric acid, the temperature employed was 25° , and the constant determined from the equation $K = 1/t \log a/a - x$. Acetic acid was esterified 50% during two minutes, phenylacetic acid during five minutes, diphenylacetic acid in one and a-half hours, and triphenylacetic acid not even after one hundred hours. Below are given the constants found during the inquiry, the initial constant being in all cases higher than those found later in the experiment.

	K .		K .
Acetic acid.....	7.758	Chloroacetic acid	2.355
Phenylacetic acid	3.566	Phenylchloroacetic acid	0.445
Diphenylacetic acid	0.202	p -Tolylacetic acid	3.752
Triphenylacetic acid	0.000503	Phenyl- p -tolylacetic acid	0.221
p -Hydroxyphenylacetic acid..	3.979	Diphenyl- p -tolylacetic acid...	0.000175
p -Hydroxydiphenylacetic acid	0.205	Glycollic acid	9.859
p -Hydroxytriphenylacetic acid	0.000339	Mandelic ,,	3.098
		Benzilic ,,	0.0177

In every instance there is a very large decrease in the esterification constant when the phenyl group is introduced.

The hydrolysis of the esters was carried out in methyl alcohol distilled over sodium, as Kremann has shown that small quantities of water have only a slight effect on the hydrolysis constant (Abstr., 1905, ii, 307). The solutions again used were $N/10$; $aK = 1/t X/a - X$.

	aK .		aK .
Methyl acetate	0.0102	Methyl triphenylacetate	—
„ phenylacetate	0.0178	„ diphenyl- p -tolylacetate	—
„ diphenylacetate	0.0031		

The introduction of one phenyl residue actually raises the constant; the triaryl esters are very stable.

The following salts of triphenylacetic acid have been prepared: the ammonium, $C_{20}H_{19}O_2N, 1\frac{1}{2}H_2O$?, easily hydrolysed by water, potassium, $C_{20}H_{15}O_2K, 1\frac{1}{2}H_2O$, barium, strontium, and copper. The ammonium, $C_{21}H_{21}O_2N, H_2O$, sodium, potassium, barium, and lead salts of diphenyl- p -tolylacetic acid have also been obtained.

A convenient method of preparing phenyl- p -tolylacetic acid by condensing mandelic acid and toluene in the presence of tin tetrachloride is described.

W. R.

Chemical Composition of Matter. EDUARD MULDER (*Rec. trav. chim.*, 1908, 27, 418).—It is suggested that Daltonian atoms contain smaller atoms, that the latter are again composite, and so on indefinitely. The final, infinitely small atoms are supposed to be beyond conception.

R. J. C.

Explanation of the Periodic System of the Elements on the Basis of the Electron Theory. HUGO STRACHE (*Ber. deut. physikal. Ges.*, 1908, 6, 798—803).—A theoretical paper in which an

attempt is made to explain a large number of different phenomena on the assumption that the atoms are aggregates of corpuscles which are identical with electrons and with the particles which constitute the ether. The distance separating two corpuscles determines the nature of their mutual action, that is to say, whether they attract or repel one another. The nature of the action of an atomic aggregate on the ether particles is supposed to determine the electro-positive or -negative character, the valency, and other properties of the atoms. Corresponding with the periodic system, the nature of this mutual action varies in a periodic manner as the atomic aggregates increase in complexity.

H. M. D.

New Periodic Function of the Atomic Weight. VIKTOR PÖSCHL (*Zeitsch. physikal. Chem.*, 1908, 64, 707—708).—When the proportions of the elements present on the earth are plotted against their respective atomic weights, a periodic curve is obtained.

G. S.

Filter Holder. ROBERT HANSEN (*Chem. Zentr.*, 1908, ii, 1145; from *Apoth. Zeit.*, 1908, 23, 652).—An arrangement is described for holding the folded filter paper in a funnel so as to leave a free space of about 6 mm. between the holder and the funnel. It is made of tinned iron with an aperture at the bottom for the filtrate to flow through, and will fit all kinds of funnels. Besides hastening filtration, it obviates the necessity of accurately folding the filter paper to fit a particular funnel.

J. V. E.

Filter Funnel and Funnel Strainer. ERNST PESSLER (*Chem. Zentr.*, 1908, ii, 1145; from *Apoth. Zeit.*, 1908, 23, 659).—The author describes a conical aluminium filter-paper holder to be placed in the ordinary funnel; it is perforated from the apex to the rim at the top by small holes, and has, in addition, several points which rest on the funnel and keep a space of about $\frac{1}{2}$ -cm. between the funnel and the strainer.

The aluminium funnel strainer described is made with a bevel edge so as to fit closely to the funnel; it is perforated by one millimetre holes, and is designed to replace the older form, in which the sieve is soldered to the funnel.

J. V. E.

A Stirrer for Vacuum-Distillation Flasks. H. SÜCHTING (*Zeitsch. anal. Chem.*, 1908, 47, 755—756).—The stirrer is constructed as follows: A glass tube, 5 mm. in diameter and about 850 mm. in length, is fixed through the rubber stopper closing the neck of the flask, the lower end of the tube projecting about 50 mm. below the stopper. A wide tube about 100 mm. in height is fixed to the long tube just above the stopper, and the space between the two is partly filled with mercury. A second long tube is passed over the first, its lower end dipping in the mercury, and its upper end being fixed by means of a piece of rubber tubing to a glass rod passing down the centre of the first tube into the flask; at the bottom of the rod is fixed a stirring device. Short pieces of tubing held in clamps serve

as bearings for the outer long tube, and the latter is rotated together with the rod by means of a pulley and motor. When the air is exhausted from the flask, the mercury rises in the space between the two tubes until the barometric height is reached. W. P. S.

Distillation and Rectification of Alcohol. (Lecture Experiment.) EDUARD DONATH (*Chem. Zentr.*, 1908, ii, 1001—1002; from *Zeitsch. chem. Appar.*, 1908, 3, 360—362).—Beer containing 3 to 4% of alcohol is boiled in a flask and the vapour led by means of a tube into a second flask, where a liquid condenses having 12 to 15% of alcohol; if a third flask is attached to the second one in a similar manner so as to condense the issuing vapour, a spirit is obtained of sufficient strength to burn. The principle of rectifying spirit is also shown by having as a condenser a series of copper vessels with outside copper jackets, so that water at various temperatures may be made to circulate round them. A third form of apparatus for demonstrating this process is described, where the vapour from boiling beer or other dilute spirituous liquid is led into a condensation vessel from which vapour still passes on through a tower fitted with frequent layers of metallic gauze, thence through a series of water-cooled bulbs, and, finally, the issuing vapour is condensed. A liquid containing 58 to 60% vol. of alcohol is obtained by this method. J. V. E.

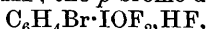
Inorganic Chemistry.

Hydrate of Iodine Oxyfluoride, Fluoroiodates, and Iodoxyfluorides. RUDOLF F. WEINLAND and FERDINAND REISCHLE (*Zeitsch. anorg. Chem.*, 1908, **60**, 163—172. Compare Weinland and Lauenstein, *Abstr.*, 1899, ii, 363).—*Iodine oxyfluoride hydrate*, $\text{IOF}_3 \cdot 5\text{H}_2\text{O}$ or $\text{IF}_3(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, is obtained in colourless needles by dissolving iodic acid in a solution of hydrofluoric acid in glacial acetic acid and evaporating. The same compound, contaminated with iodine, is obtained when alcohol is used as solvent. The crystals fume in the air, giving off hydrogen fluoride.

Four salts containing pyridine have also been prepared. When 1 mol. each of iodic acid and pyridine are dissolved in an acetic acid solution of hydrofluoric acid and the solution evaporated over sulphuric acid, *pyridine trifluoroiodate*, $\text{IF}_3(\text{OH})_2 \cdot \text{C}_5\text{NH}_5$, separates in colourless, prismatic needles. When a concentrated aqueous solution of this salt is allowed to crystallise slowly, *pyridine difluoroiodate*, $\text{IF}_2\text{O}(\text{OH}) \cdot \text{C}_5\text{NH}_5$, is obtained in colourless crystals. When the pyridine salt first mentioned is dissolved in a mixture of hydrofluoric acid and glacial acetic acid, and 1 mol. of iodic acid is added, *pyridine pentafluorodiiodate*, $\text{IF}_2\text{O}(\text{OH}) \cdot \text{C}_5\text{NH}_5 \cdot \text{IOF}_3 \cdot \text{H}_2\text{O}$, is obtained. Finally, from a solution of 2 mols. of iodic acid, 1 mol. of

pyridine, and excess of hydrofluoric acid in alcohol, *pyridine heptafluorodi-iodate*, $\text{IF}_4(\text{OH})\cdot\text{C}_5\text{NH}_5\cdot\text{IOF}_3$, is obtained in colourless needles. All the pyridine salts are stable in air.

The following five compounds are obtained by dissolving the corresponding iodo-compounds (iodobenzene and the iodotoluenes) in very concentrated alcoholic hydrofluoric acid. *Phenyl iodoxyfluoride hydrofluoride*, $\text{C}_6\text{H}_5\cdot\text{IOF}_2\cdot\text{HF}$, the *p*-bromo-derivative,



and *o*-, *m*-, and *p*-*tolyl*iodoxyfluoride hydrofluoride, $\text{C}_6\text{H}_4\text{Me}\cdot\text{IOF}_2\cdot\text{HF}$, all form colourless crystals, which readily give up hydrogen fluoride. The compound, $\text{IOF}_3\cdot\text{C}_6\text{H}_5\cdot\text{IOF}_2$, separates in colourless needles from a solution of 1 mol. of iodobenzene and 3 mols. of iodic acid in alcoholic hydrofluoric acid; it is readily decomposed by water. G. S.

Ozone. III. STEPHAN JAHN (*Zeitsch. anorg. Chem.*, 1908, **60**, 292—336. Compare Abstr., 1905, ii, 16; 1906, ii, 292).—The sources of error in measurements of the electrical potential of ozone are discussed. The velocity of rotation of the electrode is without influence, and the anomalies are therefore not to be explained by diffusion (compare Luther and Inglis, Abstr., 1903, ii, 406). The effect is shown to be probably due to the adsorption of ozone by platinum.

Measurements of potential were made against hydrogen with platinum electrodes in sulphuric acid, with and without the addition of cobaltic sulphate. The results show that over the interval where Co''' forms 2.5—8.0% of the total Co, the potential of the cell corresponds closely with that required by the ratio $\text{Co}''' : \text{Co}''$. When $\text{Co}'''/\text{Co}'' = 1$, the potential is 1.785 volt, a value employed in calculating the ozone potential.

The *E.M.F.* of a cell in which the reaction $\text{O}_3 + \text{H}_2 = \text{H}_2\text{O} + \text{O}_2$ occurs, is probably 1.90 volt at 0° .

An equation is given by means of which the temperature-limits of stability of ozone may be determined, derived from the Gibbs-Helmholtz equation, but the uncertainty of the values for potential and for specific heat is so great that no accurate calculation can be made. It appears, however, that ozone should be formed from oxygen by the action of heat alone in quite measurable quantity at a temperature of 2000° (compare Fischer and Marx, Abstr., 1906, ii, 224, 606).

C. H. D.

Ozone. IV. STEPHAN JAHN (*Zeitsch. anorg. Chem.*, 1908, **60**, 337—357. Compare preceding abstract).—The development of heat in the decomposition of ozone has been measured by a method similar in principle to that of van der Meulen's, soda-lime being employed as catalyst, and a current of ozonised oxygen of constant composition led through the calorimeter. The catalyst was contained in a glass tube connected with a copper spiral tube in a vacuum-jacketed vessel.

The heat of dissociation of ozone is found to be 34,100 cal. per gram-molecule, with a probable error of 1%. C. H. D.

Investigation of the System : Sulphur-Iodine. F. OLIVARI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 512—521).—The freezing-

point curve of mixtures of sulphur and iodine is of the type of a cryohydric curve, the eutectic point, corresponding with 80.8 atom % of sulphur, being at 65.7°. The formation of compounds by fusion of these two elements is hence excluded, the supposed melting point of the two iodides, S_3I_2 and S_2I_2 , being the cryohydric point.

Cryoscopic measurements of sulphur dissolved in iodine show that the molecular weight has the value 256, corresponding with S_8 in dilute solution, but increases as the concentration is raised; there is therefore no isomorphism between the two elements. The specific volume curve for mixtures of sulphur and iodine is a straight line joining the specific volumes of the two elements. The supposed iodides, S_3I_2 and SI_6 , obtained by crystallisation from solution, are mechanical mixtures of sulphur and iodine, as also is probably the iodide, S_3I_2 .
T. H. P.

Absolute Sulphuric Acid: its Preparation from Sulphur Trioxide and Water: its Specific Electrical Conductivity and that of more Dilute Acid. DAVID M. LICHTY (*J. Amer. Chem. Soc.*, 1908, 30, 1834—1846).—During a study of the decomposition of oxalic acid by sulphuric acid (Abstr., 1907, ii, 445), it was observed that the rate of decomposition was decreased to a surprising extent by the addition of only 0.01% of water to sulphuric acid supposed to be of 100% strength. Since analytical methods are not sufficiently accurate to determine the presence of very small quantities of water, recourse was had to determination of the specific electrical conductivity of the acid. This method, however, could not serve to establish the composition of the acid, since the exact conductivity of any one concentration was not known.

A method has therefore been devised for the preparation of absolute sulphuric acid by the direct interaction of sulphur trioxide and water in stoichiometrical proportions. The specific conductivity of the acid obtained in this way has been determined at 25°, and found to be 0.01041 reciprocal ohm, which is also the minimum specific conductivity of concentrated sulphuric acid. It has also been found that the maximum f. p. of concentrated sulphuric acid is identical with the f. p. of the absolute acid, namely, 10.43—10.45°. It is proved, therefore, that the preparation of absolute sulphuric acid may be based on the minimum specific conductivity and on the maximum f. p.

It is shown that, for acid of not less than 95% strength, the results of analysis by means of conductivity determinations are accurate to within 0.01%. A table of specific conductivities is given, which may be used for analytical purposes.
E. G.

Mixed Anhydrides of Sulphuric Acid. AMÉ PICTET and GEORGES KARL (*Bull. Soc. chim.*, 1908, [iv], 3, 1114—1126; *Arch. sci. phys. nat.*, 1908, 26, 437—454).—In preparing the mixed anhydride of nitric and sulphuric acids, $(SO_3)_4N_2O_5$, already described (Abstr., 1907, ii, 758), there is also formed some *sulphonitrous anhydride*, $(SO_3)_5(N_2O_3)_2$, m. p. 198—200°, b. p. 302—305°/728 mm., which is better prepared by dissolving sulphur trioxide and nitrogen trioxide separately in carbon tetrachloride and mixing the two solutions. It

is a hard, colourless substance crystallising in needles. Its properties are very similar to those of the nitryl tetrasulphate described previously, and, like the latter, it gradually liquefies, but does not fume in moist air. Since Provostaye's nitrosyl sulphate (*Ann. Chim. phys.*, 1840, [ii], 73, 362) has m. p. 217—230° and distils at 360°, according to various authors, it is suggested that it cannot have the formula, $(\text{SO}_3)_2\text{N}_2\text{O}_3$, generally assigned to it, but should probably be represented as $(\text{SO}_3)_6(\text{N}_2\text{O}_3)_3$.

D'Arcy's observation (*Trans.*, 1889, 55, 157), that boron and sulphur trioxides do not combine when heated together in open vessels, is confirmed, but combination takes place when the operation is carried out in a closed vessel, *boryl sulphate*, $\text{SO}_2(\text{Q}\cdot\text{BO})_2$, being formed at 115—120°, *boryl disulphate*, $(\text{SO}_3)_2\text{B}_2\text{O}_3$, at 230°, and mixtures of the two at intermediate temperatures. Both are colourless, amorphous, bulky, brittle, hygroscopic substances, which have no definite melting point, do not fume in moist air, but dissociate when heated, leaving eventually residues of boron trioxide. They dissolve in water, yielding solutions of boric and sulphuric acids. Boryl disulphate reacts with alcohol to form alkyl borates and alkyl-sulphuric acids. In the last respect, its behaviour differs somewhat from that of other mixed anhydrides (compare Friedel and Ladenburg, *Compt. rend.*, 1865, 64, 84; Pictet and Geleznoff, *Abstr.*, 1903, i, 309, 601; Pictet and Bon, *Abstr.*, 1906, i, 3).

When chromium trioxide and sulphur trioxide are heated in closed tubes at 75° or at a higher temperature, a yellow mass of the *mixed anhydride*, $\text{SO}_3\cdot\text{CrO}_3$, is formed, together with some chromium sesquioxide, from which it could not be separated.

T. A. H.

Molecular Weight of Selenium. F. OLIVARI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 389—391).—Cryoscopic measurements of solutions of selenium in iodine (compare Timmermans, *Abstr.*, 1906, ii, 429) give for the molecular weight of selenium the values 150·2—167·7, the number calculated for Se_2 being 158·4; thus selenium has the molecular weight corresponding with Se_{10} at 4° (compare Beckmann, *Abstr.*, 1904, ii, 235), with Se_8 at 42° (compare Beckmann and Pfeiffer, *Abstr.*, 1897, ii, 363), and with Se_2 at 113·9° (compare also Pellini and Pedrina, *Abstr.*, 1908, ii, 833). T. H. P.

Volumetric Composition of Gaseous Ammonia and Atomic Weight of Nitrogen. PHILIPPE A. GUYE and A. PINTZA (*Compt. rend.*, 1908, 147, 925—928).—Ammonia prepared from pure ammonium chloride and lime was decomposed by a hot platinum wire, and the nitrogen and hydrogen obtained were passed, after purification, into a vacuum vessel of about $3\frac{1}{2}$ litres capacity until the pressure was about one atmosphere at 0°. The loss in weight of the complete generating apparatus being known, the weight and density of the mixed gases could be calculated. One litre of the mixed gases at 0° and 760 mm. was found to weigh 0·37989 gram when corrected for traces of sulphur dioxide and trioxide. Knowing the densities of hydrogen and nitrogen, and making allowance for their slight expansion on mixing, the volumetric ratio of nitrogen to hydrogen in ammonia is 1:3·00172. It follows that the atomic weight of nitrogen is 14·014 (O=16).

Consideration of the sources of error, however, showed that any value from 14.002 to 14.022 might well have been obtained. The authors consider their method less accurate than direct gravimetric determinations.

R. J. C.

Oxidation of Ammonia by Potassium Permanganate and the Effect of Ammonium Salts on the Reaction. MORDKO HERSCHKOWITSCH (*Zeitsch. physikal. Chem.*, 1908, 65, 93—96).—Dilute solutions of ammonia and of potassium permanganate, in varying concentrations, with or without the addition of ammonium salts, have been heated for definite periods in a large flask at 40°, and the relative proportions of nitrogen, nitrous and nitric acids in the mixture determined.

Increase in the proportion of ammonia increases both the nitrogen and the nitrous acid, and diminishes the nitric acid; increasing the concentration of both reagents has much the same effect, except that the proportion of nitrous acid is not much altered. Addition of ammonium salts diminishes the amounts of nitrogen and nitrous acid, and greatly increases the nitric acid. Ammonium salts are formed in the course of the reaction, even when none are present originally, and, in order to eliminate their action, experiments have been made in which excess of alkali is added previously. In these circumstances, less nitrous acid and more nitrogen are formed.

G. S.

The Hydrazinates of some Metallic Salts. HARTWIG FRANZEN and O. VON MAYER (*Zeitsch. anorg. Chem.*, 1905, 60, 247—291).—Hydrazinates of metallic salts have been prepared by Curtius and Schrader (Abstr., 1895, ii, 10) and by Hofmann and Marburg (Abstr., 1899, i, 486). A number of new methods of preparation are now described. On the addition of hydrazine to a solution of a cobalt-ammine salt, reduction always takes place, nitrogen being evolved, and the hydrazine compound of a cobaltous salt being precipitated.

One mol. of hydrazine replaces 2 mols. of ammonia. The double compounds form crystalline powders, insoluble in water, soluble in acids or ammonia. Sulphates and nitrates tend to combine with 3 mols. of hydrazine, whilst chlorides, bromides, and oxalates, with the exception of nickel chloride and bromide and of calcium and strontium bromides, retain only 2 mols. The following compounds have been prepared:

With $3\text{N}_2\text{H}_4$: Nickel chloride, bromide, sulphate, nitrate, and dithionate; cobaltous sulphate and nitrate; zinc nitrate; cadmium nitrate; calcium bromide; strontium bromide.

With $2\text{N}_2\text{H}_4$: Nickel chloride, bromide, and oxalate; cobaltous chloride, bromide, and oxalate; zinc chloride, bromide, iodide, oxalate, and sulphate; cadmium chloride, bromide, iodide, oxalate, sulphate, carbonate, and phosphate; ferrous chloride and oxalate; manganous chloride, sulphate, and nitrate; cupric oxalate; calcium chloride and nitrate; strontium chloride; barium chloride and bromide.

Full analyses and descriptions of the compounds are given.

C. H. D.

Chlorine Azide [Chloroazoimide], N_3Cl . FRITZ RASCHIG (*Ber.*, 1908, 41, 4194—4195).—*Chloroazoimide*, N_3Cl , is liberated as a colourless gas, having an odour similar to hypochlorous acid, when an aqueous solution of sodium azoimide (1 mol.) and sodium hypochlorite (1 mol.) is acidified even with weak acids, such as acetic acid or boric acid. It is slightly soluble in water, forming a yellow solution, and explodes with extraordinary violence when brought into contact with a flame or glowing splinter, and sometimes spontaneously with the production of a pale blue flame. It is decomposed by aqueous sodium hydroxide, thus: $N_3Cl + 2NaOH = NaN_3 + NaOCl + H_2O$.

W. H. G.

Preparation of Crystalline Silicon. A. J. KIESER (*Chem. Zeit.*, 1908, 32, 1161—1162).—With the object of ascertaining whether combination takes place between aluminium and silicon when methods involving the use of aluminium are employed for preparing silicon, careful tests have been made for aluminium in the silicon and for silicates in the slag. For the first tests, crystalline silicon was prepared by Vigouroux's method, and for the second the slag from Wöhler's method was examined. In each case the quantity of aluminium and silica respectively obtained was so small as to make it evident that combination between aluminium and silicon does not take place.

J. V. E.

New Formation of Liquid Alloys of Potassium and Sodium. GEORGE F. JAUBERT (*Bull. Soc. chim.*, 1908, [iv], 3, 1126—1131; *Ber.*, 1908, 41, 4116—4120*).—The liquid alloys obtained by the action of (1) sodium on potassium hydroxide and (2) potassium on sodium hydroxide are described.

When sodium hydroxide is melted in a vacuous Jena flask with potassium, reaction occurs at 200—250°, bubbles of gas (hydrogen?) are evolved, the temperature rises to 300°, and a layer of the alloy, NaK_2 , having the appearance of mercury is formed and floats on the excess of alkali hydroxide used.

When potassium hydroxide (6 parts) and sodium (11 parts) are melted together in the same way at 250—275°, the alloy, NaK , is formed, but by modifying the quantities of the hydroxide and metal used and raising the temperature to 350°, the chief product is the alloy, NaK_2 . Both alloys are liquid, and do not solidify even at 10°. They oxidise rapidly in cold air, especially if fresh surfaces are continually exposed, and even when kept under liquid petroleum the potassium slowly oxidises. The alloy, NaK_2 , is now made commercially, and is being applied in a number of industries.

T. A. H.

Cæsium Chromates. FRANS A. H. SCHREINEMAKERS and D. J. MEYERINGH (*Chem. Weekblad*, 1908, 5, 811—816).—The following chromates of cæsium have been prepared (at 30°): Cs_2CrO_4 ; $Cs_2Cr_2O_7$; $Cs_2Cr_3O_{10}$, and $Cs_2Cr_4O_{13}$. Their properties are similar to those of the corresponding chromates of potassium, ammonium, and rubidium. The mono- and di-chromates dissolve in water without decomposition;

* and *Ann. Chim. anal.*, 1909, 14, 1—5.

the tri- and tetra-chromates are decomposed by water. The solubility of the monochromates of ammonium, potassium, rubidium, and caesium increases in the order given; that of the dichromates diminishes in the same order.

A. J. W.

Action of Carbon Dioxide under Pressure on Metallic Hydroxides at 0°. FRANK K. CAMERON and WILLIAM O. ROBINSON (*J. Physical Chem.*, 1908, 12, 561—573).—The authors have determined the solubility of carbon dioxide in water at various pressures in presence of an excess of the solid hydroxides or carbonates. Successive small quantities of carbon dioxide were forced into a tube containing the hydroxides or carbonates, vigorously stirred with a small known weight of water, and curves were obtained connecting pressure with weight of carbon dioxide in the apparatus. Breaks in these curves at any pressure indicate absorption of carbon dioxide by the solid phase, that is, the formation of solid carbonates or hydrogen carbonates.

The only authentic solid hydrogen carbonates appear to be those of the alkali metals, excluding lithium. Calcium, ferrous iron, and magnesium do not form solid hydrogen carbonates at 0° even under 5 atmospheres pressure. The hydroxides of aluminium, ferric iron, and glucinum do not appear to combine with carbonic acid.

The authors regard the solubility of calcium carbonate in carbon dioxide solution as due to a specific solvent action of the carbon dioxide-water mixture rather than as indicating the formation of a hydrogen carbonate (compare, however, Raikow, *Abstr.* 1905, ii, 85).

R. J. C.

The Solvent Action of Carbon Dioxide up the Carbonates of the Heavy Metals. CLARENCE A. SEYLER (*Analyst*, 1908, 33, 454—457).—It has been shown by Free (*Abstr.*, 1908, ii, 848) that the solubility of basic copper carbonate increases with the concentration of the free carbon dioxide, and the author now shows that Free's results exhibit regularities similar to those found for other carbonates, and that these can be deduced from the principles of chemical equilibrium. The solubility of the basic carbonates of zinc and lead is governed by the same law. In all three cases the effect of a hydrogen carbonate would be to diminish the solubility, according to the law $\sqrt{M} \times \text{HCO}_3 = \text{constant}$, when the carbon dioxide is kept constant. The protective action of calcium in solution as hydrogen carbonate on waters which act on lead and zinc is thus explained.

W. P. S.

Mixed Barium-Strontium Chromate Precipitate. LIONEL H. DUSCHAK (*J. Amer. Chem. Soc.*, 1908, 30, 1827—1833).—Hulett and Duschak (*Abstr.*, 1904, ii, 616) have stated that the occlusion of barium chloride by precipitated barium sulphate is most easily explained by regarding the precipitate as an isomorphous mixture of barium sulphate with one or more complex barium salts, and that cases of isomorphism in which one component, owing to its ready solubility, is present in only a minute quantity are probably not uncommon.

A study has now been made of the precipitate of mixed barium and strontium chromates formed as an intermediate product in the separation of barium and strontium by the usual analytical method. The results of the experiments show that a crystalline precipitate of barium and strontium chromates of definite composition is formed in a saturated solution of barium chromate containing given concentrations of strontium chromate and acetic acid. It has been found that diffusion takes place within this substance, and that, therefore, it must either be regarded as a solid solution or else diffusion must be recognised as a possible property of isomorphous mixtures.

E. G.

Silico-thermic Experiments. PAUL ASKENASY and CHARLES PONNAZ (*Zeitsch. Elektrochem.*, 1908, 14, 810—811).—Barium peroxide and silicon react very violently when the reaction is initiated by means of a fuse. By using coarsely-powdered barium peroxide (50 parts) and silicon (15 parts), a barium silicide with 30% of barium is obtained. The mixture (with less silicon and a little sodium peroxide) may also be used to fuse iron or copper, or powdered ferro-silicon or titanium silicide may be used in place of silicon.

T. E.

Estimation of the Valency of Glucinum by Colloidal Experiments. ANT. GALECKI (*Zeitsch. Elektrochem.*, 1908, 14, 767—768).—The quantities of barium, calcium, potassium, glucinum, magnesium, lanthanum and aluminium salts required to coagulate a colloidal solution of arsenic sulphide are compared. Glucinum behaves in exactly the same way as barium, calcium, and magnesium, very much larger quantities of potassium salts and very much smaller quantities of aluminium or lanthanum salts being required to produce the same effect. The results point to glucinum being bivalent.

T. E.

Compounds of Lead with Nitrous Acid. ALBERTO CHILESOTTI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 377—384, 474—483. Compare Abstr., 1908, ii, 948).—When treated with water, the basic salt, $\text{Pb}(\text{OH})_2, \text{Pb}(\text{NO}_2)_2, \text{H}_2\text{O}$, undergoes hydrolysis, yielding the compound $3\text{PbO}, \text{N}_2\text{O}_3, x\text{H}_2\text{O}$ (*loc. cit.*). The latter then undergoes further hydrolysis, during which the ratio $\text{Pb}:\text{NO}_2$ increases to a value indicating the formation of the salt $4\text{PbO}, \text{N}_2\text{O}_3, \text{H}_2\text{O}$.

The experiments carried out up to the present time show that the following basic salts must be regarded as definite compounds: $\text{Pb}(\text{OH})_2, \text{Pb}(\text{NO}_2)_2$, and its hydrate with $1\text{H}_2\text{O}$; $3\text{PbO}, \text{N}_2\text{O}_3$ or $2\text{PbO}, \text{Pb}(\text{NO}_2)_2$, and $4\text{PbO}, \text{N}_2\text{O}_3, \text{H}_2\text{O}$; the first two of these salts may be regarded as derivatives of ortho-nitrous acid, H_2NO_3 .

The salt $3\text{PbO}, \text{N}_2\text{O}_3$ may be prepared as follows: The basic salt, $\text{Pb}(\text{NO}_2)_2, \text{Pb}(\text{OH})_2, \text{H}_2\text{O}$, is treated with increasing quantities of water, the limpid, yellow solution formed being replaced by water, by which means an almost colourless, turbid liquid is obtained, from which the suspended substance is gradually deposited; the substance then remaining undissolved consists of the salt $3\text{PbO}, \text{N}_2\text{O}_3, x\text{H}_2\text{O}$.

Study of the electrolysis of the salt $4\text{PbO}, \text{N}_2\text{O}_3, \text{H}_2\text{O}$ in

dilute acetic acid shows that the ions NO_2' or the molecules of the neutral nitrite, $\text{Pb}(\text{NO}_2)_2$, do not form complex cations with lead, and that the ions NO_3' and NO_2' move, for the most part, independently of one another, and in proportions corresponding with the stronger dissociation of $\text{Pb}(\text{NO}_3)_2$ and with the greater mobility of the NO_3' ion; the current is carried only in small proportion by lead ions.

In order to ascertain whether lead nitrate combines with the nitrite in small proportion to form complex anions, the author uses a method devised by Miolati and Pizzighelli (*Abstr.*, 1908, ii, 595). Conductivity measurements of solutions containing lead nitrite and nitrate show that the specific conductivity curve changes direction when the two salts are present in molecular proportions. It is hence probable that, to a certain small extent, these two salts combine in the proportion $\text{Pb}(\text{NO}_3)_2 : \text{Pb}(\text{NO}_2)_2$ to form a complex salt.

Attempts to separate such a complex salt in the solid state from solutions containing the components in molecular proportions were unsuccessful.

T. H. P.

Optical Investigation of the Copper Complex in Ammonia and Pyridine Solutions. ARTHUR HANTZSCH and PHILIP WILFRED ROBERTSON (*Ber.*, 1908, 41, 4328—4340. Compare *Abstr.*, 1908, ii, 447, 646).—The method previously described has been extended to the coppertetrammine complex, and the following conclusions have been arrived at. All cupric compounds whether in aqueous or alcoholic ammonia solutions are optically identical, and contain exclusively the coppertetrammine complex, $\text{Cu}(\text{NH}_3)_4$; the base is coppertetrammine hydrate, $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$, and not the diammine hydrate. The colour is not materially altered whether the temperature, degree of dissociation, or solvent is changed, and apparent departures from this are ascribed to chemical change; as for example the formation of a triammine-aquo-complex, $\text{Cu}(\text{NH}_3)_3(\text{OH}_2)$. The solutions in aqueous pyridine of copper salts are likewise identical; the complex is less stable than that with ammonia, and is probably $\text{Cu}(\text{Py}_3\text{OH}_2)$. Copper acetate in pure or alcoholic pyridine contains another, less intensely coloured, complex, probably $\text{Cu}(\text{Py}_2\text{OAc})_2$.

The chemical influence of the solvent is exhibited in the water and methyl, ethyl, and amyl alcoholic solutions of copper acetate, probably due to the addition of solvent to the unsaturated complex, $\text{Cu}(\text{OAc})_2$. Copper forms in solutions only the complex CuR_4 , and has co-ordination number 4.

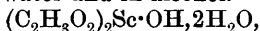
W. R.

Scandium. SIR WILLIAM CROOKES (*Phil. Trans.*, 1908, 209, A, 15—46. Compare *Abstr.*, 1908, ii, 695).—About thirty scandium salts, both of inorganic and organic acids, have been prepared and analysed, and their properties are described in detail. Some of the inorganic salts have already been described by previous observers.

The chloride, Sc_2Cl_6 , and the corresponding bromide crystallise with $12\text{H}_2\text{O}$; the fluoride is anhydrous. Scandium potassium sulphate,

$\text{Sc}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$, is, contrary to the statement of Cleve, and in agreement with Nilson, only slightly soluble in a saturated solution of potassium sulphate. The *selenate*, $\text{Sc}_2(\text{SeO}_4)_3 \cdot 8\text{H}_2\text{O}$, rhombic prisms, loses $6\text{H}_2\text{O}$ at 100° , and becomes anhydrous at 400° ; it decomposes at a yellow heat. The *nitrate*, $\text{Sc}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, prismatic crystals, is rendered anhydrous on heating over a water-bath, and decomposes at a high temperature. When dried in a vacuum at 100° for seventeen hours, a basic nitrate, $\text{Sc}(\text{OH})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, is obtained, and another basic nitrate, $\text{Sc}_2\text{O}(\text{NO}_3)_4$, is obtained by heating the nitrate for twelve hours in a hot-air oven at 120° .

The majority of the organic scandium salts were prepared by interaction of scandium hydroxide and the corresponding acid. Most of the salts with fatty acids are more soluble in cold than in hot water. The *formate*, $(\text{HCO}_2)_2\text{Sc} \cdot \text{OH} \cdot \text{H}_2\text{O}$, occurs in hard, lustrous crystals, soluble in hot water and in alcohol. The *acetate*,



forms fine white crystals, which, on being kept for some days, lose $1\text{H}_2\text{O}$. The *propionate*, $(\text{C}_3\text{H}_5\text{O}_2)_2\text{Sc} \cdot \text{OH}$, occurs as a voluminous, white powder, easily soluble in alcohol; the *butyrate*, $(\text{C}_4\text{H}_7\text{O}_2)_2\text{Sc} \cdot \text{OH}$, the *isobutyrate*, with $2\text{H}_2\text{O}$, and the *isovalerate*, $(\text{C}_5\text{H}_9\text{O}_2)_2\text{Sc} \cdot \text{OH} \cdot 2\text{H}_2\text{O}$, are also amorphous and soluble in alcohol.

Scandium oxalate, $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$, occurs as a crystalline powder, which loses $2\text{H}_2\text{O}$ over sulphuric acid at the ordinary temperature, $3\text{H}_2\text{O}$ in air at 100° , and $4\text{H}_2\text{O}$ in air at 140° . It is moderately soluble in a solution of ammonium oxalate, on which fact a method of separating scandium from other rare earths may be based. The *succinate*, $\text{C}_2\text{H}_4[\text{CO}_2\text{Sc}(\text{OH})_2]_2 \cdot \text{H}_2\text{O}$, is a white powder, insoluble in water and alcohol; the *picrate*, $(\text{C}_6\text{H}_2\text{O}_7\text{N}_3)_2\text{Sc} \cdot \text{OH} \cdot 14\text{H}_2\text{O}$, occurs in yellow, needle-shaped crystals, which explode faintly on heating. The salt loses $9\text{H}_2\text{O}$ at 100° . The *benzoate*, $(\text{C}_6\text{H}_5 \cdot \text{CO}_2)_3\text{Sc}$, and the *o-toluate*, $(\text{C}_6\text{H}_4\text{Me} \cdot \text{CO}_2)_3\text{Sc} \cdot \text{OH} \cdot 3\text{H}_2\text{O}$, form crystalline powders; a *basic o-toluate*, $2\text{C}_8\text{H}_7\text{O}_3\text{Sc} \cdot \text{Sc}(\text{OH})_3$, obtained by using excess of the hydroxide, occurs as a white powder. The *m-* and *p-toluates*, both with $3\text{H}_2\text{O}$, form white, curdy precipitates, insoluble in water; the *phenylacetate*, $(\text{C}_7\text{H}_7 \cdot \text{CO}_2)_2\text{Sc} \cdot \text{OH} \cdot 3\text{H}_2\text{O}$, is also practically insoluble in water. The *pyromellitate*, $\text{C}_6\text{H}_2[\text{CO}_2\text{Sc}(\text{OH})_2]_4 \cdot 2\text{H}_2\text{O}$, a white, amorphous powder, loses $1\text{H}_2\text{O}$ at 100° , and the remaining molecule at 140° . The *camphorate*, $\text{C}_{10}\text{H}_{14}\text{O}_4 \cdot \text{ScOH}$, is a white, insoluble powder, which is very electrical in the dry state.

The atomic weights of the closely-related elements, scandium, yttrium, and ytterbium, are approximately simple multiples of that of boron, and as they occur together in nature, it is suggested that the elements of lower atomic weight may be formed from those of higher atomic weight by successive sub-division.

Photographs of those parts of the spectrum containing the more prominent scandium lines are given. G. S.

Scandium. I. RICHARD J. MEYER (*Zeitsch. anorg. Chem.*, 1908, 60, 134—151).—The extraction of scandium from wolframite (from Zinnwald, Saxony) is described. The mineral contains 0.14—0.16% of rare earths, in which scandium oxide predominates. The ore is

first fused with sodium hydroxide and extracted with water; the residue (chiefly the oxides of iron, manganese, calcium, and lead) contains practically all the scandium (0.30—0.33% of the oxide).

Two methods have been used for separating the scandium from the mixed oxides: (1) To a neutral or slightly acid solution of the oxides a saturated solution of oxalic acid is added, and the mixture kept for twenty-four hours. The precipitate, which is richer in the rare earths than the original mixture, is washed, ignited, dissolved in excess of hydrochloric acid, and excess of hydrofluoric acid is added. The precipitate thus obtained is quite free from manganese, and consists of the fluorides of lead, calcium, iron, and of the rare earths. The remaining metals are removed by special methods, and the rare earth residue finally obtained contains about 95% of scandium oxide.

According to the second method, the mixture of oxides is dissolved as completely as possible in hydrochloric acid, solid sodium silicofluoride is then added, and the mixture boiled for half an hour, when a precipitate containing all the scandium and practically none of the other rare earths is obtained. Iron, calcium, etc., are then removed as before, and, finally, a very pure scandium oxide is obtained.

The other rare earths, except thorium, can be separated from scandium by adding sodium thiosulphate to a neutral solution and boiling for some time; the precipitate consists of scandium thiosulphate. The final product was tested for purity spectroscopically and by an atomic weight determination; it contained about 1% of thorium oxide, for which no quite satisfactory method of separation has been found.

G. S.

Heats of Combustion of Aluminium, Calcium, and Magnesium. FRANK E. WESTON and HENRY R. ELLIS (*Trans. Faraday Soc.*, 1908, 4, 130—133).—Both magnesium and calcium reduce aluminium oxide on ignition with a fuse; magnesium also reduces lime. Lime and magnesia are partly reduced by aluminium and calcium respectively at high temperatures.

C. H. D.

Aluminium Carbide. PAUL ASKENASY, W. JARKOWSKY, and A. WANICZEK (*Zeitsch. Elektrochem.*, 1908, 14, 811—813).—When pure crystalline aluminium carbide is heated above the melting point of aluminium in air or in an indifferent gas, metallic aluminium exudes from it. In making the carbide from alumina and carbon in the electric furnace, the best yield of carbide is obtained by rapidly cooling the contents of the furnace. When the cooling is slow, the product consists mainly of the apparently unchanged mixture. The authors believe that the reaction $\text{Al}_4\text{C}_3 \rightleftharpoons 4\text{Al} + 3\text{C}$ has a transition point; at high temperatures the carbide is the stable system, at lower temperatures it decomposes into the metal and carbon. At the melting point of aluminium, the velocity of decomposition is very considerable. These observations explain the presence of hydrogen in the gas evolved by the action of acids on aluminium carbide, and also the fact that a copper-aluminium alloy is formed when it is fused with copper.

T. E.

Fused Alumina in the Amorphous State, and Reproduction of Blue Colour of Sapphires. LOUIS PARIS (*Compt. rend.*, 1908, 147, 933—935).—Pure alumina in the oxyhydrogen flame, although it is only superficially fused, absorbs chromic oxide throughout its mass, giving artificial rubies. Oxides of cobalt, iron, etc., which would give a blue coloration, are insoluble in pure alumina. Nickel oxide, however, dissolves, giving a greenish-blue colour.

If a small percentage of another oxide, such as lime, is added to the fused alumina, cobalt and other colouring oxides dissolve, giving a blue product, the optical properties of which show it to be amorphous, whereas pure alumina and artificial rubies are crystalline.

Stones, weighing as much as 20 carats, can be obtained indistinguishable from natural sapphires, except by a slight difference in refractive index.

R. J. C.

Reproduction of the Blue Colour of Oriental Sapphires. AUGUSTE VERNEUIL (*Compt. rend.*, 1908, 147, 1059—1061).—The author contends that the process described by Paris (preceding abstract) does not accurately reproduce the colour of Oriental sapphires.

W. O. W.

Alum. ROBERT MARC (*Zeitsch. anorg. Chem.*, 1908, 60, 193—207).—Whilst a specimen of alum obtained from Kahlbaum had a solubility in water of about 10 grams per litre at 17°, being independent of the degree of supersaturation before cooling, and it readily formed supersaturated solutions, a specimen obtained from Merck was less soluble, had very little tendency to form supersaturated solutions, and the solubility depended on the degree of supersaturation before the excess of salt was caused to separate by inoculation; the higher the supersaturation the greater the final solubility. It was then found that the alum which separated from dilute solutions contained more alkali, that is, it was more basic than that separating from more concentrated solutions. The original alum of Merck, however, was of the usual composition, as was that of Kahlbaum.

No adequate explanation of these phenomena has so far been found. Of the commercial alums examined, only Merck's showed the peculiarity in question.

G. S.

Solidification Curves of Certain Molten Silicates. EMIL DITTLER (*Monatsh.*, 1908, 29, 1037—1074).—The freezing-point curves for mixtures of ægirite and nephelin, labradorite and nephelin, and labradorite and diopside, have been determined. Comparative measurements were made for mixtures of the minerals and of the artificial substances. In general, the melting-point curves for mixtures of the artificial products are higher than those for the minerals. The melting points of the crystalline mixtures lie in all cases approximately on a straight line, whilst in the case of the glasses the melting points are considerably lower than those of the two components. The order in which the silicates separate out is: magnetite, augite, ægirite, labradorite, diopside, nephelin, and sodium augite. This succession is in agreement with Rosenbusch's rule.

The experimental data lead the author to doubt whether the solidification of complex silicate mixtures is even approximately regulated by the factors which determine the same process in the case of simple systems.

H. M. D.

Action of Hydrochloric Acid on Permanganates. RUDOLF F. WEINLAND and P. DINKELACKER (*Zeitsch. anorg. Chem.*, 1908, **60**, 173—177).—Meyer and Best (Abstr., 1900, ii, 77) have obtained double salts of manganese tetra- and tri-chloride with potassium permanganate in glacial acetic acid. The authors now show that these and corresponding double salts can be obtained by the action of aqueous concentrated hydrochloric acid on permanganates.

The compound, $\text{MnCl}_4 \cdot 2\text{KCl}$, is best obtained by adding calcium permanganate and a concentrated solution of potassium chloride to a 40% aqueous solution of hydrochloric acid cooled with ice and salt; it forms small, dark red crystals. The corresponding rubidium and ammonium salts have been obtained in the same way.

From the solutions from which the double salts of quadrivalent manganese have separated, double salts of trivalent manganese of the type $\text{MnCl}_3 \cdot 2\text{KCl}$ are obtained on adding excess of the alkali chlorides in concentrated aqueous solution. The *rubidium*, *cæsium*, potassium, and ammonium salts have been prepared; all except the rubidium salt have been described by previous observers.

G. S.

Action of Chlorine on Ferrobore and Manganese Bore at High Temperature. JOSEF HOFFMANN (*Zeitsch. angew. Chem.*, 1908, **21**, 2545—2546).—When Goldschmidt's ferrobore is heated to 300—400° in a long combustion tube in a current of dry chlorine, there is produced near the heated substance a small quantity of a dark green sublimate having the composition $\text{Fe}_3\text{Cl}_5\text{B}$. The chief product, however, condenses farther away on the cooler parts of the tube as a brown solid, and is probably a complex substance composed of boron chloride and ferrous chloride. A still more volatile compound was condensed in a U-tube connected to the combustion tube and kept in a cooling mixture; this was a pale yellow, highly refractive liquid, b. p. 24—28°, which appears to be impure boron chloride.

Manganese bore, heated in dry chlorine in a similar manner, also gave complex manganese boro-chlorides, but in such small quantities that at present it has not been possible to ascertain their composition.

J. V. E.

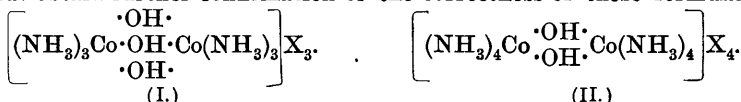
Composition of Colloidal Ferric Hydroxy-chlorides. LÉOPOLD MICHEL (*Compt. rend.*, 1908, **147**, 1052—1054. Compare Malfitano, Abstr., 1906, ii, 450).—This paper contains details of the method adopted for studying the composition of colloidal ferric chloride solutions by filtration through collodion membranes. Experiments have been made to determine the ratio Fe : Cl in the micro-cells of ferric hydroxy-chloride to which the membranes are impermeable, and in the filtrate which constitutes the intercellular liquid. From the

analytical data obtained, the author arrives at the conclusion that the colloidal solution contains several physical units of variable composition.

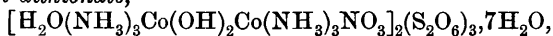
In one series of experiments carried out on an ochreous solution of ferric chloride containing a precipitate, the intercellular liquid was found to be of uniform composition throughout. The micro-cells suspended in the top layer contained iron and chlorine in the atomic ratio Fe : Cl = 2.4 : 1, whilst in the lower layer containing the sediment the ratio was 4.5 : 1.

In the stable colloidal solution obtained by adding ferric chloride to boiling water, a separation of micro-cells of different composition was effected by means of the centrifuge. W. O. W.

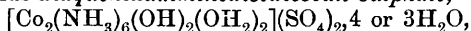
Complex Metal Ammonias. VIII. Transformation of Hexamminetrioldicobalt Salts into Octamminedioldicobalt Salts. ALFRED WERNER (*Ber.*, 1908, 41, 3879—3884. Compare Abstr., 1908, ii, 42, 43).—It has been found possible to pass from a hexamminetrioldicobalt salt having the constitutional formula (I) to an octamminedioldicobalt salt having the formula (II), that is, to replace an "ol-bridge" in the former by 2 mols. of ammonia, and thus obtain further confirmation of the correctness of these formulæ :



Hexamminetrioldicobalt sulphate (compare this vol., ii, 43) is converted by cold 50% nitric acid into *dinitratohexamminedioldicobalt nitrate*, $[\text{NO}_3(\text{NH}_3)_3\text{Co}(\text{OH})_2\text{Co}(\text{NH}_3)_3\text{NO}_3](\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, which crystallises in pale violet, glistening scales. Its aqueous solutions quickly decompose; consequently, other salts of this series could not be prepared in a pure state. A freshly-prepared solution when treated with sodium dithionate slowly deposits *nitratoaquohexamminedioldicobalt dithionate*,



as small, pale violet scales. An aqueous solution of the nitrate which has been kept for some time, when treated with sodium sulphate, yields *diaquohexamminedioldicobalt sulphate*,



an intense, bluish-violet, sparingly soluble salt which could not be obtained pure. The nitrate is converted by liquid ammonia and subsequent treatment with ammonium bromide into octamminedioldicobalt bromide (compare Abstr., 1907, ii, 965). W. H. G.

Complex Metal Ammonias. IX. Decammine- μ -aminodicobalt Salts. ALFRED WERNER (*Ber.*, 1908, 41, 3912—3921. Compare Abstr., 1908, ii, 42).—When octammine- μ -amino-ol-dicobalt nitrate is treated with nitric acid in the cold, *nitratoaquooctammine- μ -aminodicobalt nitrate*, $\left[\begin{array}{c} (\text{NH}_3)_4\text{Co}\cdot\text{NH}_2\cdot\text{Co}(\text{NH}_3)_4 \\ \text{H}_2\text{O} \quad \text{NO}_3 \end{array} \right] (\text{NO}_3)_4$, is obtained quantitatively as a violet salt. This, on addition in small quantities to well-stirred liquid ammonia, is converted into the decammine- μ -aminodicobalt nitrate, a small quantity of the octammine-

μ -amino-ol-dicobalt nitrate being regenerated. The constitution of this salt was determined independently of the octammine series, as chloropentammine-cobalt and hexammine-cobalt salts are obtained by the action of a mixture of hydrochloric and sulphuric acids, from which the deduction is made that five molecules of ammonia are attached to each of the cobalt atoms, thus: $[(\text{NH}_3)_5\text{Co}\cdot\text{NH}_2\cdot\text{Co}(\text{NH}_3)_5]\text{Cl}_5 + \text{HCl} = \left[\text{Co}^{\text{Cl}}(\text{NH}_3)_5\right]\text{Cl}_2 + [\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. That the decammine salt is not an imino-derivative of the type $[(\text{NH}_3)_5\text{Co}\cdot\text{NH}(\text{HCl})\cdot\text{Co}(\text{NH}_3)_5]\text{Cl}_4$ is shown by its behaviour towards alkalis, the elements of hydrogen chloride not being withdrawn.

These salts have all a bluish-red colour, and correspond with the rhodochromium salts, $\left[\text{Cr}_2\left(\frac{\text{NH}_3}{\text{OH}}\right)_{10}\right]\text{X}_5$, from which the conclusion is drawn that the hydroxyl in the chromium compound plays the same part as the μ -amino-radicle in the cobalt derivatives.

The *nitrate*, $\text{Y}(\text{NO}_3)_5, \{\text{Y} = [(\text{NH}_3)_5\cdot\text{Co}\cdot\text{NH}_2\cdot\text{Co}(\text{NH}_3)_5]\}$, forms dark bluish-red needles; the *chloride*, $\text{YCl}_5\cdot\text{H}_2\text{O}$, precipitated from the solution of the nitrate by addition of ammonium chloride, crystallises in glistening, reddish-violet needles, and is not decomposed on boiling with concentrated hydrochloric acid. It is only decomposed by the mixture of sulphuric acid and hydrochloric acid by long-continued heating. The *bromide*, $\text{YBr}_5\cdot\text{H}_2\text{O}$, forms slender, reddish-violet needles; the *dithionate*, $\text{Y}_2(\text{S}_2\text{O}_6)_5\cdot 6\text{H}_2\text{O}$, forms a rose-red powder, which, on heating at $60-80^\circ$, loses $4\text{H}_2\text{O}$ and is converted into the hexammine and hydroxyl pentammine salts. This was shown by treatment with aqueous ammonium bromide, when the hexammine bromide was precipitated. The filtrate on addition of alcohol deposited a bluish-red powder free from sulphur, which, on boiling with hydrochloric acid, gave chloropentammine-cobalt chloride. The *sulphate*, $\text{Y}_2(\text{SO}_4)_5\cdot 3\text{H}_2\text{O}$, crystallises in red needles and thin prisms. W. R.

True Peroxide of Nickel. GIOVANNI PELLINI and D. MENEGHINI (*Zeitsch. anorg. Chem.*, 1908, 60, 178—190).—A nickel peroxide of the formula $\text{NiO}_2\cdot x\text{H}_2\text{O}$ has been obtained as follows. A dilute solution of nickel chloride is cooled to -50° , an equal volume of 30% hydrogen peroxide added, and, finally, potassium hydroxide in alcoholic solution. The precipitate is washed several times with cold alcohol and then with ether, and forms a greyish-green powder, stable in the air. The pure peroxide has not been obtained, but in one case the ratio $\text{Ni}:\text{O}$ was as high as 1:1.98. The same peroxide is obtained by the action of hydrogen peroxide on free nickel hydroxide, but the reaction is comparatively slow, a large proportion of the hydroxide remaining unchanged. The proportion of water associated with the peroxide has not been determined.

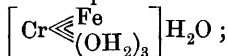
The greyish-green peroxide gives all the reactions of hydrogen peroxide, and its behaviour is quite different from that of the peroxide of the same formula described by Bellucci and Clavari (*Abstr.*, 1905, ii, 823); it is therefore suggested that the former oxide has the constitution $\text{Ni} < \overset{\text{O}}{\text{O}}$, and that described by Bellucci, $\text{Ni} \leq \overset{\text{O}}{\text{O}}$. G. S.

Chromium Compounds. VII. Hydrates of Chromium Fluoride and an Example of Co-ordinate Isomerism among Hydrates. ALFRED WERNER and W. COSTACHESCU (*Ber.*, 1908, 41, 4242—4246).—The compounds CrF_3 , $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$, $2\text{CrF}_3 \cdot 7\text{H}_2\text{O}$, and $\text{CrF}_3 \cdot 9\text{H}_2\text{O}$ are described in chemical literature.

The authors have examined the compounds with 7 and $9\text{H}_2\text{O}$, and the following new compounds: $\text{CrF}_3 \cdot 6\text{H}_2\text{O}$, $2\text{CrF}_3 \cdot 7\text{H}_2\text{O}$, and $\text{CrF}_3 \cdot 3\text{H}_2\text{O}$.

Hexaquo chromium fluoride, $[\text{Cr}(\text{OH}_2)_6]\text{F}_3$, forms a violet, crystalline powder, and is obtained by adding a concentrated solution of potassium fluoride to a similar solution of violet chromium nitrate. Its electrical conductivity (in paraffin vessels) is about half that of the violet chloride, and treatment with sulphuric acid gives rise to hexaquo chromium sulphate. When the moist crystals are kept, they yield the violet hydrate, $\text{CrF}_3 \cdot 9\text{H}_2\text{O}$. This conversion occurs spontaneously when the crystals are washed, especially when they are pressed slightly with a spatula. This hydrate yields hexaquo chromium sulphate when treated with sulphuric acid, and the formula $[\text{Cr}(\text{OH}_2)_6](\text{OH}_2\text{F})_3$ is suggested. The hexahydrate loses $3\text{H}_2\text{O}$ at $60\text{--}70^\circ$.

Hexaquo chromium chromium hexafluoride, $[\text{Cr}(\text{OH}_2)_6]\text{CrF}_6$, is obtained as an insoluble green product when the hexaquo chromium fluoride is warmed with water. A *monohydrate*, $[\text{Cr}(\text{OH}_2)_6]\text{CrF}_6 \cdot \text{H}_2\text{O}$, is obtained by double decomposition between hexaquo chromium chloride and ammonium chromium hexafluoride, $(\text{NH}_4)_3\text{CrF}_6$. It forms a pale green, crystalline powder with a pearly lustre, and when heated at 105° loses a molecule of water, yielding the insoluble green compound. The monohydrate is isomeric with Poulenc's salt (*Abstr.*, 1893, ii, 321), which is regarded as trifluorotriaquo chromium monohydrate,

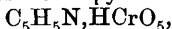


its aqueous solution has a distinctly acid reaction, but does not give the reactions of fluorides. J. J. S.

Higher Oxidation Products of Chromium. V. Perchromates. ERNST H. RIESENFELD (*Ber.*, 1908, 41, 3941—3951. Compare *Abstr.*, 1908, i, 963).—There are two classes of perchromates: the salts derived from the penta-acid, HCrO_5 , are blue in colour, those derived from the octa-acid, H_3CrO_8 , are red. The salts of chromatodiperacid do not exist (*Abstr.*, 1904, ii, 410, 737).

A red, hydrated *potassium perchromate*, analogous to the sodium salt, has been prepared by the action of chromic acid on potassium cyanide in the cold. This salt crystallises in rhombic plates, and very quickly loses its water of crystallisation.

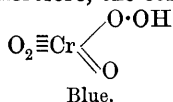
The constitution of these salts has been investigated by determining their molecular weights. The blue pyridine perchromate,



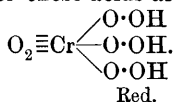
is unimolecular, and from determinations of the freezing points in aqueous solution, the red potassium and ammonium perchromates have also the simple formula M_3CrO_8 . The solutions are good electrolytes. Determination of the mol.-wt. of the free acid is not possible, because of its rapid decomposition in water; this decom-

position has been measured in a mixture of ether, glacial acetic acid, and water, and obeys the unimolecular law. As this argument for the simple formula in the case of the free acid is not conclusive, the electrochemical equivalent of the chromium was determined, and shown to be $1\text{Cr}:6\text{Ag}$ in the case of the red potassium salt. It is not possible to assign a formula to this salt on the assumption of the univalency of potassium, the bivalency of oxygen, and the sexavalency of chromium.

Although hydrogen peroxide cannot be proved to be a product of the decomposition of these salts, yet alkaline gold chloride and permanganate are reduced during the change, and the assumption is made that these salts are analogous to alkali peroxides. The equivalent of permanganate reduced is held to be a measure of the "holoxide" oxygen groups. The blue pyridine perchromate decomposed very rapidly, and so this could not be measured, but in the decomposition of the red salts, 5.5 equivalents of the permanganate were reduced. The conclusion is drawn that this is due to the formation of $3\text{H}_2\text{O}_2$, and that, therefore, the constitutions of these acids are:



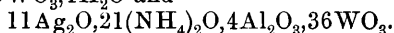
Blue.



Red.

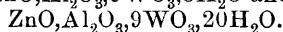
W. R.

Derivatives of Complex Inorganic Acids: Aluminotungstates and Aluminophosphotungstates. LLOYD C. DANIELS (*J. Amer. Chem. Soc.*, 1908, 30, 1846—1857).—Balke and Smith (*Abstr.*, 1904, ii, 179) have described the aluminotungstates, $3(\text{NH}_4)_2\text{O}, \text{Al}_2\text{O}_3, 9\text{WO}_3, 4\text{H}_2\text{O}$ and

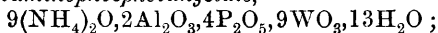


The present investigation was carried out with the object of ascertaining whether the ratio $\text{Al}_2\text{O}_3:9\text{WO}_3$ would exist in other derivatives. The following salts have been prepared and described,

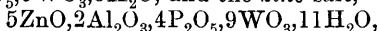
Copper aluminotungstate, $2\text{CuO}, \text{Al}_2\text{O}_3, 9\text{WO}_3, 16\frac{1}{2}\text{H}_2\text{O}$; the *barium* salt, $8\text{BaO}, \text{Al}_2\text{O}_3, 9\text{WO}_3, 7\text{H}_2\text{O}$; the *mercurous* salt, $5\text{Hg}_2\text{O}, \text{Al}_2\text{O}_3, 9\text{WO}_3$, and the *zinc* salts, $1\frac{1}{2}\text{ZnO}, \text{Al}_2\text{O}_3, 9\text{WO}_3, 8\text{H}_2\text{O}$ and



Ammonium aluminophosphotungstate,



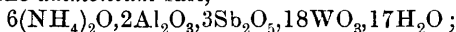
the *silver* salt, $4\text{Ag}_2\text{O}, 2\text{Al}_2\text{O}_3, 4\text{P}_2\text{O}_5, 9\text{WO}_3, 6\text{H}_2\text{O}$; the *barium* salt, $4\text{BaO}, 2\text{Al}_2\text{O}_3, 4\text{P}_2\text{O}_5, 9\text{WO}_3, 3\text{H}_2\text{O}$, and the *zinc* salt,



are also described.

The following aluminarsenotungstates have been prepared. The *ammonium* salt, $6(\text{NH}_4)_2\text{O}, 2\text{Al}_2\text{O}_3, 3\text{As}_2\text{O}_5, 18\text{WO}_3, 14\text{H}_2\text{O}$; the *barium* salt, $4\text{BaO}, 2\text{Al}_2\text{O}_3, 3\text{As}_2\text{O}_5, 18\text{WO}_3, 12\text{H}_2\text{O}$, and the *cadmium* salt, $4\text{CdO}, 2\text{Al}_2\text{O}_3, 3\text{As}_2\text{O}_5, 18\text{WO}_3, 17\text{H}_2\text{O}$.

A description is also given of the following aluminioantimoniotungstates. The *ammonium* salt,



the *silver* salt, $6\text{Ag}_2\text{O}, 2\text{Al}_2\text{O}_3, 3\text{Sb}_2\text{O}_5, 18\text{WO}_3, 12\text{H}_2\text{O}$, and the *barium* salt, $5\text{BaO}, 2\text{Al}_2\text{O}_3, 3\text{Sb}_2\text{O}_5, 18\text{WO}_3, 6\text{H}_2\text{O}$.

E. G.

Compounds of Silicon and Uranium. **Uranium Disilicide, USi_2 .** ÉDOUARD DEFACQZ (*Compt. rend.*, 1908, 147, 1050—1052.* Compare Abstr., 1907, ii, 475, 696).—The silicides of tungsten and molybdenum of the type MSi_2 having been prepared previously, the author completes the series by describing the preparation and properties of the corresponding uranium compound. *Uranium disilicide, USi_2 ,* obtained in small yield from silica and the oxide, U_3O_8 , by the aluminothermic method, occurs as brilliant microscopic crystals, D^{20}_D 8, belonging to the regular system. Chlorine attacks this silicide at 500° , giving the chlorides of uranium and silicon. Cold hydrogen fluoride dissolves it readily, whilst oxidising agents have little action. Although stable in air at a red heat, it burns slowly in oxygen at 800° , and is decomposed on fusion with alkalis, alkali carbonates, or potassium hydrogen sulphate.

Details are given of the method adopted for the analysis of this compound. W. O. W.

Thorium. WERNER VON BOLTON (*Zeitsch. Elektrochem.*, 1908, 14, 768—770).—The metal is prepared in minute crystals by reduction of the tetrachloride by sodium. By hammering the metal into a thick-walled copper tube 10 mm. in diameter, rolling this down to 1 mm. wire, and removing the copper with dilute nitric acid, a spongy wire of thorium is obtained, which can be rolled out to a band. The melting point is 1450° ; it burns in the air; potassium hydroxide and nitric acid have little action; sulphuric acid slowly attacks it, yielding the sulphate, and hydrochloric acid acts quickly, leaving about 15% of the metal undissolved in the form of lower oxides, which are possibly formed during the action. The density of the powder is 11.32, that of the rolled band, 12.16.

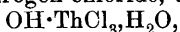
When the powder is shaken with cold 5% hydrochloric acid, the first portion which dissolves (about 10% of the whole metal) forms a complex acid, $(\text{ThO}_2)_{10}(\text{HCl})_4$, the solution of which contains neither thorium nor chlorine ions; its principal reactions are: with oxalic acid or sulphuric acid, a small precipitate, soluble in excess, is produced; ammonium oxalate gives a gelatinous precipitate, insoluble on boiling; ammonium carbonate and citric acid give gelatinous precipitates, insoluble in excess. The metal reduced from this compound is ordinary thorium. T. E.

Thorium. RICHARD J. MEYER (*Zeitsch. Elektrochem.*, 1908, 14, 809—810).—The reduction of thorium oxide by carbon tetrachloride yields a metal containing considerable quantities of oxide (Abstr., 1901, ii, 106). The oxide left by Bolton's thorium when dissolved in acid (preceding abstract) was therefore doubtless present in the metal. This also explains the action of dilute hydrochloric acid; the dissolved substance was probably metathorium chloride derived from the oxide. T. E.

Chlorides and Oxychlorides of Thorium. ÉDOUARD CHAUVENET (*Compt. rend.*, 1908, 147, 1046—1048. Compare Matignon, Abstr., 1901, ii, 106).—Thorium tetrachloride is most conveniently prepared free

* and *Bull. Soc. chim.*, 1909, [iv], 5, 3—5.

from oxychloride by heating thorium dioxide in a current of carbonyl chloride. A deliquescent, white powder, which is formed at the same time, has been proved to be identical with the crystalline chloride by analysis and by measurement of its heat of solution in water (56.75 Cal. at 12.5°). An aqueous solution of the tetrachloride deposits $\text{ThCl}_4 \cdot 7\text{H}_2\text{O}$ on evaporation (compare Krüss, Abstr., 1897, ii, 456). The heat of dissolution of this hydrate is 14.75 Cal. at 13.5°. When heated at 120—160° in hydrogen chloride, the oxychloride,



is obtained as a very hygroscopic powder, of which the heat of dissolution is 47.63 Cal. at 13.5° (compare Rosenheim, Abstr., 1900, ii, 351). The chloride, $\text{ThCl}_4 \cdot 7\text{H}_2\text{O}$, is converted into the oxychloride, ThOCl_2 , at 250°; the heat of dissolution of the latter is 28.15 Cal. at 13°.

W. O. W.

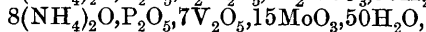
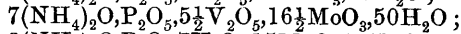
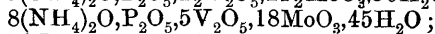
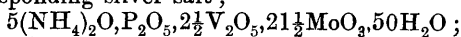
Basic Sulphates of Thorium and Cerium. OTTO HAUSER and F. WIRTH (*Zeitsch. anorg. Chem.*, 1908, 60, 242—246).—Dilute solutions of thorium sulphate deposit flocculent thorium hydroxide, containing some adsorbed sulphate, on boiling; thus resembling zirconium sulphate (Abstr., 1907, ii, 626). Concentrated solutions, heated in sealed tubes at 160—180°, deposit crystals of $\text{ThOSO}_4 \cdot \text{H}_2\text{O}$. At 105—115°, the same salt is deposited, mixed with the normal hydrated sulphate.

A dilute ice-cold solution of ceric sulphate deposits, after twenty-four hours, pale yellow crystals of $4\text{CeO}_2 \cdot 3\text{SO}_3 \cdot 12\text{H}_2\text{O}$, completely analogous to the basic zirconium sulphate. Boiling saturated solutions of ceric sulphate deposit crystals of $2\text{CeO}_2 \cdot 3\text{SO}_3 \cdot 4\text{H}_2\text{O}$, which, however, could not be obtained in a pure state, since they rapidly redissolve on cooling, and some reduction to cerous sulphate takes place.

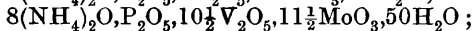
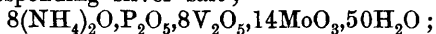
C. H. D.

Derivatives of Complex Inorganic Acids: Phosphovanadomolybdates. WILLIAM BLUM (*J. Amer. Chem. Soc.*, 1908, 30, 1858—1862).—Wolcott Gibbs (Abstr., 1884, 713) described two phosphovanadomolybdates, $8(\text{NH}_4)_2\text{O} \cdot 2\text{P}_2\text{O}_5 \cdot 8\text{V}_2\text{O}_5 \cdot 14\text{MoO}_3 \cdot 50\text{H}_2\text{O}$ and $7(\text{NH}_4)_2\text{O} \cdot 2\text{P}_2\text{O}_5 \cdot \text{V}_2\text{O}_5 \cdot 48\text{MoO}_3 \cdot 30\text{H}_2\text{O}$, and suggested that it was probable that the vanadium pentoxide, considered as $\text{V}_2\text{O}_5 \cdot \text{O}_3$, might replace the molybdenum trioxide of the phosphomolybdate. He was unable, however, to obtain a salt containing a higher proportion of vanadium pentoxide than that in the first compound mentioned. The present author is of opinion that this was probably due to the fact that an excess of ammonium vanadate was used in all the experiments.

The formation and composition of the ammonium phosphovanadomolybdates has now been further studied, and the following compounds have been obtained: $6(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 4\text{V}_2\text{O}_5 \cdot 18\text{MoO}_3 \cdot 52\text{H}_2\text{O}$, and the corresponding silver salt;



and the corresponding silver salt;



and $8(\text{NH}_4)_2\text{O}, \text{P}_2\text{O}_5, 11\text{V}_2\text{O}_5, 11\text{MoO}_3, 50\text{H}_2\text{O}$. All these ammonium salts crystallise in the tetragonal system, and are soluble in water.

E. G.

Action of Antimony Trichloride on Cobalt and on its Alloys with Antimony. F. DUCELLIEZ (*Compt. rend.*, 1908, 147, 1048—1050. Compare Abstr., 1908, ii, 853).—When cobalt is submitted to the action of antimony trichloride at 700—1200°, *cobalt monoantimonide*, CoSb , is formed as a crystalline, non-magnetic powder, D^{20}_4 8.12, m. p. about 1200°. This undergoes slight oxidation in air, and burns readily in oxygen; hydrogen chloride has little action on it, but hot concentrated sulphuric acid dissolves it rapidly. At 700—1450° it attacks antimony trichloride, forming antimony and cobalt chloride; the composition of the residual substance, however, remains unaltered. At 1200°, cobalt is attacked by antimony trichloride, and forms magnetic alloys containing less antimony than the foregoing antimonide; this compound remains as a non-magnetic powder when these alloys are treated with sulphuric acid.

Three classes of alloys of cobalt and antimony have been prepared by direct union of the elements at 500° in a current of hydrogen. (1) Magnetic alloys containing less than 67.04% antimony. When heated with antimony trichloride at 800°, or when treated with sulphuric acid, these lose their magnetic properties, and leave a residue of the monoantimonide, CoSb . (2) Alloys containing 67.04—80.27% of antimony, which decompose readily on heating, and form the monoantimonide when heated at 1200° in hydrogen. Substitution of antimony trichloride for hydrogen gives the same compound, together with antimony and cobalt chloride. (3) Alloys containing more than 80.27% antimony, which, on treatment with nitric acid followed by hydrogen chloride, give *cobalt diantimonide*, CoSb_2 , a grey, crystalline powder, D^{20}_4 7.76, m. p. about 700°; this closely resembles the monoantimonide in its chemical properties.

W. O. W.

Atomic Weight of Bismuth. III. Analysis of Bismuth Bromide. ALEXANDER GUTBIER and HANS MEHLER (*J. pr. Chem.*, 1908, [ii], 78, 409—420. Compare Abstr., 1906, ii, 92; 1908, ii, 600).—The bismuth bromide employed in this investigation was prepared by the action of bromine on four specimens of bismuth. The percentage of bromine present in each of the four samples of bromide was determined by dissolving the latter in 2*N*-nitric acid and precipitating with silver nitrate. As the result of eight experiments, it was found that 34.81207 grams of bismuth bromide gave 43.80773 grams of silver bromide. The extreme values obtained were $\text{Bi} = 208.18$ and $\text{Bi} = 207.88$. The value 208.0 ± 0.06 ($O = 16$) for the atomic weight of bismuth determined by this method is in agreement with the result ($\text{Bi} = 208.0$) obtained by Gutbier and Birckenbach (Abstr., 1908, ii, 600) by the synthesis of bismuth oxide.

W. H. G.

Atomic Weight of Bismuth. IV. Synthesis of Bismuth Sulphate. ALEXANDER GUTBIER and RUDOLF LÉON JANSSEN (*J. pr. Chem.*, 1908, [ii], 78, 421—436. Compare preceding abstract).—The atomic weight of bismuth was determined in this investigation as follows: a known weight of the element was dissolved in nitric acid (D 1.05), the nitrate obtained evaporated with sulphuric acid, and the sulphate heated to constant weight in an electric-oven at 380° . Two specimens of bismuth were used; three experiments with one sample gave the mean value $\text{Bi} = 208.04$, whilst two experiments with the second sample gave $\text{Bi} = 208.17$. The extreme values obtained were $\text{Bi} = 208.26$ and 207.92 . The atomic weight of bismuth determined by this method is 208.1 ($\text{O} = 16$).

From the results of the investigations of Marignac (*Abstr.*, 1884, 813), Lowe (*Abstr.*, 1884, 558), Schneider (*Abstr.*, 1895, ii, 114), and of Gutbier and his co-workers, it follows that bismuth has the atomic weight 208.0 ($\text{O} = 16$).
W. H. G.

Carbonates and Oxalates of Bismuth. LUDWIG VANINO and EMILIE ZUMBUSCH (*Ber.*, 1908, 41, 3994—3999).—Attempts to prepare normal bismuth carbonate and oxalate show that these substances are extremely sensitive to the hydrolytic action of water. Only by working under strictly defined conditions can substances of definite composition be obtained. The normal carbonate has not been isolated, but the oxalate is obtained when a solution of bismuth nitrate and mannitol in equal molecular quantities (0.1 gram-mol. per 100 c.c.) is treated at 25° with the calculated quantity of a saturated solution of oxalic acid and the precipitate washed with cold water. If the washing is performed with hot water, the precipitate, after drying, has the composition $\text{OH} \cdot \text{Bi} : \text{C}_2\text{O}_4$.
C. S.

Mineralogical Chemistry.

Action of Oxidising and Reducing Gases on the Colour of Minerals. WALTER HERMANN (*Zeitsch. anorg. Chem.*, 1908, 60, 369—404).—A number of coloured minerals have been heated in oxidising and reducing gases in order to determine the nature of the constituent causing colour ; borax glasses coloured with known oxides being heated under the same conditions for comparison.

The results indicate that oxides of iron occur as colouring material in zircon, corundum, spinel, epidote, and beryl. Chromium and manganese, together with iron, bring about colorations in green zircon, garnet, and tourmaline. The results with quartz and topaz were indecisive. Organic substances, when present, occur together with metallic oxides, so that, on heating, the colour due to the oxide remains. Certain minerals, halite, fluorite, smoky quartz, amethyst, and citrine, lose their colour when heated in all cases, and this cannot therefore be attributed to oxides of heavy metals.

The colorations are mostly to be regarded as due to dilute solutions

of colouring matters, but garnet and epidote are probably coloured in themselves to some extent.

The conditions prevailing in minerals are of a complicated nature.

C. H. D.

Minerals of the Fumaroles of Vesuvius. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1908, 31, 260—264).—The fumaroles due to the 1903 eruption are still active, and are of two types. Those of one type deposit sodium and potassium chlorides together with cotunnite and tenorite. These saline encrustations contain a rather large quantity of calcium chloride, indicating the presence of the mineral chlorocalcite. The formula of the new mineral palmierite (Abstr., 1897, ii, 628), discovered in these deposits, was given previously as $\text{PbSO}_4 \cdot (\text{K}, \text{Na})_2\text{SO}_4$; the published analysis agrees better with the formula $4\text{PbSO}_4 \cdot 3[(\text{K}, \text{Na})_2\text{SO}_4]$. It is to be noted, however, that the very small amount of material available for analysis was isolated from the associated apthitalite by dissolving the latter in cold water; but as palmierite is quickly decomposed by hot water and more slowly by cold water, with the separation of lead sulphate, it is probable that the material analysed contained some free lead sulphate, and consequently the true formula of the mineral is more likely to be $\text{PbSO}_4 \cdot (\text{K}, \text{Na})_2\text{SO}_4$. Fumaroles of the acid type deposit crystals of erythrosiderite and sassolite.

L. J. S.

Occurrence of Boric Acid in Vesuvianite. EDGAR T. WHERRY and WILLIAM H. CHAPIN (*J. Amer. Chem. Soc.*, 1908, 30, 1684—1687).—Vesuvianite from twenty-five different localities was specially examined for boric acid; in nine cases it was absent, in four present only in traces, and in only four was there more than 1%. The largest amount, 4.14%, was found in the vesuvianite from the Wilui river in Siberia.

F. W. Clarke's formula for vesuvianite is $\text{R}_2^{\text{II}}\text{Ca}_7\text{Al}_2(\text{SiO}_4)_6$, where R^{II} may be H_2 , K_2 , Na_2 , Mg , Ca , Fe^{II} , Mn^{II} , and especially AlOH and AlF , and Al may be replaced by Fe^{III} , Mn^{III} , or B^{III} . The small amount of ferric iron (never exceeding 5%) present in vesuvianite, however, rather suggests that there is only a limited amount of basic aluminium capable of being replaced by ferric iron, and consequently, that the aluminium and boron play the part of acids. Clarke's formula would then become $\text{Ca}_7(\text{R}^{\text{II}}\text{AlO}_2)_2(\text{SiO}_4)_2(\text{SiO}_3)_4$, or, if part of the aluminium is basic and part acidic, $\text{Ca}_7\text{R}^{\text{II}}(\text{R}^{\text{II}}\text{AlO}_2)(\text{SiO}_4)_4(\text{SiO}_3)_2$.

L. J. S.

Gibbsite from India. LEWIS LEIGH FERMOR (*Chem. Zentr.*, 1908, ii, 1062; from *Rec. Geol. Survey, India*, 34, 167—171).—Gibbsite occurs in association with manganese ores at Talevadi, in the Belgaum district, Bombay, where it forms a layer 2—6 mm. in thickness on psilomelane in a ferruginous laterite; the small, scaly crystals form greyish-white, radially-fibrous aggregates; anal. I, by S. S. Rama Rau. Anal. II, by J. C. Brown, is of amorphous gibbsite, resembling halloysite in appearance, from Bhekowli, in the Sátará district.

	Al_2O_3 .	SiO_2 .	H_2O (hygr.).	H_2O (comb.).	Total.	Sp. gr.
I.	63.59	2.01	34.75		100.35	2.40
II.	64.20	0.39	0.62	34.51	99.72	2.35

L. J. S.

Argyrodite from Bolivia. V. MORITZ GOLDSCHMIDT (*Zeitsch. Kryst. Min.*, 1908, 45, 548—554. Compare Abstr., 1898, ii, 436).—A description is given of some unusually large crystals (3—5 cm. across) of argyrodite found on pyrrargyrite from Colquechaca. The habit is dodecahedral {110}, or less frequently octahedral, and the character of the faces, as well as some ill-defined etching-figures, point to holohedral-cubic symmetry, D 6·235. The following analysis agrees with Penfield's formula Ag_8GeS_6 .

Ag.	Cu.	Hg.	Fe.	Zn.	Ge.	Sn.	As.	S.	H ₂ O.	Total.
75·67	0·08	0·03	0·03	0·11	6·55	0·10	0·05	17·15	0·18	99·95

In spite of the difference in crystal-symmetry, argyrodite appears to fall best in the tetrahedrite group, and in this case the formulæ, $3\text{R}_2^{\text{IS}}, \text{R}^{\text{IIR}^{\text{IV}}}\text{S}_3$, for tetrahedrite and, $3\text{R}_2^{\text{IS}}, \text{R}_2^{\text{IR}^{\text{IV}}}\text{S}_3$, for argyrodite show an analogous homœomorphic relation similar to that between Fe_2O_3 , FeTiO_3 , etc.

L. J. S.

Composition of Morinite. ADOLPHE CARNOT and ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1908, 31, 149—152).—Morinite, of which a preliminary description was given by Lacroix in 1891, is found in the deposits of tin ore at Montebbras, dep. Creuse, as small and indistinct, monoclinic crystals, or more usually as crystalline masses with an easy cleavage and a rose-red colour. It occurs embedded in amblygonite, of which it is an alteration product, and is associated with quartz, cassiterite, and wavellite. Analysis of the massive material gave (after deducting 1·50 SiO_2 , 0·20 H_2O lost at 120°):

P_2O_5 .	F.	Al_2O_3 .	Ca.*	Na_2O .	H_2O .	Total.
33·50	13·20	17·80	13·80	5·20	17·90	101·40

* CaO , 19·0; traces of Li_2O , MgO , FeO .

The formula $3\text{AlPO}_4, \text{Na}_2\text{HPO}_4, 3\text{CaF}_2, 8\text{H}_2\text{O}$, when expressed in the form $(\text{AlF})_3^{\text{II}}\text{Na}_2\text{H}(\text{PO}_4)_3, (\text{CaF})_3^{\text{I}}\text{PO}_4, 8\text{H}_2\text{O}$, shows in the first molecule a relation to amblygonite, $[\text{Al}(\text{F}, \text{OH})]_{\text{II}}^{\text{I}}(\text{Li}, \text{Na})\text{PO}_4$. The alteration of the amblygonite has thus been accompanied by a loss of aluminium and a gain of calcium. The aluminium phosphates, wavellite, and a kind of turquoise are abundant at Montebbras, and they represent the last stage in the alteration of the amblygonite. Morinite is remarkable in containing more fluorine than any other phosphate, this element being usually largely replaced by hydroxyl in other minerals.

L. J. S.

Minerals of the Pegmatite-veins with Lithia-tourmaline in Madagascar. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1908, 31, 218—247).—The mineral occurrences in the neighbourhood of Mt. Bity,* in Madagascar, have already been briefly mentioned in connexion with the new species bityite (Abstr., 1908, ii, 705); a more detailed description is now given. Beryl is represented by two varieties: normal beryl, of which the colour is white, blue, or green; and beryl rich in alkalis (caesium, lithium, and sodium), which is pink.

* i.e., Mt. Ibity, south of Antsirabe.—L.J.S.

The following new analyses are given. Lazulite is found on the surface as dark blue fragments; analysis by F. Pisani gave:

P_2O_5 .	Al_2O_3 .	MgO.	FeO.	H_2O .	Total.	Sp. gr.
45·30	35·22	9·19	3·95	5·80	99·46	3·12

Another mineral found loose on the surface is doubtfully referred to hatchettolite; this is brown and resinous, with an irregular fracture, transparent in thin flakes, and optically isotropic, D 3·95. A partial analysis by Urbain gave: Cb_2O_5 (with Ta_2O_5 and TiO_2), 56·61; uranium oxide (weighed as U_3O_8), 14·15; GIO , 2·37; Fe_2O_3 , 1·13; Mn_3O_4 (with a little cerium and yttrium earths), 1·46; ThO_2 , 0·96; SiO_2 , 2·31; Pb, Bi, Sn, Cu (weighed as sulphides), 1·52; oxides of alkaline earths, 1·64; loss at 300° , 11·51; loss on ignition, 3·81.

L. J. S.

Alunite from Réalmont, dep. Tarn. PIERRE TERMIER (*Bull. Soc. franç. Min.*, 1908, 31, 215—216).—The mineral is very compact, and has a pale rose colour with black patches and streaks, the latter being due to the presence of bituminous matter. Analysis by F. Pisani agrees with the usual formula $K_2O, 3Al_2O_3, 4SO_3, 6H_2O$:

SO_3 .	Al_2O_3 .	K_2O .	CaO.	H_2O .	Insol.	Total.	Sp. gr.
36·80	36·36	10·40	0·76	13·60	2·20	100·12	2·8

The mineral occurs as a stratum, 10 cm. in thickness, between schists and a bed of kaolin, and has evidently been formed by the action of water containing sulphuric acid (derived by the weathering of the iron pyrites in the schists) on a rhyolite rich in orthoclase. The complete separation of these two products of decomposition of the rhyolite into two sharply-defined beds is curious.

L. J. S.

The Scheelite of Otago. A. M. FINLAYSON (*Trans. New Zealand Inst.*, 1908, 40, 110—122).—Scheelite occurs as yellowish-white masses in many of the veins of auriferous quartz in the gold-fields of Otago. Analysis of a commercial sample gave:

WO_3 .	CaO.	MgO.	FeO.	Fe_2O_3 .	MnO.	CO_2 .	Total.
80·58	18·98	0·20	0·24	nil			100·00

Molybdenum is also often present in varying amounts up to 1%. The mineral sometimes occurs in contact with corroded calcite, and has evidently been formed by the action of solutions containing tungstic acid on the lime minerals of the surrounding rocks.

L. J. S.

Tantalite and Gadolinite from Western Australia. ANDREW GIBB MAITLAND (*Chem. Zentr.*, 1908, ii, 1062; from *Bull. Geol. Survey Western Australia*, 23, 65—74).—Mangano-tantalite (hübnerite) occurs as large masses, weighing as much as five hundred weight, in pegmatite-veins traversing greenstone in the Wodgina tin-field, and

it is also found in the alluvial deposits ; anal. I by Simpson. Gadolinite occurs in granite in the Cooglegong tin-field ; anal. II by Davis :

	Ta ₂ O ₅ .	Cb ₂ O ₅ .	SiO ₂ .	TiO ₂ .	Ce ₂ O ₃ .	(La,Di) ₂ O ₃ .	Y ₂ O ₃ .	SnO ₂ .	WO ₃ .	GIO.
I.	68·65	15·11	—	0·40	—	—	—	0·48	trace	—
II.	—	—	23·33	—	2·50	18·30	33·40	—	—	12·28

	FeO.	MnO.	NiO.	CaO.	MgO.	H ₂ O.	Loss on ignition (He, H, N, CO ₂).	Total.	D.
I.	1·63	14·15	trace	trace	0·15	0·07	—	100·64	7·03
II.	10·38	—	—	—	0·69	—	0·32	101·20	4·14

L. J. S.

Risörite, a New Mineral. OTTO HAUSER (*Zeitsch. anorg. Chem.*, 1908, 60, 230—236).—The new yttrium columbium mineral from Risör, Norway (Abstr., 1907, ii, 704), has been further examined, and shown to be a definite species. The mean of four analyses gives :

Cb ₂ O ₅ .	Ta ₂ O ₅ .	TiO ₂ .	SnO ₂ .	ThO ₂ .	UO ₂ .	(Y,Er) ₂ O ₃ .	Ce(La,Di) ₂ O ₃ .	
36·21	4·00	6·00	0·01	trace	0·10	36·28	2·88	
CaO.	FeO.	PbO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	CO ₂ .	N,He.	H ₂ O.	Total.
1·93	2·61	0·20	1·20	0·81	0·23	0·90	7·11	100·67

It is a glassy, isotropic mass, D¹⁶ 4·179, hardness 5·5, with considerable β -radioactivity. It may be regarded as an isomorphous mixture of fergusonite with metatitanates.

C. H. D.

The So-called Dysanalyte from Vogtsburg, in the Kaiserstuhl. OTTO HAUSER (*Zeitsch. anorg. Chem.*, 1908, 60, 237—241).—The Kaiserstuhl mineral described by Knop (Abstr., 1878, 385) as dysanalyte appears to consist of perowskite contaminated with enclosures. An analysis of selected crystals gave :

	TiO ₂ .	SiO ₂ .	Cb ₂ O ₅ .	FeO.	CaO.	MnO.	Na ₂ O.	Ce ₂ O ₃ .	Total.
	50·93	2·21	4·86	9·22	25·60	0·23	4·37	2·80	100·22

C. H. D.

Naegite. TSUNASHIRŌ WADA (*Chem. Zentr.*, 1908, ii, 1063 ; from *Beiträge zur Mineralogie von Japan*, 1906, 23—25).—A new analysis by Haga of "naegite" (Abstr., 1905, ii, 177) shows that the mineral consists largely of zirconia and silica.

	ZrO ₂ .	ThO ₂ .	SiO ₂ .	Cb ₂ O ₅ , Ta ₂ O ₅ .	UO ₃ .	Y ₂ O ₃ .	Total.
	55·30	5·01	20·58	7·69	3·03	9·12	100·73

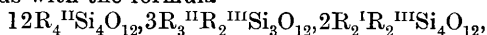
L. J. S.

[Analyses of Hornblende.] LOUIS DUPARC and FRANCIS PEARCE (*Bull. Soc. franç. Min.*, 1908, 31, 94—135).—Numerous determinations are given of the optical constants of several rock-forming minerals, and analyses of the following : (I) hornblende from amphi-

bolite from the Island of Coll, Hebrides; (II) hornblende from amphibolite from Chester, Massachusetts.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Cr ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	Total.
I.	51.50	0.23	2.88	0.14	6.25	5.39	0.05	13.26	16.95	1.61	0.32	98.58
II.	42.74	1.08	5.48	—	11.92	11.46	0.06	12.72	11.60	2.25	0.56	99.69

(I) corresponds with the formula



and (II) with $10R_4^{II}Si_4O_{12}, 9R_3^{II}R_2^{II}Si_3O_{12}, 4R_2^IR_2^{III}Si_3O_{12}$. L. J. S.

Zeolites from the Basalt of Montresta, Sardinia. JACQUES DEPRAT (*Bull. Soc. franç. Min.*, 1908, 31, 181—192. Compare Abstr., 1908, ii, 864).—Cavities in the basalt contain heulandite, stilbite, mesolite, chabazite, and rarely analcite and thomsonite. The following were analysed: (I) heulandite, crystals; (II) stilbite, crystals; (III) mesolite, as finely-fibrous, radial aggregates intimately associated with chabazite.

	SiO ₂ .	Al ₂ O ₃ .	CaO.	Na ₂ O.	H ₂ O.	Total.
I.	59.00	16.70	8.20	1.30	14.70	99.90
II.	57.70	17.10	7.70	0.50	17.60	100.60
III.	47.70	24.10	10.00	5.80	12.41	100.01

L. J. S.

[Anorthoclase] from Port Victor, South Australia. H. W. GARTRELL (*Chem. Zentr.*, 1908, ii, 1063; from *Trans. Roy. Soc., South Australia*, 27, 256—260).—The granite of this locality contains large porphyritic crystals of anorthoclase, which are flesh-red and translucent to opaque; D 2.58. The following analysis corresponds with $Or_{28}Ab_8An_4$:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	Loss on ignition.	Total.
64.54	19.34	traces			1.24	2.89	11.84	0.58	100.43

L. J. S.

Cordierite-pinites from Central France. FERDINAND GONNARD (*Bull. Soc. franç. Min.*, 1908, 31, 171—181).—A description is given of the occurrence of the pseudomorphs after cordierite in the departments of Puy-de-Dôme, Loire, and Rhône. The following analysis, by P. Barbier, is given of large, dark green crystals, with a perfect cleavage and D 2.77, which occur with microcline, smoky quartz, and apatite in a pegmatite at Vizézy:

SiO ₂ .	Al ₂ O ₃ .	FeO	MnO, CaO.	MgO.	K ₂ O.	Loss on ignition.	Total.
42.43—42.66	33.21—32.95	10.58	traces	2.61	4.75	6.29	99.87

L. J. S.

Contact Minerals (Gehlenite, Spurrite, and Hillebrandite) from Mexico. FRED. E. WRIGHT (*Amer. J. Sci.*, 1908, [iv], 26, 545—554).—These minerals were formed near the junction of altered limestone and intrusive basic diorite in the Velardeña mining district in Durango.

Gehlenite occurs as massive, granular aggregates together with spurrite, yellow garnet, and calcite. It is dark grey in colour, owing to abundant minute inclusions of magnetite, and only rarely are small pieces, free from magnetite inclusions, of an amber-yellow colour; D^{25} 3.039. Analysis I is very similar to previous analyses of gehlenite, but no simple formula can be deduced, the mineral probably representing a solid solution of several end members of a series :

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.
I.	26.33	0.03	27.82	1.43	0.50	0.01	2.44
II.	26.96	0.01	0.39	0.11		0.03	0.23
III.	32.59	0.02	0.23	0.15		0.01	0.04
	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	CO ₂ .	Total.	
I.	39.55	0.21	0.10	1.85	nil	100.27	
II.	62.34	0.05	trace	nil	9.73	99.85	
III.	57.76	0.03	0.05	9.36	nil	100.24	

Spurrite occurs as granular masses with glistening cleavages, resembling crystalline marble in appearance; no crystals were observed. The mineral is transparent to translucent, and colourless to pale grey with tints of blue or yellow; lustre, vitreous to resinous; hardness, 5; D^{25} 3.014. The optical characters indicate that the symmetry is probably monoclinic; the birefringence is high ($\gamma - \alpha = 0.039$), the axial angle small ($2E = 70^\circ$), the sign negative, and there is a noticeable crossed dispersion. Lamellar twinning occurs on more than one plane perpendicular to the plane of symmetry, and there are two cleavages, with an angle of 79° , perpendicular to the same plane. Before the blowpipe, the mineral becomes white and porcelain-like, and is infusible. It effervesces in dilute hydrochloric acid, and is readily dissolved with the separation of gelatinous silica. Analysis II corresponds with the formula $2Ca_3SiO_4, CaCO_3$.

Hillebrandite possesses a fibrous structure, the fibres being often aggregated as radial sperulites; it is associated with yellow garnet and wollastonite. The material is white, often with a tinge of green, and porcelain-like, and is translucent only in small chips; hardness, $5\frac{1}{2}$; D^{25} 2.692. The optical characters of the fibres suggest orthorhombic symmetry. Before the blowpipe, the mineral fuses to a colourless glass. It readily dissolves in hydrochloric acid, with the separation of some silica, and is slowly decomposed by water. Analysis III gives the formula $2CaO, SiO_2, H_2O$.

Attempts to prepare the new minerals spurrite and hillebrandite synthetically have so far been unsuccessful. L. J. S.

Mineralogy of the Færoe Islands. MATTHEW F. HEDDLE (*Chem. Zentr.*, 1908, ii, 1061; from *Trans. Geol. Soc. Glasgow*, 1906, 12, 1—15).—Anal. I of bluish-white spheres of faröelite from Nolsö; II, of mesolite occurring on sphærostilbite from Nolsö; III, of stilbite from Bordö.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.	42.50	28.06	—	11.35	5.60	—	13.02	100.53
II.	46.80	26.46	—	9.08	5.14	—	12.28	99.76
III.	58.79	14.613	0.47	9.534	0.324	0.232	17.298	101.261

L. J. S.

Phillipsite from Mont Simiouse, Loire. FERDINAND GONNARD (*Bull. Soc. franç. Min.*, 1908, 31, 269—271).—Analysis by P. Barbier of crystals of phillipsite associated with chabazite and offretite lining cavities in basalt at Mont Simiouse gave:

SiO ₂ .	Al ₂ O ₃ .	CaO.	BaO, MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
52.10	18.33	4.96	traces	6.88	1.10	16.55	99.92

This agrees with the formula $\text{RAl}_2\text{Si}_5\text{O}_{14}, 5\text{H}_2\text{O}$ (where R = Ca, K, Na), whilst some analyses of phillipsite from other localities have given the formulæ $\text{RAl}_2\text{Si}_4\text{O}_{12}, 5\text{H}_2\text{O}$, $\text{RAl}_2\text{Si}_4\text{O}_{12}, 4\text{H}_2\text{O}$, and $\text{RAl}_2\text{Si}_3\text{O}_{10}, 3\frac{1}{2}\text{H}_2\text{O}$. The present mineral therefore represents an acid type of phillipsite, similar to that from Giessen and the Kaiserstuhl. L. J. S.

The Pumice of the Volcano of Mont Dore. ALFRED LACROIX (*Compt. rend.*, 1908, 147, 778—782).—A description is given of the fragmentary materials, more particularly the pumice, of this extinct volcano. Rhyolitic pumice (anal. I and II, by F. Pisani) with a fibrous structure occurs only in small pieces; it consists almost entirely of a colourless glass with very few phenocrysts of anorthoclase, surrounded by orthoclase. The composition is identical with that of the rhyolite (anal. III). Trachytic pumice (anal. IV) has a cellular structure and is less glassy, containing phenocrysts of orthoclase, anorthoclase, biotite, and augite, together with microlites of orthoclase.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	TiO ₂ .	H ₂ O.	Total.
I.	73.90	10.95	0.08	1.06	1.08	1.58	4.08	4.60	—	3.35	100.68
II.	73.90	11.93	0.15	0.87	0.13	0.34	4.10	4.62	trace	4.00	100.04
III.	75.50	13.50	0.95	—	0.39	0.99	4.35	4.15	trace	0.37	100.20
IV.	60.50	18.20	1.20	1.08	0.26	0.68	5.10	5.23	0.39	7.00	99.64

L. J. S.

Rare Renfrewshire Minerals. ROBERT S. HOUSTON (*Chem. Zentr.*, 1908, ii, 1062; from *Trans. Geol. Soc. Glasgow*, 1906, 12, 354—361).—Several minerals are described, and analyses given of the following: I, labradorite from Gleniffer Hills, south of Paisley; II, pectolite, massive and fibrous, from South Quarry, Craigenfeoch, near Johnstone; III, stilbite, red, from near Kilbarchan.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	MnO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
I.	53.82	28.09	2.88	3.62	4.24	trace	2.25	3.70	2.00	100.60
II.	55.38	trace	—	33.68	trace	—	—	7.20	3.30	99.56
III.	55.02	16.48	trace	7.24	0.58	—	—	4.46	17.00	100.78

L. J. S.

Weathering and Formation of Kaolinite in the Halle Quartz-porphry. VICTOR SELLE (*Chem. Zentr.*, 1908, ii, 1203; from *Zeits. Naturw.*, 1907, 79, 321—421).—Analysis I is of the white product of weathering, and II, of the portion insoluble in concentrated sulphuric acid; the latter consists of quartz, 3.58%, and felspar, 7.97%. Deducting from the soluble portion the alkalis as sericite, the sulphuric anhydride as gypsum, and neglecting the magnesia, the remainder has the composition $2\text{Al}_2\text{O}_3, 5\text{SiO}_2, 4\text{H}_2\text{O}$, whereas kaolinite has the formula $2\text{Al}_2\text{O}_3, 4\text{SiO}_2, 4\text{H}_2\text{O}$.

The mineralogical composition of the sample is given as : quartz, 11·56 ; felspar, 7·97 ; kaolinite, 71·45 ; sericite, 4·06 ; other minerals, 4·96%.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	SO ₃ .	H ₂ O.	Alkalis.	Total.
I.	51·05	27·07	5·51	1·01	2·09	1·45	10·30	1·52	100·00
II.	8·88	1·44	0·08	0·12	0·04	—	—	1·04	11·55

The alteration of the felspar in the rock has given rise, first to mica, and this has subsequently been altered to kaolinite. In the Halle district the decomposed porphyries are richer in kaolinite nearer the surface, and minerals of pneumatolytic origin are absent. The conclusion is therefore drawn that the formation of kaolinite is dependent on the ordinary processes of weathering, only these were more intense in their action in former times than at present.

L. J. S.

Analysis of London Clay. JOHN H. B. JENKINS (*Geol. Mag.*, 1908, [v], 5, 265—266).—In a well-boring at East Ham, the stratum of clay extends from 17 to 76 feet below the surface. The wet, stiff clay of dark grey colour loses 20·1% at 120°, and on ignition there is a further loss of 6·3%. The ignited material is brick-red, and contains :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	Total.
67·9	18·3	8·7	1·3	1·2	1·6	1·4	100·4

L. J. S.

Red Porphyry [Porfido Rosso Antico]. J. COUYAT (*Compt. rend.*, 1908, 147, 988—990).—The ancient quarries whence this celebrated ornamental stone was obtained by the Romans are situated along the Wadi Abu Maammel, on the north-west slopes of the Jebel Dokhan, in Egypt. The crystalline schists of the district are penetrated by necks of hornblende-andesite and by veins of various other igneous rocks (this vol., ii, 65). This andesite, when unaltered (anal. II), is greenish-black or ebony-black, and contains phenocrysts and microlites of andesine and hornblende together with much apatite and magnetite. The hornblende (anal. I) contains some manganese ; it has a maximum extinction angle of 22°, and its pleochroic colours are pale yellow to green. The red porphyry (anal. III) is found in the central, more crystalline portions of the necks, and it is an altered form of the hornblende-andesite ; there is a gradual passage from one rock to the other, a violet porphyry forming an intermediate zone. The simultaneous decomposition of the hornblende and felspar has given rise to much manganiferous epidote (withamite), but the red colour of the rock is mainly due to the large quantity of finely-divided hæmatite ; other secondary minerals are damourite, actinolite, and biotite.

SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	MnO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.	44·5	1·5	12·5	12·2	4·0	9·5	11·1	0·4	3·9	0·5	100·1
II.	64·3	0·45	16·4	1·85	2·5	4·7	3·0	trace	4·3	2·0	100·1
III.	64·4	0·65	16·1	3·5	1·0	5·0	2·7	trace	4·2	1·6	100·25

L. J. S.

[Hypersthene-Augite from Lake Onega.] WALTER WAHL (*Fennia, Helsingfors*, 1908, 24, No. 3, 1—94).—In a paper on the geology of the west coast of Lake Onega, Russia, are given several rock analyses, together with the following analysis of a pyroxene isolated from a coarse-grained quartz-diorite from Schtscheliki.

SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	NiO.	MnO.	MgO.
50·36	0·80	2·49	2·35	18·15	0·04	0·56	11·37
	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.	Sp. gr.	
	13·97	0·26	0·19	0·55	101·09	3·46	

The crystals show a zonal structure with varying optical characters; in the inner portion, $2E = 48^{\circ}42'$, and in the outer, $2E = 73^{\circ}8'$; $c:c = 45^{\circ}$. The mineral belongs to the group of enstatite-augites, and is a hypersthene-augite.

L. J. S.

Gabbro and Iron-ore of the Jubrechkin Kamen, Northern Urals. LOUIS DUPARC (*Compt. rend.*, 1908, 147, 1061—1063).—This mountain is formed entirely of uralitised gabbro (anal. I) of various types, and irregularly distributed through the rock are basic segregation patches (anal. II), often of considerable size. These patches consist largely of magnetite, together with hornblende and a little epidote and kaolin.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	Loss on ig- nition.	Total.
I.	47·97	1·30	13·50	3·55	11·47	trace	10·63	6·51	0·26	2·78	1·60	99·57
II.	26·62	9·50	11·62	19·50	21·87	0·20	6·47	2·57	0·34	1·06	1·30	101·05

L. J. S.

Mode of Formation of the Puy de Dôme. ALFRED LACROIX (*Compt. rend.*, 1908, 147, 826—831).—The structure of this extinct volcano is compared with the recent West Indian volcanoes, and found to resemble that of Guadeloupe rather than Mt. Pelée. Analyses are given of domites with biotite or with hornblende, and of the fragmentary derivatives of these rocks.

L. J. S.

Eruptive Rocks of Jebel Dokhan, Red Sea. J. COUYAT (*Compt. rend.*, 1908, 147, 867—869).—Veins and bosses of the eruptive rocks penetrate the conglomerates and schistose sediments which rest on a granitic massif. Analyses are given of granite, microgranite, micropegmatite, rhyolite, andesite, and labradorite.

L. J. S.

Possible Existence of a Nickel-Iron (Fe₅Ni₃) in Meteorites. LAZARUS FLETCHER (*Min. Mag.*, 1908, 15, 147—152).—In the analysis of the meteoric stone of Zomba (Abstr., 1901, ii, 400), the repeated extractions of the nickel-iron with mercuric ammonium chloride showed that the residue became gradually richer in nickel. This was at the time attributed to the rusting of the iron in the minute particles of the alloy, but is now explained by the presence of a nickel-iron constituent, Fe₅Ni₃, containing 38·50% Ni(Co), which is not

readily attacked by the mercuric solution. This constituent is identical with the "taenite" containing 38.13% Ni(Co) isolated, by reason of its insolubility in dilute hydrochloric acid, from the Youndegin iron (Abstr., 1900, ii, 27). From an examination of the thermo-magnetic characters of the Sacramento iron, S. W. J. Smith (*Phil. Trans.*, 1908, A, 208, 21) has recently concluded that this meteorite contains a nickel-iron with not less than 37% Ni, thus confirming the above results. L. J. S.

Investigations on the Gases of the Wiesbaden Thermal Springs. FERDINAND HENRICH (*Ber.*, 1908, 41, 4196—4209. Compare Abstr., 1905, ii, 6, 221; 1907, ii, 150).—The gases evolved by some of the thermal springs at Wiesbaden have been analysed, and found to contain carbon dioxide, nitrogen, oxygen, methane, hydrogen sulphide, argon, neon, helium, and radium emanation in the following proportions, the values given being volume percentages. *Kochbrunnen* ($t = 68.7^\circ$): gas absorbed by potassium hydroxide 84.8, oxygen 0.2, nitrogen 12.7, methane 0.6, rare gases (argon, etc.) and emanation 1.7; *Adlerquelle* ($t = 64.6^\circ$): gas absorbed by potassium hydroxide 77.6, oxygen 1.2, nitrogen 18.4, methane 0.8, rare gases and emanation 2.0; *Schützenhofquelle* ($t = 49.2^\circ$): gas absorbed by potassium hydroxide 32.4, oxygen 0.2, nitrogen 62.05, methane 0.45, rare gases and emanation 4.9. The composition of the evolved gas varies slightly and irregularly throughout the year.

It is probable that the gases are derived from the rocks in the vicinity of the springs, since it has been found that these rocks when heated alone or with potassium hydrogen sulphate evolve oxygen, nitrogen, helium, and argon. The oxygen is absorbed by the ferrous carbonate present in the spring-water. W. H. G.

Physiological Chemistry.

Effects of Low Pressures on Respiration. ARTHUR BOYCOTT and JOHN S. HALDANE (*J. Physiol.*, 1908, 37, 355—377). **Alveolar Air on Monte Rosa.** R. OGIER WARD (*ibid.*, 378—389). **Effects of Want of Oxygen on Respiration.** JOHN S. HALDANE and EDWARD P. POULTON (*ibid.*, 390—407).—The experiments on the effect of low atmospheric pressure on respiration were carried out on men, partly on Monte Rosa and partly in a specially-constructed steel chamber. When the pressure is diminished, the alveolar carbon dioxide pressure remains constant during short exposures. When the air pressure reaches 550 mm., or the alveolar oxygen pressure 62 mm., the alveolar carbon dioxide pressure falls, and as the air pressures fall, the fall in the carbon dioxide pressure occurs with increasing rapidity. In long exposures, the fall in the carbon dioxide pressure occurs earlier

and further ; the alveolar oxygen pressure is correspondingly higher ; the process is one of gradual adaptation to low pressures or great altitudes. The fall in alveolar carbon dioxide pressure is due to hyperpncea dependent on the low oxygen pressure, and is absent if oxygen is added to the air. The hyperpncea is, however, not directly due to want of oxygen, since it takes time to develop, and may persist for days after the want of oxygen is removed. It is probably due to the gradual formation, in consequence of insufficient oxygen, of lactic acid or other substances which have the same influence as carbon dioxide on the respiratory centre, so that less carbon dioxide is required to excite the centre. When the alveolar oxygen pressure falls to 30 mm., urgent symptoms are produced. Exposure to cold causes a slight rise, and to heat, a slight fall in the alveolar carbon dioxide pressure.

If sufficient of the preformed carbon dioxide is first removed by forced breathing, want of oxygen has no exciting influence on the centre, and apncea will be produced, and does not cease until the alveolar carbon dioxide pressure rises to normal, unless abnormal products produced by want of oxygen reinforce the action of the carbon dioxide ; the development of these other products is, however, a gradual process.

W. D. H.

Experiments on the Gaseous Metabolism of Infants carried out by means of Zuntz and Oppenheimer's Modification of the Regnault-Reiset Respiration Apparatus. ARTHUR SCHLOSSMANN, CARL OPPENHEIMER, and HANS MURSCHAUSER (*Biochem. Zeitsch.*, 1908, 14, 385—406).—The experiments were carried out by means of the apparatus described by two of the authors (*ibid.*, 361—368, 369—384). In the case of a healthy child ($4\frac{1}{2}$ —5 months old) sleeping for eight hours after feeding, the oxygen utilised was 0.731 gram, and the carbon dioxide excreted, 0.931 gram per kilo. per hour. The respiratory quotient was 0.911. These numbers were greater for the first three hours after the meal than for the later period. In similar experiments, when the child was awake for a part of the experimental period, the oxygen consumed was 0.853 gram, and the carbon dioxide excreted 1.046 grams per kilo. per hour, the respiratory quotient being 0.896. Experiments were also carried out on children during a period of fast; in pathological cases, and results differing markedly from the above were obtained.

S. B. S.

Effect of Salt Solutions on the Heart and Respiration of the Skate. IDA H. HYDE (*Amer. J. Physiol.*, 1908, 23, 201—213).—As a rule, increase of heart-beat produced by various salts is accompanied by rise of blood-pressure and increase of respiratory activity. Ammonium chloride, however, increases blood-pressure without increasing cardiac force ; disodium hydrogen phosphate increases the force of the heart, but not that of respiration, and urea increases cardiac and respiratory activity without raising the blood-pressure. The salts which are specially depressing are potassium chloride and magnesium sulphate. Many other details are added in relation to concentration, etc., of these and other salts.

W. D. H.

Coagulation-time of Blood in Man. T. ADDIS (*Quart. J. exp. Physiol.*, 1908, 1, 305—334).—Daily variations in the coagulation-time of the blood do not occur; the administration of citric acid or of calcium salts also makes no difference. The contrary result is due to errors in technique, the influence of temperature having been disregarded in all previous measurements of coagulation-time. The coagulation-time is shortest between 36° and 40°; at temperatures above and below this, it increases. A new method is described in which temperature and other factors are kept constant; the observation is made with a microscope, and depends on the fact that when a current of oil streams along the side of a drop of blood, a smooth flow of the corpuscles is induced. The movement stops suddenly when coagulation takes place. W. D. H.

Blood-Clot of the King-crab. CARL L. ALSBERG and E. D. CLARK (*J. Biol. Chem.*, 1908, 5, 323—330).—The blood-clot is considered to consist of the agglutinated cells of the blood only, without admixture with any substance akin to fibrin. The solubilities and the low sulphur and tyrosine contents are thought to point to the protein present as being a member of the gelatin-elastin group. W. D. H.

The Sugar in Blood. IV. The Method of Osmotic Compensation. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1908, 14, 476—483).—Experiments were carried out with the object of determining whether the sugar in blood exists free or combined in some form as a colloidal complex. For this purpose, the total sugar was estimated polarimetrically after precipitating the proteins by colloidal ferric hydroxide. Portions of the blood were then dialysed against an isotonic salt solution (containing a small quantity of sodium fluoride) to which varying amounts of sugar had been added. After twenty-four hours, the sugar was estimated in the dialysate. An increase in the latter, after the dialysis, would denote that the original liquid contained less sugar than the blood, whereas a diminution would indicate that it contained more. It was found that the amount of sugar in the dialysate did not alter after dialysis, when it contained the same percentage of sugar as was found in the blood by the method described above; hence the sugar in the blood exists in a free state. S. B. S.

The Total Sugar of the Blood. RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1908, 147, 1028—1031. Compare Abstr., 1908, ii, 957).—The amount of sugar obtained from the blood-clot depends to a somewhat considerable extent on the duration of the hydrolysis by hydrofluoric acid, for, besides liberating the sugar, the acid also slowly destroys it. The sugar obtainable from the clot is in any case a considerable portion of the total sugar of the blood. G. B.

Diastases in the Blood and Body Fluids. ANTON J. CARLSON and A. B. LUCKHARDT (*Amer. J. Physiol.*, 1908, 23, 148—164).—The diastases in blood and lymph are mere "discards" of the tissues on the road to destruction or elimination, and serve no essential end in

the body processes. Their amount is not related to pancreatic activity, to changes in the diet, or to the rate of oxidation in the body. Such differences as are noticeable in different fluids, or in the same fluid at different times, appear to be of an accidental nature.

W. D. H.

The Maltase of the Blood-serum and Liver. CHOSABURŌ KUSUMOTO (*Biochem. Zeitsch.*, 1908, 14, 217—233).—This is a comparative study of the action of the maltase of the blood and liver extract in different animals. The absolute and relative strength of the action varies considerably, being greatest in the pig and least in the sheep, of the animals examined, so far as relates to the maltase of the blood, but the liver extract is more powerful in the sheep than in the pig or dog. In the calf and horse, the two ferments act about equally. This varying action may depend on the amount of ferment present, or on the presence of such inhibitory substances as anti-maltase.

W. D. H.

The Occurrence of Proteic Acids in Blood. JÓZEF BROWIŃSKI (*Zeitsch. physiol. Chem.*, 1908, 58, 134—146. Compare Abstr., 1908, ii, 205).—The proteic acids described by Bondzynski in the urine of men and dogs are also present in blood; one litre of horse's serum contains 0.137 gram of oxyproteic acid.

W. D. H.

Cytolysis. ALONZO E. TAYLOR (*J. Biol. Chem.*, 1908, 5, 311—314).—Injections of salmon sperm into rabbits renders the blood capable of causing cytolysis of the spermatozoa. The serum was inactive if the spermatozoa used were stale, so also was the sera from animals inoculated with the lipoidal, protamine, or nucleic acid fractions obtained from the cells.

W. D. H.

Precipitin Reactions. W. A. SCHMIDT (*Biochem. Zeitsch.*, 1908, 14, 294—348).—If dried serum is heated at 110°, it does not lose its power of reacting to precipitin; if heated at 130°, this property is lessened, and at 150° almost entirely lost. If the serum is not dried, heating at 70° for an hour does not destroy the property, and the reaction may be obtained even after heating at 90°. These temperatures are higher than those given by previous observers. Passing from the precipitable substance to the precipitin, this is not so thermostable; still heating at 75° for several hours does not entirely destroy it, and precipitin serum, after heating at 70°, is still capable of producing immunisation. If heated with alkali, similar results are obtained. Various theoretical deductions from these experiments are discussed.

W. D. H.

Sensibilising Action of Animal Pigments. I. WALTHER HAUSMANN (*Biochem. Zeitsch.*, 1908, 14, 275—278).—Vegetable extracts which contain chlorophyll act hæmolytically on red corpuscles in the light, but not in the dark. This is not a property confined to chlorophyll, but is also possessed by certain animal pigments, and in the present paper, bile pigment is shown to possess it. This may play a

part in diseases where pigmentary changes occur in parts exposed to light, such as the skin. Hæmatoporphyrin acts in the same way both on red corpuscles and on other animal cells, such as paramœcium.

W. D. H.

The Influence of Neutral Salts on Hæmolysis. RUDOLF HOBER (*Biochem. Zeitsch.*, 1908, 14, 209—216).—The action of weak hypotonic solutions of neutral salts of the alkalis is to cause discharge of the hæmoglobin from the red corpuscles of the ox. The anions favour hæmolysis in the following order: $\text{SO}_4 < \text{Cl} < \text{Br}, \text{NO}_3 < \text{I}$, and the cations in the following: $\text{Li}, \text{Na} < \text{Cs}, \text{Rb} < \text{K}$. The action probably depends on an action on the membrane increasing its permeability.

W. D. H.

The Hæmolysin of Human Pancreatic Juice. II. JULIUS WOHLGEMUTH (*Chem. Zentr.*, 1908, ii, 1111; from *Berl. Klin. Woch.*, 1908, 45, 1304—1305).—Inactive pancreatic juice, in spite of its lipolytic properties, does not contain hæmolysin. On activating with enterokinase or calcium chloride, or by keeping, it acquires the property of dissolving red blood-corpuscles under certain conditions. The addition of lecithin also causes the juice to acquire hæmolytic properties, although it is not thereby activated as regards trypsin. The hæmolytic properties are possibly due to the setting free by the activated trypsin of lecithin from some protein lecithide complex.

S. B. S.

Effect of Diet on Saliva. CHARLES HUGH NEILSON and M. H. SCHEELE (*J. Biol. Chem.*, 1908, 5, 331—338).—Saliva hydrolyses starch to maltose and maltose to dextrose, and so probably contains two enzymes. A carbohydrate diet increases both actions, and a protein diet lessens both in the same proportion. These facts are considered to prove adaptation to diet. The experiments were conducted on men.

W. D. H.

Assimilation of Formaldehyde and of Glycerol and Sugar. THOMAS BOKORNY (*Pflüger's Archiv*, 1908, 125, 467—491).—If, as is believed, carbon dioxide is changed into formaldehyde by the action of chlorophyll granules, the condensation of the latter substance must occur with great rapidity, for, except in minimal amount, it is very toxic to life, and to the chlorophyll apparatus. On treatment with dilute formaldehyde, starch formation is increased, and this occurs in the dark and under the influence of light with equal rapidity. The energy of light is necessary in the formation of formaldehyde from carbon dioxide. Oxygen is not essential either for the assimilation of formaldehyde, glycerol, or sugar.

W. D. H.

Metabolism of Glycine in Liver Affections. HERMANN JASTROWITZ (*Arch. exp. Path. Pharm.*, 1908, 59, 463—472).—In normal persons, the administration of 20 grams of glycine does not lead to its appearance in the urine, but in those with liver disease

and in dogs suffering from phosphorus poisoning, if glycine is given, a good deal escapes conversion into urea and passes into the urine.

W. D. H.

Liebig's Extract of Meat. R. ENGELAND (*Zeitsch. Nahr. Genussm.*, 1908, 16, 658—664).—The following bases were separated and identified in Liebig's extract of meat, the method employed being a modification, in part, of that described by Kutscher and Steudel: creatinine, neosine, carnitine (Abstr., 1905, i, 726), vitiatine (Abstr., 1907, ii, 708), histidine, methylguanidine, and alanine. W. P. S.

The Assimilation of Carnitine in the Animal Body. R. ENGELAND (*Zeitsch. Nahr. Genussm.*, 1908, 16, 664—666).—It is shown that carnitine when administered to dogs is entirely decomposed, and is probably converted into dimethylguanidine, as this base was detected in the urine. In the case of rabbits, it appears that carnitine is reduced during its passage through the body, but the small quantity of base recovered from the urine did not allow of its identity being established with certainty.

W. P. S.

Hydrolytic Enzymes of Invertebrates. HERBERT E. ROAF (*Bio-Chem. J.*, 1908, 3, 462—472).—Glycerol extracts of the digestive glands of various invertebrates (arthropods, molluscs, echinoderms) were employed, or in some cases, the alcohol precipitate from such extracts. Enzymes capable of hydrolysing starch and glycogen, fats, and proteins were found. The addition of these extracts to milk and oxalated blood-plasma caused coagulation. Variations as to the presence and activity of all these ferments occur, and many results are stated quantitatively. In relation to the proteo-clastic enzymes, the Congo-red fibrin method of the author was mainly employed; variations are noted in the reaction of the medium which gives the best results.

W. D. H.

Is Choline Present in the Cerebro-spinal Fluid of Epileptics? S. KAJIURA (*Quart. J. exp. Physiol.*, 1908, 1, 291—296).—Relying on Rosenheim's periodide test, which is both trustworthy and sensitive, choline was not found in the cerebro-spinal fluid in cases of epilepsy. The detection of a few fragments of anisotropic crystals by Donath's micro-polariscopic test is not in itself sufficient evidence of the presence of choline; treated in the same way with platinic chloride, etc., the same result may be obtained with normal cerebro-spinal fluid, or even with distilled water.

W. D. H.

Chemico-physical Investigations on the Crystalline Lens. III. Imbibition of the Crystalline Lens in Water and in Water Vapour. FILIPPO BOTTAZZI and NOÈ SCALINCI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 445—454. Compare Abstr., 1908, ii, 966, 1054).—The penetration of water into the crystalline lens, and the swelling and increase in weight of the latter, is due to some extent to a process of imbibition, and not, as is usually supposed,

solely to the osmotic pressure of the lens. As there is not an imbibition equilibrium between the lens and the water in which it is immersed, the water penetrates the lens, at first rapidly and subsequently more slowly. The lens tends towards a maximum of imbibition, which is, however, only attained if the capsule is ruptured. In this imbibition, there are two distinct periods, in the first of which water penetrates the lens and causes it to swell uniformly, whilst in the second the water accumulates between the lens and the capsule. Experiment shows that the percentage increase of weight of a lens from which the capsule has been removed is less than in the case of a lens which retains its capsule. When no capsule is present, the lens increases rapidly in weight during about the first half-hour of immersion, after which the increase is first checked for a time and then proceeds more gradually; this is due to the diffusion from the lens of the soluble facoprotein, the loss thus caused being sufficient to compensate, for a time, the increase in weight due to imbibition.

When suspended in saturated water vapour at 38°, the crystalline lens does not increase, but gradually diminishes, in weight, a process of disimbibition taking place. From this point of view, the crystalline lens may be regarded as a block of solid hydrogel, since swollen gelatin behaves in the same way when suspended in water vapour (compare Schroeder, *Abstr.*, 1903, ii, 721). The amount of disimbibition of the lens in water vapour is, for a definite time, directly proportional to the initial weight of the lens, whilst the increase in weight of a lens due to imbibition in water is inversely proportional to that weight. The mechanism of the process of disimbibition is essentially different from that of the process of imbibition.

T. H. P.

Effect of Stimulation of the Accelerator Nerve on the Saline Metabolism of the Isolated Heart. WILLIAM H. HOWELL and W. W. DUKE (*Amer. J. Physiol.*, 1908, 23, 174—179).—A comparatively small supply of Locke's fluid was continuously perfused through isolated cats' hearts by the method described by Locke and Rosenheim. Neither the calcium nor the potassium in the fluid showed any variation in amount after a perfusion lasting for hours, and after long-continued excitation of the cardiac accelerator nerve. No trace of hypoxanthine was discovered in the fluid, although Burian describes this substance as being continuously formed in skeletal muscle, and increased in amount during its contraction. The difference may be due to an essential difference between the two kinds of muscle, or to the presence of dextrose in Locke's fluid. The heart, however, gives off creatinine (or creatine) to the circulating fluid.

W. D. H.

Action of Barium Chloride on the Normal Heart, and the Heart which has Undergone Fatty Degeneration. RENATO DE NICOLA (*Chem. Zentr.*, 1908, ii, 961; from *Arch. Farm. speriment.*, 1908, 7, 130—138).—Barium chloride is a myocardial poison with marked action on the muscle, but influences little, or not at all, the heart movements of an organ which has undergone fatty degeneration, and only causes death by exhaustion.

S. B. S.

The Sugar Utilised in the Isolated Heart. MARIO CAMIS (*Chem. Zentr.*, 1908, ii, 1194; from *Zeitsch. allg. Physiol.*, 1908, 8, 371—404).—The relationship between the amount of work done by an isolated heart and the amount of sugar utilised from a Ringer-Locke solution was investigated. The apex of the heart (from rabbits, cats, and a fox), which was perfused in a Langendorff apparatus, was weighted by different loads, and from the number and size of the contractions, the amount of work performed was calculated. It was found in the case of the rabbit that, for the same amount of mechanical work, the larger was the amount of sugar utilised the greater the load attached to the heart. A direct proportionality between the sugar utilised and the work of the heart could not, however, be ascertained. The hearts of cats and of foxes utilised no sugar under the same conditions of experiment. In these cases, glycogen seems to disappear, the fresh hearts of cats and foxes containing more of this carbohydrate than was found in those organs which had been employed in the perfusion apparatus. A similar difference was not found in the case of rabbits. The conclusion was drawn that in herbivora the source of muscular energy is the sugar which is obtained directly from the food-stuffs, or by degradation of other carbohydrates, whereas, in the case of carnivora, the source is the glycogen of the muscles, which has been prepared from the proteins of the food-stuffs.

S. B. S.

Fate of Glycerol in the Body. FELIX REACH (*Biochem. Zeitsch.*, 1908, 14, 279—285).—The liver was perfused with Ringer's solution by a method similar to that used by Locke and Rosenheim in their investigations on the utilisation of sugar by the beating heart. It is shown that the liver has the power of synthetically forming acetoacetic acid in small quantities from glycerol. This is not in contradiction to the antiketogenic action of glycerol.

W. D. H.

Liver Cells and their Permeability to Sugar. P. C. ROMKES (*Biochem. Zeitsch.*, 1908, 14, 254—274).—The author claims to have proved by four distinct methods that the walls of liver cells are permeable to dextrose. The wall of the nucleus, on the other hand, appears to be impermeable to dextrose. These facts have an important bearing on the reversible hydrolysis of glycogen to dextrose:

$$\text{C}_6\text{H}_{10}\text{O}_5 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_{12}\text{O}_6.$$

J. J. S.

Conversion of Glycogen into Sugar by the Liver. ALONZO E. TAYLOR (*J. Biol. Chem.*, 1908, 5, 315—318).—Flask experiments on the liver of the giant clam show a post-mortem conversion of its glycogen into sugar, which is believed to be analogous to what occurs during the life of the animal. The conversion is a function of two variables and is proportional directly to them, namely, the masses of glycogen and of glycolytic ferment in the liver cells.

W. D. H.

The Animal Fats and the Extract by Light Petroleum from the Liver. YUTAKA NUKADA (*Biochem. Zeitsch.*, 1908, 14, 419—429).—The content of animal fats in lower fatty acids was estimated by hydrolysing the fats, adding to the soaps just sufficient acid to

neutralise the alkali used, and washing the separated fatty acids with water until the washings were no longer acid ("filtration method"). The volatile acids in the washings were also estimated by distillation. The acetylation number was determined by similar processes. The acetylation numbers of the fats, fatty acids, and light petroleum extracts were determined. It was found that the fatty acids in the fats from adipose tissues, which are soluble in water and volatile with steam, amount to 0.4 to 0.7% of the total. These fats contain, when fresh, only small quantities of substances with a free hydroxyl group; with the age of the fat, however, the number of these groups increases. On hydrolysis of the fats, substances containing free hydroxyl groups are obtained, amongst which are cholesterol and appreciable quantities of hydroxy-acids. Liver extracts contain cholesterol, but not cholesterol esters; hydroxy-acids also seem to be present.

S. B. S.

The Influence of Radium Emanations on Autolysis. SIMON LÖWENTHAL and E. EDELSTEIN (*Biochem. Zeitsch.*, 1908, 14, 484—490).—Radium emanations appreciably increase the rate of autolysis of tissues, especially in the expressed juices from certain carcinomatous growths.

S. B. S.

The Influence of Inorganic Colloids on Autolysis. V. M. ASCOLI and G. IZAR (*Biochem. Zeitsch.*, 1908, 14, 491—503).—In the experiments, colloidal silver, prepared by Bredig's method, was employed. It was used in two forms, "stabilised" by the addition of gelatin, and "non-stabilised." Both forms increase the rate of autolysis of liver tissue, whereas the former alone, when in very small doses, causes a rise of temperature when administered to animals. Both forms, however, when given in sufficient doses, cause this rise of temperature, the "stabilised" to a greater extent than the "non-stabilised." The addition of defibrinated blood inhibits the effect of the non-stabilised blood on liver autolysis, but not that of the stabilised; serum, on the other hand, exerts the same effect on both forms of colloidal silver. The addition of sodium chloride inhibits the action of the non-stabilised colloid, but not that of the stabilised.

S. B. S.

The Preparation and Chemical Properties of the Xanthoma Substance, with some Investigations of the Fat-like, Doubly-refracting Substance in Large, White Kidneys. J. PRINGSHEIM (*Biochem. Zeitsch.*, 1908, 15, 52—75).—The material for investigation of the xanthoma was obtained from the dura mater and the skin of a woman who suffered from chronic icterus with hypertrophic cirrhosis of the liver. The material was extracted with alcohol and then with acetone, and from the latter solvent, crystals separated which, after repeated recrystallisations from the same solvent, melted at 67.5°. The dura mater material contained 14.2% of this substance. It was free from phosphorus and nitrogen, and yielded, on hydrolysis with sodium ethoxide in benzene solution, a residue which, on recrystallisation from alcohol, melted at 144.5° and gave the characteristic

cholesterol reactions. The fatty acids obtained by hydrolysis were not identified; the lead salts were partly soluble in ether. There is evidence, therefore, that the doubly-refracting substance is an ester of cholesterol. Similar substances, melting at 54° and 52° , were obtained from the kidneys of a woman who had died from tuberculosis of the lungs, and of a child who had died from uræmia. In these cases, there was not sufficient evidence to determine whether the doubly-refracting substance consisted entirely of cholesterol esters, as the yield obtained was small. The author calls attention to the pathological significance of the facts, and the need for chemical identification of the doubly-refracting substances. S. B. S.

Spontaneous Movements of Amphibian Muscle in Saline Solutions. GEORGE RALPH MINES (*J. Physiol.*, 1908, 37, 408—444).—The rhythmical periods in the contractions produced by exposing amphibian muscles to a 0.7% solution of sodium chloride vary from 6 to 0.06 sec., and the movements continue in the presence of curare; large doses of curare abolish them, owing to the inorganic salts in the curare employed. The appearance of movements is accompanied by increased excitability to galvanic currents. The addition of calcium chloride lessens the movements and the excitability. Potassium chloride first increases and then stops both phenomena. The movements are regarded as myogenic. W. D. H.

Comparative Effect of Alcohol, Ether, and Chloroform on Striped Muscle. Effects of Muscarine and Atropine on Striped Muscle. AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1908, lxxi—lxxiv, lxxxi—lxxxiv; *J. Physiol.*, 37).—The comparative anæsthetic effect on the frog's sartorius was tested by the contractions obtained by stimulation when subjected to immersion in various strengths of alcohol, ether, and chloroform respectively in 0.6% sodium chloride solution. The strengths, $N/\text{alcohol}$, $N/10$ ether, and $N/100$ chloroform, are very nearly physiologically equivalent.

The action of muscarine and atropine was tested in a similar way. Both alkaloids act as paralysants, the former more powerfully. The chief difference is that muscarine produces a temporary contracture not unlike that caused by nicotine and caffeine. The muscle recovers when placed in normal saline solution, but this is less complete after atropine than after muscarine. The antagonism of the two drugs is best shown by mixing them together, when the contracture is not observed. W. D. H.

Action of Sodium Cyanide on Muscles and Nerves of Cold-blooded Animals. S. DONTAS (*Arch. exp. Path. Pharm.*, 1908, 59, 430—443).—In frogs, sodium cyanide acts not only on the central nervous system, but also on peripheral nerves. Muscles will not contract on stimulation of their nerves when these are exposed to the action of a 0.005% solution of the salt. This is a reversible action, and can be removed by washing with Ringer's solution. In the early stages of poisoning in the intact animal, the toxic effects are removable by the injection of sodium thiosulphate. W. D. H.

Chemical Investigations of Placenta. S. HIGUCHI (*Biochem. Zeitsch.*, 1908, 15, 95—104).—The mean percentage result of the analysis of six placenta: water, 84.91; dry substance, 15.09; fat, 0.846; unsaponifiable substance, 0.283; glycogen, 0.032; total S., 0.120; total P., 0.140; lecithin, 0.899; total N., 2.266; albumin, 14.16; aqueous extract, 3.974 (containing N., 10.38%; ash, 0.387%); alcoholic extract, 2.070 (containing N., 3.521%; ash, 0.492%); total ash, 0.878. S. B. S.

The Effect of Hydrochloric Acid on the Composition of the Subcutaneous Connective Tissue of Rabbits. J. PH. STAAL (*Zeitsch. physiol. Chem.*, 1908, 58, 97—117. Compare Loghem, *Abstr.*, 1904, ii, 751).—The following determinations have been made with the extract from the subcutaneous connective tissue of normal rabbits and of rabbits to which hydrochloric acid was administered: freezing point, electrical conductivity, and percentage of sodium and of chlorine. It is shown that the percentage of sodium increases rapidly (some 4 to 15 times) after the administration of 0.5% hydrochloric acid during two to seven days. The ratio Na/Cl also increases, and thus Loghem's view, that by the administration of hydrochloric acid alkali is removed from the tissue, is not correct.

Similar experiments were made on the blood of rabbits. These new facts can only be brought into harmony with Loghem's experimental data by concluding that, although the percentage of sodium increases, the sodium concentration decreases in the case of rabbits to which hydrochloric acid has been given. J. J. S.

Arsenic in the Animal Organism. W. H. BLOEMENDAL (*Arch. Pharm.*, 1908, 246, 599—616).—The occurrence and distribution of arsenic in the animal organism, both before and after the administration of arsenical preparations, have been investigated. Full details are given in the original as to the methods used in preparing arsenic-free reagents. The method adopted of destroying the organic matter was that of Fresenius and von Babo, involving the use of hydrochloric acid and potassium chlorate. For the detection of the arsenic, an electrolytic form of Marsh's apparatus was employed, capable of revealing the presence of 0.0001 mg. of arsenic. The formation of an arsenic mirror was depended on for the detection of the poison, and in quantitative work the mirrors formed were dissolved in a sulphuric acid solution of potassium dichromate of known strength and titrated back with *N*/1000 or *N*/4000 sodium thiosulphate.

After administration of arsenic, the latter can be detected in all parts of the organism, but the various parts can be arranged in the following descending order as regards their arsenic content: nails, hair, spleen, thyroid gland, skin, lungs, liver, kidneys, heart, sacrum, muscle, generative organs, and brain (compare Scodosuboff, *this Journ.*, 1876, i, 92; Gautier, *Abstr.*, 1900, ii, 152, 168, 226; 1902 ii, 517; Besredka, 1900, ii, 156; Denigés, 1905, ii, 745). Arsenic commonly occurs in the hair, even when absent from all other parts. Normally, urine contains no arsenic, or only traces. Soon after administration it can be detected in the urine, and disappears again in

ten to twelve days after administration ceases (compare Carlson, Abstr., 1907, ii, 130). In man a greater percentage of the arsenic is eliminated in the hair than is the case with rabbits, goats, or cows. Cacodylic acid is converted in the organism into arsenious oxide, but it is not certain that this is the case with atoxyl. The arsenic in sodium cacodylate is eliminated partly in a gaseous form, but this does not appear to be the case with arsenious oxide. No arsenic, or only traces, appears in the milk in the case of the cow, goat, cat, or rabbit, but a small amount appears in human milk. Both in man and animals, only traces of arsenic are found under normal conditions (compare Gautier, *loc. cit.*), and this appears to have no physiological significance and to be absorbed merely in the form of impurities in food, etc. No arsenic is passed from the parent to the fœtus.

T. A. H.

The Relationships of Cycloses to the Animal Organism. EMIL STARKENSTEIN (*Zeitsch. physiol. Chem.*, 1908, 58, 162—164).—Rosenberger's conclusion, that inosite is present in tissues partly as a mother substance (inositogen), is dissented from. The conclusion drawn from quantitative experiments is that the animal organism contains free inosite.

W. D. H.

Oxidation of Products of Cholesterol in the Animal Organism. III. ISAAC LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1908, 58, 175—184. Compare Abstr., 1907, ii, 899).—This paper deals with the methods for the detection of oxysterol, and further proofs are given that this substance and its precursor exist preformed in blood and bone-marrow. The first oxidation product passes easily into the second.

W. D. H.

The Origin of Glycine from Uric Acid. L. HIRSCHSTEIN (*Arch. exp. Path. Pharm.*, 1908, 59, 401—406).—Further proofs are advanced that glycine originates from uric acid both in the body and *in vitro*. It does not, however, appear to be an end-product of uric acid breakdown, for in alkaline solutions it is destroyed, in part, as soon as it is formed, and if the concentration of the alkali is sufficient, it is difficult to detect any at all.

W. D. H.

Storage and Retention of Quinine in the Human Organism. G. GIESMA (*Chem. Zentr.*, 1908, ii, 1053; from *Arch. Schiffs-Tropen-hyg.*, 1908, 12, 78—81).—The observation of Schaumann, that quinine can be found in the organs of a dog even when the urine is free from alkaloid, applies also to the case of man. The quantities found were, however, as a rule, so small that they could not be estimated quantitatively. In a kidney weighing 420 grams, 6 mg. were found. The blood was free from quinine, and this observation does not confirm the general opinion that the alkaloid circulates in the blood-stream. The hæmolysis of black-water fever probably occurs in the kidneys.

S. B. S.

The Extractives from Fish Flesh. A. SUWA (*Chem. Zentr.*, 1908, ii, 1112; from *Zentr. Physiol.*, 1908, 22, 307—310).—The extract

from the flesh of cod was treated with tannin, barium hydroxide, and lead salts. From the concentrated purified extract, creatinine separated. From the filtrate, the bases were separated by phosphotungstic acid. From the carbonates, the alloxuric bases were precipitated with 20% silver nitrate. Other bases were obtained by fractional precipitation with silver nitrate and barium hydroxide. Creatinine and methylguanidine were obtained in these fractions. After separating excess of silver, other bases were obtained by fractional precipitation of solutions of chlorides with mercuric chloride. S. B. S.

Osmotic Concentration in Body-Fluids of Aquatic Animals. WILLIAM J. DAKIN (*Bio-Chem. J.*, 1908, 3, 473—490).—Further experiments are recorded on fishes and invertebrates which show that changes in the water in which they live brings about sooner or later an alteration in the electrolytes and non-electrolytes of the body-fluids, followed by an alteration in the chemical constitution of their cells. Whether the interchange occurs by the gills or the alimentary canal is left undecided. W. D. H.

Characteristic Principles of Sclerostomum equinum. Presence in this Parasite of an Intensely Hæmolytic Crystalline Alkaloid. TH. BONDROY (*Compt. rend.*, 1908, 147, 928—930).—This worm, which occurs in the intestine of horses, contains an oily base crystallising in prisms, yielding precipitates with general alkaloidal reagents, furnishing a crystalline picrate, and reducing auric chloride in the cold; less than 0.0001 gram produces hæmolysis in seven to eight minutes. G. B.

The Sensitising Action of Vegetable and Animal Pigments on Paramœcia. WALTHER HAUSMANN and W. KOLMER (*Biochem. Zeitsch.*, 1908, 15, 12—18).—It has been shown already that certain pigments, on exposure to light, bring about rapid hæmolysis of red blood-corpuscles. In a similar way, they can kill paramœcia. The pigments investigated were chlorophyll, animal bile from different sources, and hæmatoporphyrin. In some cases, the pigment was added in alcoholic solutions, it being determined by preliminary experiments that the alcohol had no deleterious influence in the strength used. S. B. S.

Sugar from Colostrum. JOHN SEBELIEN and EINAR SUNDE (*Zeitsch. angew. Chem.*, 1908, 21, 2546—2550).—The authors reply to Schiebe's criticism (*Abstr.*, 1901, ii, 204). Independent evidence is given of the presence of lactose in colostrum, and the results of estimating this substance by the optical method and by Kjeldahl's method are compared. Differences are found of about the same magnitude and in the same direction as was observed when lactose was estimated in milk, the optical method giving higher values than the gravimetric method. It is suggested that some small quantity of arabinose causes this difference, the amount being put at about 0.05% of the colostrum. J. V. E.

Excretion of Iodine and Lithium by the Bile. F. FRICKER (*Biochem. Zeitsch.*, 1908, 14, 286—293).—After the administration of lithium iodate in doses of 1 gram by the mouth in man, the excretion of iodine by the bile reaches its maximum in the third hour. Some also leaves the body by the urine, but later. If lithium iodide is given, 0.86% leaves the body by the bile within twenty-four hours. Lithium also appears in the bile, and its excretion by this channel lasts seven hours. The excretion of the two elements does not run parallel. The observations were made on a patient with a biliary fistula. W. D. H.

Condition in which Iodine Occurs in the Urine after Ingestion of Iodides and Iodates. ELI CRESPOLANI (*Boll. chim. farm.*, 1908, 47, 679—685).—The author confirms the presence of organic iodo-compounds in the urine after ingestion of potassium iodide. Further, when alkali iodates are administered, the reduction which they undergo takes place only during the gastric digestion, and is complete when the quantities of iodate taken are not too great; this reduction is affected by the action of the peptones in a solution which is faintly acidified with hydrochloric acid. T. H. P.

The Influence of Tolylenediamine on the Cholesterol Content of the Fæces. CHOSABURŌ KUSUMOTO (*Biochem. Zeitsch.*, 1908, 14, 407—410).—Tolylenediamine has been stated to cause a destruction of the red blood-corpuscles, to which fact has been ascribed the increased amount of cholesterol found by the author in the bile of a dog with a biliary fistula. Further experiments with a normal dog show that subcutaneous injection of the drug causes also an increased excretion of cholesterol in the fæces. The increase, like that in the bile, is only transitory. S. B. S.

The Cholesterol Content of Dogs' Fæces with Ordinary Nutrition and after Administration of Cholesterol. CHOSABURŌ KUSUMOTO (*Biochem. Zeitsch.*, 1908, 14, 411—415).—With a meat diet, more cholesterol was ingested than excreted. Addition of cholesterol to the diet caused increased cholesterol excretion. The increase in the amount excreted was, however, less than the increase in the amount ingested, part disappearing presumably either through resorption in the alimentary tract or through destruction by bacteria. S. B. S.

The Content of Dogs' Fæces in Cholesterol and Coprosterol. CHOSABURŌ KUSUMOTO (*Biochem. Zeitsch.*, 1908, 14, 416—418). The acetylation number of the cholesterol isolated from fæces indicated that the crude product contained only cholesterol and coprosterol. The relative amounts of these substances found in the fæces after different diets were determined by means of the iodine number. S. B. S.

Uric Acid Excretion in Normal Man. PAUL J. HANZLIK and PHILIP B. HAWK (*J. Biol. Chem.*, 1908, 5, 355—366).—The average daily excretion of ten healthy students of ages from nineteen to

twenty-nine years on a normal mixed diet containing 91.2 grams of protein (or 1.33 grams per kilo. of body-weight) was 0.597 gram. The generally accepted average is 0.7 gram. W. D. H.

Changes in the Circulation of Nitrogen Produced by Colloidal Silver Prepared by the Electrical Method. EDUARDO FILIPPI and LEONARDO RODOLICO (*Chem. Zentr.*, 1908, ii, 1052; from *Arch. Farm. speriment.*, 1908, 7, 313—328).—Quantities of 5 c.c. of a reddish-brown colloidal silver solution containing 0.025—0.035% of metal were injected for eight days, partly subcutaneously and partly intravenously, into rabbits. There was a decrease in the nitrogen ingested during this period, but an increase in the nitrogen excreted, the latter being chiefly in the form of urea. S. B. S.

Hydrochloric Acid in the Stomach in Cancer. BENJAMIN MOORE (*Bio.-Chem. J.*, 1908, 3, 449—461).—Although the lessening of free hydrochloric acid in the gastric contents of cases of cancer is not absolutely diagnostic, the author holds that it occurs in the majority of cases, in spite of the opposite results obtained by Copeman and Hake in mice. He replies to the criticisms of these authors. W. D. H.

The Occurrence of Lævulose in Diabetic Urines. WILHELM VOIT (*Zeitsch. physiol. Chem.*, 1908, 58, 122—133).—The unsatisfactory nature of both Rosin's and Borchard's tests for lævulose in urine is pointed out; they frequently give contradictory results, and sometimes positive results with normal urine. In no case of diabetic urine was the lævulose osazone obtainable. W. D. H.

Inhibiting Effect of Potassium Chloride on Sodium Chloride Glycosuria. THEO. C. BURNETT (*J. Biol. Chem.*, 1908, 5, 351—355).—After glycosuria has been produced in rabbits by the injection of sodium chloride solutions, the injection of a mixture of that salt with potassium chloride (100:2.2) markedly lessens the amount of sugar excreted. W. D. H.

The Lipolytic Powers of Syphilitic Sera, and the Diagnostic Value of Lipolysis by Sera. JULIUS CITRON and KARL REICHER (*Chem. Zentr.*, 1908, ii, 1197; from *Berl. Klin. Woch.*, 1908, 45, 1398—1400).—Syphilitic sera have a lipolytic power of 2.8—3.5 for monobutyrin and 0.7—1.4 for lecithin, as compared with the values 1.25—2.5 and 0.05—0.5 for normal sera. In view of the fact that Neuberg and Reicher have shown that most immune sera have a high lipolytic capacity, this high lipolytic power of syphilitic sera cannot be considered specific. S. B. S.

Anæsthesia and Paralysis Caused by Magnesium Salts. SAMUEL J. MELTZER and JOHN AUER (*Amer. J. Physiol.*, 1908, 23, 141—147).—Ryan and Guthrie's view that the symptoms caused by magnesium salts are due to asphyxia (increase of carbon dioxide in the blood) is an incorrect conclusion they have drawn from a single experiment, and is entirely unsupported by analytical evidence. The

magnesium salts affect the respiratory centre without any preliminary excitation, such as is caused by carbon dioxide poisoning.

W. D. H.

Antagonism of Alcohol and Carbolic Acid. ALONZO E. TAYLOR (*J. Biol. Chem.*, 1908, 5, 319—322).—As tested by its behaviour towards yeast, there is no chemical detoxication of carbolic acid by ethyl alcohol. The effect noted by surgeons, that alcohol applied to carbolised wounds checks the internal action of the phenol, must therefore depend, as Sollman has suggested, upon some physical basis.

W. D. H.

Behaviour of the Three Isomeric Phthalic Acids in the Dog's Organism. CH. PORCHER (*Biochem. Zeitsch.*, 1908, 14, 351—360).—Animals received doses of the three acids *per os*, generally in small quantities at a time, over periods of several days. The urine excreted during these periods was collected, and the amounts of the phthalic acids therein estimated. It was found that phthalic acid was almost completely burnt in the organism, whereas the *isophthalic* and *terephthalic* acids were recovered unchanged to the extent of 75%. No glycine conjugated acids were isolated.

S. B. S.

Physiological Action of Products of Metabolism. III. Action of Scatole on the Frog's Heart. IV. Action of Indole on the Frog's Heart. B. DANILEWSKY (*Pflüger's Archiv*, 1908, 125, 349—360, 361—377).—The frog's heart was perfused with Ringer's solution containing scatole or indole. Both substances depress the activity and frequency of the heart-beat, the action being on the cardiac muscle direct. These substances are also deleterious to ciliated epithelium and low organisms.

W. D. H.

Physiological Effect of Alkaloids from Hemlock (*Conium maculatum*). JACQUES M. ALBAHARY and KARL LÖFFLER (*Compt. rend.*, 1908, 147, 996—999).—Given hypodermically to intact guinea-pigs, these bases produce a fall of body-temperature, sometimes followed by convulsions and death. The action of *d*- and *l*-coniine is identical. The introduction of a hydroxyl group in conhydrine and in ψ -conhydrine lessens the toxicity, which is, on the other hand, increased by the double linking in the coniceines, derived from the conhydrines by elimination of water. The action of ψ -coniine (obtained by reduction of ψ -coniceine) is not identical with that of coniine.

G. B.

Action of Tobacco Smoke. W. EMERSON LEE (*Quart. J. exp. Physiol.*, 1908, 1, 335—372).—Nicotine is the most important poison in tobacco smoke; pyridine bases in the quantities present are not injurious. The amount of nicotine inhaled does not depend on the amount in the tobacco, but on the form in which it is smoked. The greater the condensation area between the point of combustion and the entrance into the mouth the more nicotine is distilled off from the hot area and will be inhaled. Smoking raises the blood-pressure by vaso-constriction, accelerates the heart and respiration, and increases intestinal movements. In excess, cerebral depression may occur, and

blood-pressure may be lowered to the point of collapse. These effects are chiefly seen in unpractised smokers. Prolonged tobacco smoking may induce arterial disease.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Action of *Oidium lactis* and *Vibrio cholerae* on Choline Hydrochloride. A. RUCKERT (*Arch. Pharm.*, 1908, 246, 676—691).—Brieger has stated (*Die Ptomaine*, Berlin, 1888) that certain bacteria have the property of removing a molecule of water from choline, thereby forming the toxic substance neurine, and this observation has been confirmed to a certain extent by E. Schmidt (Abstr., 1892, 219). With a view to further confirmation, the author has grown pure cultures of *Oidium lactis* and *Vibrio cholerae* in solutions of choline hydrochloride with bouillon as a nutritive medium, and finds that these decompose choline, forming ammonia and carbon dioxide, but he was unable to detect any neurine in the reaction products.
T. A. H.

The Formation by Microbial Activity from Starch of Crystalline Substances which do not reduce Fehling's Solution. FRANZ SCHARDINGER (*Centr. Bakt. Par.*, 1908, ii, 22, 98—103).—The substances in question were obtained by the growth of *Bacillus macerans* in a medium, two litres of which contained 100 grams of starch, 2 grams of ammonium phosphate, 0.5 gram of magnesium sulphate, and sodium chloride. The mixture was filtered after four days' incubation, and the filtrate, which smelt strongly of acetone and was acid in reaction, was neutralised and evaporated. On cooling, a crystalline product separated, which was extracted with 50% alcohol. To the concentrated cooled alcoholic extract, ether was added. A precipitate was thereby obtained which consisted chiefly of regular, hexagonal plates; intermixed with these were aggregates of needles. The substances do not reduce Fehling's solution, and give reactions with iodine solutions.
S. B. S.

Reduction of Nitrates during Alcoholic Fermentation. GIULO PARIS and T. MARSIGLIA (*Chem. Zentr.*, 1908, ii, 966; from *Staz. sperim. agrar. ital.*, 1908, 41, 223—232).—During the process of alcoholic fermentation, the nitrates present are found to be reduced, in varying quantity, to oxides of nitrogen. The action is sufficiently vigorous to reduce completely all the nitrates naturally present in the must; in some cases the reducing action is so vigorous that a relatively large amount of added nitrate may also be reduced, whilst in other cases the greater part remains unchanged. In these circumstances of varying intensity of reduction during fermentation, little value is to be attached to the amount of nitrate present in a wine as affording an indication of its dilution.
J. V. E.

Nitrification of Calcium Cyanamide in Various Types of Soil. SANTE DE GRAZIA (*Chem. Zentr.*, 1908, ii, 1060; from *Staz. sperim. agrar. ital.*, 1907, 41, 241—257. Compare Müntz and Nottin, this vol., ii, 88).—The nitrification of calcium cyanamide differs mainly from that of ammonium sulphate in that the former substance acts injuriously on the soil micro-organisms so long as it remains undecomposed. The rate of nitrification is not particularly slow, although in comparison with that of ammonium sulphate there is some retardation; it is much quicker in clay soils and in those rich in organic matter, but not acid, than in sandy or chalky soils. The chief factors seem to be the water capacity and the absorptive power of the soils; the fermenting power is also important. E. J. R.

The Influence of Oxygen on the Decomposition of Plants (Contribution to the Study of Humus Formation). DOMENICO CARBONE and RENATO MARINCOLA-CATTANEO (*Chem. Zentr.*, 1908, ii, 1049; from *Arch. Farm. sperim.*, 1908, 7, 265—301).—The decomposition of plants is mainly brought about by *Eumycetes*, which break down the dead tissues chiefly in presence of oxygen, but also in its absence. They not only attack the intracellular pectic substances, but also the cellulose of the cell walls, and in many cases even the starch. E. J. R.

The Amounts of Calcium and Magnesium in Plant Seeds. ERNST SCHULZE and CH. GODET (*Zeitsch. physiol. Chem.*, 1908, 58, 156—161).—Analyses of the ashes of the husks and kernels of various seeds show that the husks contain relatively more calcium than magnesium, but that the kernels are richer in magnesium.

The following numbers are given :

		Per cent. of ash.	100 parts of ash contained			
			K ₂ O.	CaO.	MgO.	P ₂ O ₅ .
<i>Pinus Cembra</i>	Kernel ...	2.90	29.4	6.7	9.9	42.8
	Husk ...	—	44.9	12.6	11.0	3.2
<i>Lupinus angustifolius</i> ...	Kernel ...	3.78	31.4	5.0	10.6	40.5
	Husk ...	—	27.5	38.7	9.4	6.1
<i>Cucurbita Pepo</i>	Kernel ...	3.67	18.8	1.1	19.0	55.8
	Husk ...	—	35.0	8.5	7.6	6.4
<i>Ricinus communis</i>	Kernel ...	3.64	—	4.0	19.8	31.9
	Husk ...	—	23.7	43.9	4.3	0.6
<i>Helianthus annuus</i>	Kernel ...	3.66	—	5.0	17.9	—
<i>Corylus avellana</i>	Kernel ...	3.09	—	9.6	15.5	—
<i>Amygdalis communis</i> ...	Kernel ...	2.86	—	12.8	13.4	—
<i>Juglans regia</i>	Kernel ...	2.40	—	3.0	11.5	—

J. J. S.

The Nutritive Effect of Amides on the Germinating Seed, the Detached Embryo, and the Green Plant. JULES LEFÈVRE (*Compt. rend.*, 1908, 147, 935—937).—The author has shown already (*Abstr.*, 1905, ii, 648) that green plants can develop perfectly and construct all their organic matter from tyrosine, leucine, oxamide, alanine, or glycine, without being supplied with any carbon dioxide whatever. He now shows that maize seeds will germinate and the

young plant grow and increase in weight under the same conditions, whilst the detached embryos of *Pinus pinea* will not; the latter, however, develop in a solution of sucrose. E. J. R.

Transformation of Cyanogenetic Glucosides during Germination. LÉON GUIGNARD (*Compt. rend.*, 1908, 147, 1023—1028).—Etiolated seedlings of *Phaseolus lunatus* lose in the first fortnight one-third of the phaseolunatin contained in the seed; in seedlings grown in the light, the disappearance of the glucoside is compensated for, from the tenth day onwards, by that which is synthesised in the leaves. Free hydrogen cyanide could not be detected at any stage; it appears to be used up as soon as it is set free. G. B.

The Relation between Plant Respiration and Alcoholic Fermentation. S. KOSTYTSHEFF (*Ber. deut. bot. Ges.*, 1908, 26, a, 565—573).—The reactions taking place during the normal respiration of plants have not yet been worked out experimentally, although several schemes have been suggested. The author deals particularly with those hypotheses in which the production of alcohol is supposed to be an intermediate stage, namely, (1) the plant sugar gives rise to alcohol, which is then oxidised by enzymes to carbon dioxide and water; (2) the alcohol formed is not oxidised, but is assimilated by the plant; (3) the plant sugar decomposes in the same way as in alcoholic fermentation, but the reaction does not go so far as alcohol production, and the intermediate substances are oxidised.

The author's experiments were made with peas, and, in his view, they confirm the last of these hypotheses. E. J. R.

Correlations in Vegetable Metabolism. BARTHOLD HANSTEEN (*Bied. Zentr.*, 1908, 37, 788; from *Landw. Jahrb.*, 1908, 262).—Under normal conditions, every plant assimilates potassium, magnesium, and phosphoric acid in such a manner that each organ of the plant contains at all times the optimum amounts, the amounts varying with different plants and different organs and according to the period of growth. The single specific optima show certain variations; exclusive addition of one of the substances modifies the process of nutrition, which, however, again becomes normal when the usual conditions are restored. N. H. J. M.

Glycogen of Ascomycetes and its Relation to Trehalose. VLADIMIR A. TICHOMIROFF (*Arch. Pharm.*, 1908, 246, 582—591).—The investigations of Clautriau, Errera, and others having shown that glycogen probably serves as a reserve material, and for this purpose is first hydrolysed into sugars, it becomes of interest to investigate the relationship in the fungi of glycogen and trehalose, the latter being the characteristic sugar of this class of plants. In all cases the distribution of glycogen was determined mainly by staining microscopic preparations with iodine, and the distribution and nature of the sugars by Senft's micro-chemical method with phenylhydrazine in glycerol (Abstr., 1904, ii, 595).

The young asci of *Terfezia transcaucasica* show much glycogen and the fully ripe ones scarcely any. With Senft's reagent, yellow spherulites of trehalosephenylosazone are formed. Similarly, *T. Boudieri* gave minute spherulites of osazone after two months, and a preparation kept in Fehling's solution showed slight reduction in the neighbourhood of some of the cell contents. *T. Leonis* was found to be rich in glycogen, especially the fructification, and in this case osazone crystals appeared after a month. *Choironomyces meandriformis*, *Hydnotria carnea*, *Tuber melanosporum*, *T. brumale*, *T. rufum*, *T. Borchii*, *T. maculatum*, *T. magnatum*, *T. aestivum*, and *T. excavatum* were also examined. The first, second, and seventh were found to contain glycogen, and also yielded spherulites of osazone after about one month, especially in the stalks and contents of the young asci. The other species mentioned had all developed ripe spores and contained no glycogen, but they formed small amounts of osazone crystals after two or three months' treatment with Senft's reagent. A preparation of *T. melanosporum* showed no reduction when warmed in Fehling's solution.

The algæ *Nostoc pruniforme* and *Fucus platycarpus* were also examined, and yielded, after two months, crystals of the same phenylosazone, which may be that of dextrose, galactose, or fucose.

T. A. H.

Occurrence of Glycyrrhizic Acid in Plants. ALEXANDER TSCHIRCH and S. GAUCHMANN (*Arch. Pharm.*, 1908, 246, 558—565. Compare Abstr., 1908, i, 898).—In extension of previous work on the isolation and characterisation of the glycyrrhizic acid of liquorice root, the authors have investigated the sweet root of *Periandra dulcis* and the bark of *Pradosia lactescens*, and find that these also contain glycyrrhizic acid, although from the second of these products it was obtained in the form of a *dihydrate*. The method of preparing the acid described by Tschirch and Cederberg (Abstr., 1907, i, 545) is not applicable in the case of the bark of *Pradosia lactescens*, or in those of the root of *Abrus precatorius* and the rhizome of *Polypodium vulgare*, in which glycyrrhizic acid also occurs.

T. A. H.

Physiological Mechanism of the Coloration of Red Grapes and of Autumn Leaves. J. LABORDE (*Compt. rend.*, 1908, 147, 993—995. Compare Abstr., 1908, ii, 774).—Certain tannins, such as gallotannin, which are not transformed into a red colouring matter by heating with hydrochloric acid (*loc. cit.*), nevertheless yield such a pigment by exposure to light in hydrochloric acid solution in the presence of formaldehyde. The latter substance, often assumed to occur in plants, is compared to a ferment; the hydrochloric acid merely produces a favourable medium, and the absence of pigmentation in white grapes is regarded as due to an unfavourable medium.

G. B.

Alkaloids of the Tubers of *Corydalis cava*. ERNST SCHMIDT (*Arch. Pharm.*, 1908, 246, 575—582).—The isolation of protopine and dehydrocorydaline from the tubers of *Corydalis ambigua* (Abstr.,

1908, i, 825) and *C. Vernyi* (*ibid.*, 908) has led the authors to re-examine the tubers of *C. cava* for these alkaloids (compare Abstr., 1897, i, 174; 1898, i, 604). Haars has already shown that the stem and leaves of *C. cava* do not contain protopine (Abstr., 1905, i, 462). Dehydrocorydaline was obtained and identified by means of the aurichloride and by its reduction to *corydaline*. An alkaloid which may be protopine was obtained mixed with bulbocapnine, from which it could not be separated. No protopine could be obtained from the seeds of *C. nobilis* or *C. lutea*. T. A. H.

Analysis of the Tubercule of *Dioscorea macabiha* from Madagascar. ÉMILE BOURQUELOT and BRIDEL (*J. Pharm. Chim.*, 1908, [iv], 28, 494—500).—The tubercules of this plant, which are reputed to be poisonous, contain no alkaloid or glucoside hydrolysable by emulsin. Starch, sucrose, a reducing sugar, and three enzymes, invertase, amylase, and an anæroxydase, were detected. The toxicity may be due to a toxin. T. A. H.

Oils from *Lycopodium*, Ergot, Areca Nut, and Aleurites cordata Seed. ARNOLD RATHJE (*Arch. Pharm.*, 1908, 246, 692—709).—Authentic specimens of these oils have been examined with the view of establishing their chief constants and their composition. The methods of investigation employed are given in detail in the original.

Lycopodium contains 49.2% of a greenish-yellow oil, which is acid in reaction, and has D 0.93617, n_D 1.4671, saponification number 195.0, acid number 18.6, iodine number 81.0, Hühner number 88.0, Reichert-Meißl number 7.3, and true acetyl value 44.1. The mixed fatty acids have m. p. 39—40°, neutralisation value 202.0, and iodine number 91.8. The percentage composition of the oil is lycopodoleic acid 81, lycopodic acid (dihydroxystearic acid) 3.2, stearic acid 1.13, palmitic acid 0.85, myristic acid 2.0, glycerol 7.8, unsaponifiable matter 0.43, and inorganic matter 0.03 (compare Langer, Abstr., 1889, 741, 1059).

Ergot oil is dark brown in colour with a slightly irritant taste. Its constants in the order given above for lycopodium oil are D 0.9250, n_D 1.4685, 179.3, 11.38, 74.0, 96.25, 0.63, 27.44, and for the mixed fatty acids m. p. 38—39°, 183.0, 77.2. The percentage composition of the oil is oleic acid 68, hydroxyoleic acid 22, palmitic acid 5, unsaponifiable matter 0.35, inorganic matter 0.2, alkaloid 0.6, and glycerol 7.5 (compare Mjøen, Abstr., 1896, ii, 506).

Two samples of areca nut fat were examined, the first having been extracted by ether (*A*), and the second by light petroleum (*B*). The constants in the order given under lycopodium oil are as follows; those for sample *A* are given first in each case. Oil, D = 0.884, 0.973; m. p. 36—37°, 37—38°; 227.4, 234.6; 91.1, 97.2; 24.3, 12.3; 92.76, 91.45; 0.2, 4.2; 11.2, 9.81; mixed fatty acids, m. p. 39°, 39—40°; 229.6, 235.5; 25.95, 13.6. The percentage composition of the mixed fatty acids in the two cases was lauric 43.6, 53.3; myristic 21.0, 24.7; palmitic 3.1, 24.7; stearic 2.25, 3.3; oleic 29.0, 14.5; decoic 1.0, 1.0. Sample *B* also yielded traces of hexoic and octoic acids. The other

constituents of the two fats in percentages were unsaponifiable matter 1.0, glycerol 5.0, and inorganic matter 0.02—0.03, and some phytosterol.

Two samples of oil from the kernels of *Aleurites cordata* (T'ung oil) were examined, the one of Chinese (No. I), and the other of Japanese (II), origin. The constants in the usual order and with those of No. I first in each case were: *oil*, D 0.9383, 0.9393; n_D 1.503, 1.504; 191.5, 189.9; 10.4, 2.1; 156.2, 153.2; 96.05, 96.48; 1.04, 0.55; 10.5, 13.42; *mixed fatty acids*, m. p. 39—40°, 40—41°; 189.4, 188.0; 163.4, 160.3. The percentage composition of the oils was fatty acids 95.6, 96.0; glycerol 9.5, 8.7; unsaponifiable matter 0.45, 0.48, and inorganic matter 0.001 and *nil*. In both cases the fatty acids consisted of elæomargaric acid 75%, and oleic acid 25% (compare Abstr., 1898, i, 628; 1899, i, 864).

T. A. H.

Composition and Toxicity of Ibervillea sonoræ. JULIA T. EMERSON and WILLIAM H. WELKER (*J. Biol. Chem.*, 1908, 5, 339—350).—The tuber of this plant contains proteins, carbohydrates (woody fibre, with small amounts of sugar and starch), fat, cholesterol, lecithin, and salts. It is used as a cathartic, and in large doses is stated to be poisonous. No alkaloid was found, and the substance responsible for its action was not discovered.

W. D. H.

Soils of Acid Reaction. YOSHINAO KOZAI (*Chem. Zeit.*, 1908, 32, 1187).—The author cites an instance of a peculiar acid-reacting soil in Nischigahara, near Tokio. It contains hydrated silicates, more especially clays, and when a sample quite free from humus is washed with water, the acidity of the soil remains unchanged and no soluble acid is dissolved out, but, after the addition of a soluble neutral salt, such as potassium chloride or ammonium sulphate, a soluble acid is at once detected.

The potassium or ammonium appears to be absorbed by the clay, causing liberation of hydrochloric or sulphuric acid, and consequently, after dressing such a soil with potassium or ammonium manures, worse results are obtained than previously.

J. V. E.

Fixation of Ammonia by Zeolites in Soils. THEODOR PFEIFFER, ALBERT HEPNER, and L. FRANK (*Bied. Zentr.*, 1908, 37, 722—723; from *Mitt. landw. Inst. k. Univ. Breslau*, 1908, 4).—Barley followed by oats were grown in pots in sand manured with blood meal, ammonium sulphate, and minerals, and in similarly prepared pots with different amounts of calcium carbonate and calcium zeolite (prepared by treating apophyllite with calcium chloride) respectively.

It was found, as in previous experiments (*Bied. Zentr.*, 1905, 510), that the absorbed ammonia was held so firmly by the calcium zeolite that it was only partly available for the second period of vegetation.

N. H. J. M.

Sodium Chloride Experiments with Mangolds. HERMANN BRIEM (*Bied. Zentr.*, 1908, 37, 731—732; from *Deut. landw. Presse*, 1907, 89).—Application of sodium chloride (2 cwt. per hectare)

in addition to superphosphate and sodium nitrate increased the yields of three varieties of mangolds (roots) and also the amount of sugar as compared with superphosphate and nitrate only. The amount of leaf was considerably increased in the case of the more leafy variety, but slightly reduced in the case of the less leafy roots (Eckendorfer).

N. H. J. M.

The Impurities of Chili Saltpetre. The Possibility of Using a Less-refined Saltpetre. SANTE DE GRAZIA (*Chem. Zentr.*, 1908, ii, 1199; from *Staz. sperim. agrar. ital.*, 1907, 41, 258—269).—The author finds that the common impurities of Chili saltpetre (sodium chloride and magnesium sulphate) are beneficial to vegetation whether applied alone or in conjunction with the pure nitrate. Potassium iodide is without effect. A less-refined saltpetre (not containing potassium perchlorate, however) might therefore be used for manure.

E. J. R.

Manurial Experiments with Two Commercial Forms of Calcium Cyanamide, Sodium Nitrate, and Ammonium Sulphate applied to Mangolds. RICHARD OTTO (*Bied. Zentr.*, 1908, 37, 787; from *Deut. landw. Presse*, 1908, 35, No. 1).—Ammonium sulphate and "stickstoffkalk" gave the highest results (991 and 984 cwt.), then "kalkstickstoff" (891 cwt.), and lastly, sodium nitrate (864 cwt.). The yield without nitrogen was 553 cwt. per hectare.

N. H. J. M.

The Employment of Calcium Cyanamide in Agriculture. ACHILLE MÜNTZ and P. NOTTIN (*Compt. rend.*, 1908, 147, 902—906; compare Sante de Grazia, this vol., ii, 83).—The authors have studied the nitrification of calcium cyanamide in the soil, and find that the process varies somewhat with the amount present, but is, in the main, quite comparable with the nitrification of ammonium sulphate. Sufficient of each of these substances was mixed with soil to add 0.25 gram of N per kilo., and the quantity of nitrate produced per kilo. after definite intervals was found to be:

	8 days.	15 days.	33 days.	2 months.	3½ months.	Relative amounts of nitrate at the end of 5 months.
Calcium cyanamide..	—0.003	—0.011	0.020	0.068	0.204	100
Ammonium sulphate	0.039	0.149	—	—	0.247	88
Dried blood.....	0.048	0.111	—	—	0.154	66
Torried leather.....	0.003	0.024	—	—	0.037	26

The large amount of cyanamide used in this experiment (10 to 20 times the quantity customary in practice) at first inhibited nitrification, and even caused some denitrification, but later on exercised no disturbing effect. Smaller amounts had no inhibiting effect; indeed, by successively adding small quantities to the soil, it is possible for large amounts to become nitrified, especially in soils where nitrification is vigorous.

Numerous field trials are recorded. These show that (1) calcium cyanamide gives substantially the same crop increases as ammonium

sulphate; (2) it does not in practice have the injurious effect on germination that would be expected from laboratory experiments, and can without any bad results be applied to the soil on the same day as the seed is sown; (3) it can be used as a top-dressing, and the slight resulting injury to the plant is only temporary.

E. J. R.

Analytical Chemistry.

A New Electrical Method for the Continuous Analysis of Gas Mixtures, and its Application to the Measurement of the Velocity of Gas Currents. ADOLF KOEPEL (*Ber. deut. physikal. Ges.*, 1908, 6, 814—827).—The method depends on the variation of the thermal conductivity of a gas mixture with its composition. In its application, the resistance of a wire suspended in the gas to be analysed is compared with that of a second wire contained in air or a gas mixture of constant composition. Both wires are traversed by a constant current, but the difference between the thermal conductivities of the surrounding gases results in temperature differences, and consequently in differences in the resistances of the two wires, which are measured. In the apparatus which has been constructed for the continuous electrical analysis, two wires are suspended in the gas to be analysed and two in the standard gas, and these are arranged so as to form the arms of a Wheatstone bridge. The method is recommended for the analysis of generator gas, flue gases, and mine gases.

In the actual apparatus, elaborate precautions are taken to avoid disturbances resulting from the action of the gas currents on the heated wires. The heated wires are so sensitive to the movements of gases that the arrangement may be utilised for the measurement of very slowly moving air-currents.

Some observations relating to the sensitiveness of the electrically-heated wires for different loads are communicated. For the wires used by the author, all the gases and gas mixtures examined were found to exhibit maximum sensitiveness when currents ranging from 0.30 to 0.34 ampere were passed through them. This variation in the current corresponded with a temperature range of 180° to 320°. H. M. D.

The Mercury Bath, a Too-little Known, Useful Expedient in Gas-analytical Work. ALFRED STOCK (*Ber.*, 1908, 41, 3834—3849).—The original contains a detailed, illustrated description of a mercury-bath, specially adapted for gas analysis, together with directions for working with it. W. H. G.

Gasometric Work by means of V. Meyer's Vapour Density Principle. JULIUS MAI (*Ber.*, 1908, 41, 3897—3904. Compare *Abstr.*, 1903, ii, 98).—The method has now been simplified, and the

sources of error reduced, so that it may be employed in actual practice. The bulb is placed near the outlet tube, and the constant temperature maintained by boiling xylene, toluene, aniline, or water. The asbestos cartridge has been displaced in favour of a glass tube, 27—35 mm. \times 6 mm., provided with one to two holes 4 to 6 mm. from the top. The results obtained from calcium, strontium, and barium carbonates are in accordance with the theoretical; magnesium carbonate gives low results.

W. R.

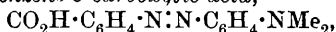
Tap Pipettes. BERNHARD TOLMACZ (*Zeitsch. angew. Chem.*, 1908, 21, 2551).—The pipette is surmounted by a tap so bored that the interior of the pipette may be in communication with the outside air, or with the suction tube, or with neither, according as it is turned. Tap pipettes with more than one bulb are found advantageous where several small quantities of the same liquid are to be measured out; thus the contents of the upper bulb, between two graduations on the stem, may be accurately measured out, and then the contents of the second bulb.

J. V. E.

Burette for Calibrating Measuring Flasks. A. MULDER (*Chem. Weekblad*, 1908, 5, 830—831).—The burette consists of a fairly narrow tube with a large bulb, and below it a smaller bulb, a side-tube being sealed on below the smaller bulb, and a glass stopcock below the side-tube. Above the larger bulb is a zero mark, between the two bulbs a 100 c.c. mark, and below the smaller bulb a 110 c.c. mark. Above and below the last two marks there are a number of divisions corresponding to tenths of a c.c. The portion of the tube below the stopcock is capillary, to admit of the introduction of the water into the flask without wetting the neck of the latter. Water is introduced into the burette from a bottle at a higher level through the side-tube and a tube fitted with a pinchcock. The apparatus is suitable for the calibration of measuring flasks intended to contain any multiple of 100 or 10 c.c.

A. J. W.

An Indicator Highly Sensitive towards Alkali and Suitable for Titrations with Centinormal Solutions. ERWIN RUPP and R. LOOSE (*Ber.*, 1908, 41, 3905—3908).—The authors find that *p*-dimethylaminoazobenzene-*o*-carboxylic acid,



surpasses other indicators, and especially hæmatoxylin and iodoeosin, when used in the titration of very dilute solutions (up to *N*/100) of weak bases (especially vegetable alkaloids). The indicator, to which is given the name "methyl-red," is prepared by combining a diazotised solution of *o*-aminobenzoic acid with dimethylaniline in alcoholic solution, and crystallises from acetic acid in glistening, violet needles. Its colour in alkaline or neutral solution is pale yellow, and in acid solution, violet-red.

J. C. C.

Burette for the Analysis of High-Grade Oxygen. H. MURSCHAUSER (*Zeitsch. angew. Chem.*, 1908, 21, 2503—2504).—A combination of two gas burettes of the Zuntz-Geppert type, surrounded by a water jacket; one serves as a thermobarometer, whilst into the other is

introduced in the usual manner about 100 c.c. of the sample, which may be measured to 1/50 c.c. By means of Hempel pipettes containing aqueous potassium hydroxide and alkaline sodium hyposulphite, the carbon dioxide and oxygen are absorbed, and the remaining gas consists of nitrogen.

L. DE K.

Detection of Hydrogen Peroxide, Formaldehyde, and Persulphates. S. ROTHENFUSSER (*Zeitsch. Nahr. Genussm.*, 1908, 16, 589—591).—Hydrogen peroxide may be detected in milk by adding about 10 drops of 2% alcoholic benzidine solution and a few drops of acetic acid to 10 c.c. of the milk; a blue coloration is obtained if hydrogen peroxide is present. For the detection of hydrogen peroxide in liquids other than milk, it is necessary to add a little milk serum as well as the reagents, as the coloration is obtained only in the presence of the protein. Persulphates give a blue coloration with the benzidine solution alone, and 1 part of persulphate in 1,000,000 may be detected by this means. Formaldehyde may be detected in milk by warming a portion of the milk with twice its volume of concentrated hydrochloric acid to which has been added 2 drops of a 2% solution of a molybdenum, uranium, cobalt, silver, mercury, or copper salt; a violet coloration being produced in the presence of formaldehyde.

W. P. S.

Analysis of a Solution containing a Mixture of Sulphides, Hydrogen Sulphides, Polysulphides, and Hyposulphites. F. DHUIQUE-MAYER (*Chem. Zentr.*, 1908, ii, 1124—1125; from *Rev. gen. Chim. pure. appl.*, 1908, 11, 273—274).—Ten c.c. of the solution are diluted to 100 c.c., and 10 c.c. of this again diluted to 200 c.c. and titrated with *N*/10 sulphuric acid, using phenolphthalein as indicator (*A*). The liquid is next titrated with *N*/10 iodine, using starch as indicator (*I*). After decolorising the liquid with a small drop of the solution, it is again titrated with *N*/10 sodium hydroxide until pink (*R*). Another 10 c.c. of the solution are diluted and shaken with 2 grams of lead carbonate, and the filtrate is titrated with *N*/10 iodine, which now only gives hyposulphite (*H*). *A* = sulphides, *R* = total sodium hydrogen sulphide, *R* - *A* = true sodium hydrogen sulphide, *I* - 2*R* = polysulphide and hyposulphite, *H* = hyposulphite, (*I* - 2*R*) - *H* = polysulphide. The coefficients used in the calculation are the tenth-part of the molecular weights; in the case of polysulphides, the titre is divided by 2, and the result is expressed as sodium disulphide.

L. DE K.

Estimation of [Ammoniacal] Nitrogen. FRITZ TAURKE (*Chem. Zeit.*, 1908, 32, 1176).—The usual plan is to distil 50 c.c. of the usual solution (= 1 gram of the sample) with magnesia; the distillate is collected in a receiver containing 50 c.c. of *N*/2 acid, and the excess of this is titrated with *N*/4 alkali. The amount of nitrogen is then calculated from the formula $(50 - a)/2 \times 0.007 \times 100 = \text{percentage}$.

In order to facilitate the operation, the author starts with 35 c.c. of the solution (= 0.7 gram of the sample), and titrates from a burette graduated to 0.1 c.c. from 25° at the top to 0° at the bottom. The

number read off then at once gives the percentage of ammoniacal nitrogen.
L. DE K.

New Mercury Nitrometer. C. ALBERTE GARCIA (*Bull. Soc. chim.*, 1908, [iv], 3, 1111—1114).—The point for which novelty is claimed in this apparatus is the device for eliminating all the air from the burette before the reaction is started. The nitrometer consists of a burette provided with a stopcock, *A*, communicating with a cylindrical reservoir of the usual pattern at the upper end, and terminating below in a cylindrical bulb of 40 c.c. capacity, which communicates laterally at its upper end with a glass funnel serving as a water reservoir, and at its lower end with a reservoir of mercury. The water and mercury reservoirs connect with the burette by flexible tubing and can be used for levelling purposes, and their connexions with the burette are controlled by stopcocks *B* and *C* respectively. In using the apparatus, the water reservoir and its connexion are filled with boiled distilled water, of which a little is allowed to run into the burette. The stopcock *B* is then closed, and the burette filled with mercury by opening stopcocks *A* and *C*. Stopcock *A* is then closed. By lowering the mercury reservoir, a reduced pressure space is created in the burette, so that solutions of reacting ingredients can be sucked in through *A*. At the termination of the reaction, water can be added through *B*, and the resulting gas, saturated with water vapour, measured in the burette in the usual manner.

T. A. H.

Volumetric Estimation of Water-Soluble Phosphoric Acid in Superphosphates. LUDWIG SCHUCHT (*Chem. Zeit.*, 1908, 32, 1201—1202).—Five hundred c.c. of the aqueous solution of the superphosphate (20 grams to 1 litre) are mixed with *N*/potassium oxalate in order to remove the calcium, but as an excess must be strictly avoided, it is best to ascertain by a special experiment how much oxalate is really required. After heating at 70° and subsequent cooling, the solution is diluted to 550 c.c., and 110 c.c. of the filtrate (= 2 grams) are titrated in presence of methyl-orange with *N*/2 alkali.

Another 110 c.c. are mixed with 25 c.c. of the oxalate solution and then titrated in presence of phenolphthalein. The following example is given. In the analysis of a superphosphate, the first titration required 2.7 c.c. alkali; the second, 11.2 c.c.; $11.2 - 2.7 \text{ c.c.} = 8.5 \text{ c.c.} \times 0.0358 \times 100/2 = 15.1\%$ soluble P_2O_5 . The amount of free acid = $2.7 \text{ c.c.} \times 0.0355 \times 100/2 = 4.8\%$ of P_2O_5 .
L. DE K.

Estimation of Boric Acid in Insoluble Silicates. EDGAR T. WHERRY and WILLIAM H. CHAPIN (*J. Amer. Chem. Soc.*, 1908, 30, 1687—1704).—*Volumetric Method* (WHERRY).—0.5 Gram of the sample is fused with 3 grams of sodium carbonate for fifteen minutes. The mass is treated with 20—30 c.c. of dilute hydrochloric acid and a few drops of nitric acid, and heated nearly to boiling in a 250 c.c. round-bottomed flask. After adding a moderate excess of pure calcium carbonate, a reflux condenser is attached, and the contents are boiled vigorously for ten minutes. The precipitate is collected on a Büchner

funnel, and washed with hot water. The filtrate is then returned to the flask, and, after adding a pinch of calcium carbonate, it is freed from carbon dioxide by boiling under reduced pressure; in this manner there is no fear of loss of boric acid by volatilisation.

The liquid is filtered, and rendered decidedly alkaline to phenolphthalein, when 1 gram of mannitol is added. The solution is now titrated for boric acid with standard sodium hydroxide until pink, when another gram of mannitol is added, and the titration continued if necessary. The sodium hydroxide must be titrated accurately as to its true hydroxide content; in that case, it matters not if a little carbonate should be present, as this is neutralised by the calcium chloride present.

Distillation Method [CHAPIN].—This method is briefly as follows: 0.5 gram of the borosilicate is fused with 3 grams of potassium sodium carbonate. The mass is decomposed by 12 c.c. of dilute hydrochloric acid (1:1), and the solution put into a distilling flask together with 12 grams of dry calcium chloride. The flask is connected with a generating flask in which methyl alcohol is being boiled, and when 25 c.c. of this have collected, heat is applied and the vapours (methyl alcohol and methyl borate) are passed through a short condenser and collected in an Erlenmeyer flask to which a water trap is attached. When 100 c.c. of distillate have collected, another 100 c.c. are collected in a second receiver.

The methyl alcohol is distilled off after addition of an amount of sodium hydroxide sufficient to retain all the boric acid. The resulting solution is then titrated for boric acid as usual, using either glycerol or mannitol as a medium.

L. DE K.

Combustion Analysis. JAMES WALKER and THOMAS BLACKADDER (*Proc. Roy. Soc. Edin.*, 1908, 28, 708—712).—The dimensions of the tube used for copper oxide combustions have been reduced so as to secure the advantages of the Dennstedt furnace, and to make this method of analysis more suitable for students working at an ordinary laboratory bench. A furnace of the Dennstedt pattern, but only 60 cm. in length, and a Jena glass combustion tube, 66 cm. long and not more than 8 mm. internal diameter, are employed. The tube is charged with coarsely powdered copper oxide, and the substance to be analysed, also mixed with copper oxide, is burnt in a moderately rapid current of oxygen at a dull red heat. Details are given for carrying out combustions of compounds containing nitrogen, and also volatile substances, such as benzene, the results obtained in each case being very good. A combustion tube of the same dimensions may also be used for estimating nitrogen by the direct method with equally satisfactory results.

J. V. E.

The Use of Sodium Peroxide for the Quantitative Analysis of Organic Compounds. III. HANS PRINGSHEIM (*Ber.*, 1908, 41, 4267—4271. Compare *Abstr.*, 1904, ii, 447; 1905, ii, 609).—A modification of the older method is described.

Substances containing 75% or more of C + H + S require eighteen times their weight of peroxide, and those with 50—75% C + H + S,

sixteen times. Substances containing 25—50% C + H + S are mixed with half their weight of a compound rich in C and H (for example, sugar); those with less than 25% C + H + S, with their own weight of the compound rich in C and H. The first of these mixtures is used with sixteen times its weight of peroxide, and the second with eighteen times its weight.

The admixing is carried out in an iron crucible by means of an iron nail. The lid is placed on the crucible, which is introduced into a dish containing cold water. The iron nail is raised to a red heat, and introduced through the hole in the lid of the crucible. If the mixture is in the right proportions, the whole mass becomes molten and, after cooling for a few minutes, is dissolved in cold water, and sulphur, halogens, arsenic or phosphorus estimated as already described.

Excellent results can be obtained.

J. J. S.

Estimation of Potassium as Phosphomolybdate. A. SCHLICHT (*Chem. Zeit.*, 1908, 32, 1125—1126, 1138—1140. Compare Abstr., 1907, ii, 130).—About 0.1 gram of potassium sulphate, free from ammonium salts, is mixed with 10 c.c. of the author's reagent and evaporated to dryness. The residue is taken up with 10 c.c. of hot 5% solution of magnesium sulphate, and when cold the precipitate is collected on a weighed asbestos filter and washed first with 10 c.c. and then with 5 c.c. of 5% magnesium sulphate, then again three times with 5 c.c. of 5% ammonium nitrate, and finally with alcohol and ether. 0.1 Gram of pure potassium sulphate thus treated yields 0.8071 gram of dry, and 0.7860 gram of ignited, residue.

The reagent is prepared as follows: 100 grams of molybdic acid are dissolved in water with addition of 250 grams of crystallised sodium carbonate, the whole is evaporated to dryness, and the residue heated for two hours at 150°. It is then dissolved in water up to 500 c.c. Meanwhile, 6 grams of magnesium pyrophosphate are dissolved in boiling nitrohydrochloric acid, and then evaporated repeatedly with nitric acid to expel the chlorine. The residue is dissolved in a little water and nitric acid, D 1.36, and diluted to 500 c.c. with acid of the same strength. To this is then added gradually and with stirring the molybdate solution, also another 500 c.c. of water, and, after standing, for two hours, the liquid is filtered.

L. DE K.

Volumetric Estimation of Potassium in Animal Fluids. W. A. DRUSHEL (*Amer. J. Sci.*, 1908, [iv], 26, 555—562 *).—The process has been described previously (Abstr., 1908, ii, 66). The only modification is that the "cobalt-yellow" is washed with weak brine (1:1) instead of with water; this permits the use of a coarser asbestos felt without danger of loss. It is then titrated with *N*/10 permanganate as usual.

Potassium in Urine.—Ten to fifty c.c. of the sample are evaporated to dryness in a small platinum dish, and the residue is heated with 5—10 c.c. of a mixture of nitric and sulphuric acids (9:1); when the first violent action is over, the acid is expelled and the residue

* and *Zeitsch. anorg. Chem.*, 1909, 61, 137—146.

ignited. The residue is then dissolved in a little water and a few drops of acetic acid, and, without previous filtration, the liquid is treated with the sodium cobalt nitrite reagent as directed.

Potassium in Circulatory Fluids.—In this case the mass (blood, serum, lymph) is oxidised with nitric acid alone, and the residue is heated, but not strongly enough to cause an explosive decomposition. The mass is then heated with sulphuric acid and finally ignited. In the case of defibrinated blood, this may be treated with about 2 c.c. of bromine, and, after an hour, it is evaporated to dryness and charred. The mass is then extracted with hot water, and the solution evaporated to dryness after adding a little sulphuric acid.

Potassium in Milk.—The milk is evaporated to dryness, and the residue treated with nitric acid. The whole is evaporated to dryness, and ignited to burn off most of the organic matter. The residue is then moistened with sulphuric acid, and once more ignited.

L. DE K.

The Determination of Calcium Carbonate in Soils by the Methods of Bernard and of Treitz, and its Significance in the Selection of Soils [for Vineyards]. KARL VOTRUBA (*Chem. Zentr.*, 1908, ii, 1065; from *Allgem. Wein-Zeit.*, 1908, No. 30).—Bernard's method consists in gently powdering the soil, passing it through a 0.3 mm. sieve, and determining the carbon dioxide evolved in a calcimeter from the fine soil. In Treitz's method, the soil is stirred with water, allowed to settle for half a minute, decanted and allowed to settle for half an hour, and the carbon dioxide given off from the deposit on treatment with acid determined. The two methods did not give concordant results in the author's tests, but, in general, it appears that the amount of carbonate in the fine soil is more important than that present in coarse lumps. Other properties of the soil, however, have to be taken into account in selecting soils for vineyards.

E. J. R.

Detection of Poisonous Metals. GEORGE D. LANDER and H. W. WINTER (*Analyst*, 1908, 33, 450—452).—The following methods are suggested for a rapid and simple qualitative search for poisonous metals in organic substances, such as viscera, etc. A Reinsch test is first made for arsenic, antimony, bismuth, and mercury; if a deposit is obtained on the copper foil, numerous methods are available for its further examination. A portion of about 50 grams of the sample is then treated with 50% nitric acid (in quantity sufficient to cover the substance), from 5 to 10 c.c. of concentrated sulphuric acid being also added. The mixture is heated until dense brown fumes are evolved, diluted, and filtered. The filtrate is rendered strongly alkaline with ammonia, a slight excess of ammonium sulphide is added, and the precipitated phosphates, chromium hydroxide, and iron, lead, mercury, copper, bismuth, and zinc sulphides are collected on a filter and washed. The metals are thus obtained practically free from organic matter, and may then be separated and identified by known methods.

W. P. S.

Microchemical Analysis. IV. Mercury, Bismuth, Lead, Copper, Cadmium. NICHOLAS SCHOORL (*Zeitsch. anal. Chem.*, 1908, 47, 729—754).—The sulphides of the metals are treated with nitric acid, and the insoluble mercuric sulphide is separated; a drop of the nitric acid solution is then heated on an object glass with a drop of sulphuric acid. If, on diluting with water, a white, insoluble residue remains, it is probably lead sulphate, and its presence is confirmed by other reactions. The sulphates of bismuth, copper, and cadmium are treated with water, and, if basic bismuth sulphate remains insoluble, it is identified by the appearance of the microscopic crystals when it is converted into potassium bismuth sulphate. The solution containing the copper and cadmium is next evaporated, the residue is heated to dull redness, and treated with water; cadmium sulphate dissolves, whilst copper oxide remains undissolved. Cadmium may be identified by the shape of the crystals when it is converted into either cadmium oxalate or cadmium tetrarubidium chloride. Copper may be identified by the reaction described by Meerburg and Filippo (*Abstr.*, 1906, ii, 52).
W. P. S.

Volumetric Estimation of Lead in Ores. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1908, [iv], 3, 1131—1133).—The author has examined the Schwatz volumetric process, both in the case of lead nitrate solutions of known strength, and of a mixture of known composition, including the usual constituents of a lead ore, and finds that it gives low results. These are due (1) to the adhesion of some lead sulphate (even in presence of excess of sodium acetate) to the lead chromate when this is precipitated by the standard dichromate used, and (2) in the case of the mineral mixture to the difficulty of extracting the whole of the lead, especially when the mixture contains ferric oxide, as this is liable to form with lead oxide, lead ferrate, which is attacked with difficulty by sodium hydroxide solution. Weighing the precipitated lead chromate gives better results, but it is preferable to weigh as the sulphide as recommended previously (*Abstr.*, 1905, ii, 118, 119).
T. A. H.

Decinormal Solution of Potassium Permanganate. BERNARD COLLITT (*Pharm. J.*, 1908, 27, 724).—Experiments showing that a standard solution of potassium permanganate suffers no loss in strength for at least twelve months if kept in the dark, even although the bottle may have to be frequently opened.
L. DE K.

Estimation of Chromic Acid. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1908, [iv], 3, 1133—1135).—The author has examined the volumetric methods described by Carnot (*Abstr.*, 1889, 311) and by Zulkowski. He finds that the former, which depends on the use of a standard solution of hydrogen peroxide, gives results which vary with the dilution of the solution titrated. Zulkowski's process, depending on the liberation from potassium iodide of iodine and titration of the latter with sodium thiosulphate, gives trustworthy results if no other oxidising agent is present. In the latter case, titration with a standard solution of a lead salt can generally be resorted to, but, as shown in a

previous paper (see preceding page), it is safer to weigh the precipitated lead chromate.

T. A. H.

Electrolytic Estimation of Nickel. AUGUST SCHUMANN (*Zeitsch. angew. Chem.*, 1908, 21, 2579—2583).—A criticism of the methods proposed from time to time. Fresenius-Bergmann's ammonia method is free from sources of error, and, contrary to general belief, it is not interfered with by the presence of nitrates or chlorides. Brand's ammonium carbonate method also gives excellent results, but the author has not as yet tried this in the presence of nitrates and chlorides. Addition of sodium pyrophosphate is unnecessary. Classen's oxalic acid method cannot be recommended, as the nickel deposit is contaminated with carbon.

The electrolysis succeeds best by the use of a platinum-gauze cathode, a platinum spiral as anode, and a weak current. A sufficiency of ammonium sulphate should be present.

L. DE K.

Volumetric Estimation of Nickel with Potassium Cyanide. HERMANN GROSSMANN (*Chem. Zeit.*, 1908, 32, 1223).—The author has applied this process to mixtures of nickel and cobalt. To the solution is added some sucrose to prevent precipitation of cobalt, and the nickel is then precipitated by means of dicyanodiamidine sulphate, ammonia, and aqueous potassium hydroxide. The precipitate is collected on a filter, and re-dissolved in warm dilute hydrochloric acid. When cold, a slight excess of ammonia is added, and the nickel is titrated with potassium cyanide as usual.

Further experiments, including the estimation of nickel in the presence of zinc, are in progress.

L. DE K.

Separation of Tin, Arsenic, and Antimony; Analysis of Bronzes. DINAM (*Chem. Zentr.*, 1908, ii, 1207—1208; from *Mon. Sci.*, 1908, [iv], 11, 600—602).—Three grams of the bronze are heated with 30 c.c. of nitric acid, D 1.4; the filtrate contains zinc, lead, and the greater portion of the copper; the precipitate contains arsenic, antimony, tin, and a little copper and lead. It is dissolved in a boiling solution of 10 grams of oxalic acid and 5 grams of ammonium oxalate, and, after adding a little hydrochloric acid, a current of hydrogen sulphide is passed through the hot liquid for two hours. The tin remains in solution, and may be deposited electrolytically, whilst the arsenic, antimony, copper, and lead are precipitated as sulphides. On treating with boiling aqueous potassium hydroxide, the copper and lead are left undissolved; these are then dissolved in nitric acid, and the solution added to the main acid liquid. The alkaline solution is heated with excess of hydrochloric acid, the filtrate is oxidised with potassium chlorate, and, after expelling the excess of chlorine, the antimony is estimated iodometrically with potassium iodide and sodium thiosulphate. The precipitated arsenious sulphide is dissolved in potassium hydroxide, and also estimated iodometrically in the same manner as the antimony. The acid liquid is concentrated to about 15 c.c., 3 c.c. of saturated sodium acetate are added, and the copper and lead are deposited by electrolysis; the liquid contains the zinc,

which is precipitated by boiling with sodium carbonate, and finally weighed as oxide.

If the bronze should contain phosphorus, this will be found in the liquid from which the tin has been deposited electrolytically, and it may be precipitated as ammonium magnesium phosphate or ammonium phosphomolybdate. If iron should be present in the alloy, a portion of it will contaminate the zinc, and another portion remains in the liquid from the tin deposit, from which it may be precipitated with ammonium sulphide.

L. DE K.

Estimation of Antimony and Arsenic in Lead-Antimony Alloys. GEO. M. HOWARD (*J. Amer. Chem. Soc.*, 1908, 30, 1789—1790).—A slight modification of the author's process (*Abstr.*, 1908, ii, 429). The finely-divided alloy is heated with hydrochloric acid until action ceases, the flask is removed from the hot plate, and 0.5 c.c. of nitric acid is added. As soon as the arsenic and antimony have dissolved, the liquid is boiled for some five minutes, and then treated as directed.

If the antimony does not exceed 0.1 gram, 5 grams of tartaric acid will be sufficient to prevent precipitation. If there is a large excess of lead chloride, a larger amount of sodium hydrogen carbonate should be used when titrating the arsenic; the blue colour should be permanent for at least one minute. In oxidising the arsenic, 10 c.c. of 3% hydrogen peroxide generally suffices, and the solution must be distinctly alkaline; if this is not so, as shown by separation of sulphur, a little more sodium hydroxide should be added.

L. DE K.

Identification of Dihydric Phenols. A Delicate Reaction for Resorcinol. T. SILBERMANN and N. OZOROVITZ (*Chem. Zentr.*, 1908, ii, 1022; from *Bul. Soc. Sci. Bucuresti*, 1908, 17, 41—42).—With formaldehyde in acid solution, the dihydric phenols give characteristic, resinous, insoluble condensation products. When resorcinol is heated with formaldehyde in presence of hydrogen chloride or sulphuric acid, a very voluminous, flocculent precipitate is slowly formed. The colour of this substance is very pale red, but when it is added to concentrated sulphuric acid, or heated with concentrated hydrogen chloride solution, it changes to a brilliant carmine-red, and, on the addition of water, or when neutralised, this colour changes to pale orange. The carmine-red or orange-coloured substance, in the presence of free alkali, changes to Bordeaux-red.

An acid solution of resorcinol (1 : 100,000) gives a white turbidity with formaldehyde, which becomes rose-pink on addition of hydrogen chloride, and yields a red solution on the addition of excess of sodium hydroxide.

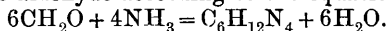
Catechol with formaldehyde in acid solution gives a very pale yellow, flocculent precipitate, which changes when boiled with concentrated hydrogen chloride solution to a violet-brown; dilution with water, or neutralisation of the acid, changes it to a flesh-pink colour; excess of alkali produces a greenish-brown colour.

Quinol requires more acid for condensation with formaldehyde

to take place ; a very pale violet, flocculent precipitate is obtained, which changes to pale brown when boiled with strong hydrogen chloride solution, diluted with water, or when neutralised, and to olive-green in presence of excess of alkali. J. V. E.

The Sodium Nitroprusside Reaction for Acetone. A. C. H. ROTHERA (*J. Physiol.*, 1908, 37, 491—494).—The following modification of the test is recommended, creatinine not reacting in the manner described. Five to ten c.c. of a solution of acetone in water or urine are taken, and a solid ammonium salt (chloride, bromide, acetate, or carbonate) added ; then 2 or 3 drops of a freshly-made 5% solution of sodium nitroprusside, and 1—2 c.c. of strong ammonia. A characteristic permanganate colour is produced. W. D. H.

Detection and Estimation of Formaldehyde in Wine Stored in Barrels which have been Disinfected with Formaldehyde. FRIEDRICH SCHAFFER (*Zeitsch. Nahr. Genussm.*, 1908, 16, 674—676).—Barrels which have been treated with formaldehyde and subsequently steamed may still contain sufficient of the aldehyde to contaminate wine which is stored in them. The author has detected traces of formaldehyde in such wines by means of the test described by Arnold and Mentzel (*Abstr.*, 1902, ii, 480). Before being tested, the wine should be distilled with phosphoric acid, and the distillate rendered alkaline with sodium hydroxide in order to decompose the aldehyde-sulphurous acid compound which distils over ; after the lapse of fifteen minutes, the mixture is acidified with sulphuric acid and the test is applied. For the estimation of formaldehyde in wine, the latter is distilled with phosphoric acid until the volume of the distillate is about three-fourths of that of the quantity of wine taken. The distillate is rendered alkaline with sodium hydroxide, and, after fifteen minutes, is exactly neutralised with sulphuric acid, using rosolic acid as indicator. The neutral solution is then shaken with a slight excess of *N*/1 ammonia (about 2 c.c. are usually sufficient), and at the end of three hours the excess of ammonia is titrated with *N*/10 sulphuric acid. The estimation depends on the combination of the ammonia with the aldehyde according to the equation :



W. P. S.

Colorimetric Method for the Estimation of Formaldehyde in Milk. EDWARD W. T. JONES (*Chem. News*, 1908, 98, 247).—The method depends on the coloration produced when a mixture of milk, formaldehyde, and hydrochloric acid containing a small quantity of ferric chloride is heated. The reagent is prepared by dissolving 0.25 gram of pure iron wire in hydrochloric acid, oxidising the ferrous salt with nitric acid, and precipitating the iron as ferric hydroxide by the addition of ammonia ; the precipitate is collected on a filter, washed, and then dissolved in 500 c.c. of concentrated hydrochloric acid. Ten c.c. of the sample of milk containing formaldehyde and 10 c.c. of the reagent are heated together for twenty-five minutes at a temperature of about 80° ; 30 c.c. of water is next added, and, when cold, the mixture is passed through

a filter, the precipitate washed with a little water, and the filtrate is diluted to a volume of 100 c.c. The blue colour of the filtrate is then compared with the colorations obtained by similarly treating quantities of pure milk to which have been added known amounts of formaldehyde.

W. P. S.

Characteristic Reaction of Uric Acid. DOMENICO GANASSINI (*Boll. chim. farm.*, 1908, 47, 715—726).—The author gives the following test for the presence of uric acid or a urate, which is not disturbed by the presence of proteins, and is not given by xanthine, hypoxanthine, caffeine, theobromine, theophylline, heteroxanthine, paraxanthine, 1:7-dimethylhypoxanthine, 3-methylxanthine, carbamide, alloxan, alloxantin, allantoin, creatine, creatinine, glycine, tyrosine, leucine, hippuric acid, nuclein, nucleic acid, or the bile acids.

To a small quantity of uric acid or a urate dissolved or suspended in water, 10% sodium hydroxide solution is added until the whole is dissolved, giving a distinctly alkaline solution. Subsequent saturation of the liquid with potassium persulphate, and gradual addition of 10% aqueous zinc sulphate until the precipitate formed no longer redissolves, causes the precipitate to assume a bluish-green colour. The reaction is shown distinctly by 10—20 c.c. of a 0.01% solution of uric acid, and is still more sensitive if carried out directly on solid uric acid or a solid urate, or the precipitated double urate of silver and magnesium.

The reaction may be applied to the detection of uric acid in urine in the following manner: Three c.c. of 10% sodium hydroxide solution are added to 10% of urine and the liquid filtered, 5 c.c. of the filtrate being treated with 2 c.c. of 10% aqueous zinc sulphate. The gelatinous white precipitate formed, when mixed on the filter with a little potassium persulphate, will assume a bluish-green colour if uric acid is present.

In blood, traces of uric acid may be detected as follows: A few c.c. of blood-serum are well mixed with one-half the volume of freshly-prepared Salkowski-Ludwig reagent, and left for about twelve hours in the dark. The faint white or grey precipitate is collected and washed five or six times with water on a small filter, being kept as far as possible away from the light. A little powdered potassium persulphate and 2 or 3 drops of 10% sodium hydroxide solution are then applied to the precipitate, in which a bluish-green colour indicates the presence of uric acid.

By this means the author has detected, although not in all cases, traces of uric acid in the blood of the ox and horse. The blood-serum of birds is also found to contain uric acid, which is further met with in samples of blood from healthy and diseased human beings.

T. H. P.

Iodometric Estimation of Uric Acid [in Urine]. FERNAND REPITON (*Chem. Zentr.*, 1908, ii, 1129; from *Rev. gen. Chim. pure appl.*, 1908, 11, 285—286).—Twenty c.c. of urine are mixed with 5 c.c. of acetic acid, and 20 c.c. of copper tartrate solution, which has been bleached by means of a saturated solution of ammonium sulphite, are

added. The copper solution should be standardised iodometrically. After the cuprous urate has settled, the liquid is made up to 100 c.c., and an aliquot portion of the filtrate is taken to ascertain the amount of copper left in solution. In order to obtain it in the higher degree of oxidation, 4 c.c. of sulphuric acid are added, and the liquid is boiled to expel the sulphur dioxide. When cold, sodium carbonate is added until a precipitate forms, which is then redissolved by means of acetic acid. Potassium iodide is now added, and the iodine liberated titrated with standard thiosulphate. The difference in the titrations represents the uric acid.

L. DE K.

Detection of Salicylic Acid in Wine, Milk, Butter, and Preserved Tomatoes. UMBERTO SAPORETTI (*Boll. chim. farm.*, 1908, 47, 751—755).—The following modified methods, based on the coloration given by dilute ferric chloride solution with salicylic acid, are more rapid and convenient than those usually employed, and are capable of detecting salicylic acid in the dilution 1 : 80,000.

Wine.—Ten c.c. of the wine are shaken in a test-tube with a mixture of 3 c.c. of ether and 1 c.c. of light petroleum previously acidified with 10% hydrochloric acid. The ethereal solution, after separation, is allowed to flow down the side of another tube containing a very dilute ferric chloride solution, as also is a further quantity of the solvent after shaking with the wine. On evaporating the ether and light petroleum by gentle heating, the lower liquid gradually assumes the characteristic violet colour. As certain substances in pure wines may give a somewhat similar coloration, the presence of salicylic acid may be confirmed by adding a little of the coloured ferric chloride solution drop by drop to water, which then turns violet.

Milk.—Ten c.c. of the milk are heated to 60—70° with 3—4 drops of acetic acid, and the clear liquid, removed by a pipette, is run to the bottom of a beaker containing dilute ferric chloride solution; the appearance of a violet ring at the surface of contact of the two liquids indicates the presence of salicylic acid.

Butter.—Five to ten grams of the butter are melted in a porcelain capsule and poured into a test-tube, the capsule being then rinsed out with 7—8 c.c. of aqueous alcohol (1 part 95% alcohol to 4 parts of water), which is added to the test-tube. After being rendered faintly acid with 10% sulphuric acid, the butter is shaken repeatedly, warmed slightly, and then allowed to set, but not solidify. The supernatant liquid is then removed in a pipette, and run to the bottom of a beaker containing dilute ferric chloride solution. If salicylic acid is present, a violet ring appears where the two liquids meet.

Preserved Tomatoes.—To 10 grams of the material, placed in a porcelain capsule, are added a few drops of 10% sulphuric acid and about 5 c.c. of ether, the whole being well mixed. The ethereal liquid is then poured into dilute ferric chloride solution, and the operation repeated with a few c.c. of light petroleum, which is also subsequently added to the ferric chloride solution. On gradually heating the latter, if salicylic acid is present, the lower liquid slowly assumes the characteristic violet colour.

T. H. P.

Bang's Method of Sugar Estimation and its Application in the Analysis of Urine. A. C. ANDERSEN (*Biochem. Zeitsch.*, 1908, 15, 76—94).—The experiments indicate that Bang's method (Abstr., 1907, ii, 136) is applicable to sugar estimations in urine. The error due to the reducing substance normally present in urine is small, and this even can be almost entirely eliminated by treatment of the urine with lead acetate or mercuric nitrate. Bang's method can also be applied to the estimation of sugar in molasses if the solutions are first clarified by the mercuric nitrate method. S. B. S.

Estimation of Reducing Sugars. PERCY H. WALKER (*Bull. Assoc. chim. suc. dist.*, 1908, 26, 341—342).—Results of experiments are given showing that slightly higher figures are obtained when the precipitated cuprous oxide is weighed as such than when it is estimated electrolytically, or converted into cupric oxide before weighing (Abstr., 1908, ii, 902). The disadvantage of weighing the copper as cupric oxide is that the tables published by the author (Abstr., 1907, ii, 585) cannot be used. W. P. S.

Estimation of Dextrose in Urine with the Weidenhaff's Fermentation Saccharometer. GEORG GREGOR (*Chem. Zentr.*, 1908, ii, 987—988; from *Zeitsch. allg. Oesterr. Apoth. Ver.*, 46, 419—420).—The author, who has successfully employed this apparatus of precision, recommends that the weight of the mercury should always be taken before each experiment, as small globules are easily lost when washing the apparatus. L. DE K.

Analysis of Camphorated Oil for Camphor Substitutes. FREDERIC W. RICHARDSON and W. WALTON (*Analyst*, 1908, 33, 463—466).—The following process is proposed for the analysis of camphorated oil in order to detect and estimate synthetic camphor, oil of turpentine, and essential oil of camphor, any or all of which may be present in addition to natural camphor. Ten c.c. of the camphorated oil are placed in a small retort, and heated to a temperature of 200° by means of an oil-bath; a current of dry carbon dioxide is passed through the retort during the heating, and the neck of the retort is connected with a weighed, two-necked Woulff's bottle. A weighed, small spiral glass condenser is fitted in the second hole of this bottle. The volatile substances collecting in the neck of the retort, the Woulff's bottle, and condenser are weighed (the neck of the retort being cut off for this purpose), dissolved in carbon tetrachloride, and the solutions are united. This solution is weighed, and portions are used for the estimation of the specific gravity, iodine number, and polymerisation with sulphuric acid. The last-mentioned process is carried out by treating a weighed portion of the solution (about one-half) with one-third of its volume of sulphuric acid, D 1.84, the acid being added slowly and the mixture cooled. The latter is then distilled in steam, and the carbon tetrachloride solution separated from the distillate and weighed; the change in specific gravity and refractive index of the solution enables the weight of the total camphors to be calculated, whilst the polarimetric reading in a

200 mm. tube, multiplied by 0.22385 and divided by 0.95, gives the amount of natural camphor. This deducted from the total camphors leaves the quantity of synthetic camphor. When the amounts of the two camphors are known, the iodine number due to turpentine and oil of camphor enables the percentages of the last-named substances to be calculated. The following iodine numbers are assumed in the calculation: natural camphor, 5; synthetic camphor, 7; essential oil of camphor, 180, and oil of turpentine, 370. W. P. S.

Gasometric Estimation of Urea. A. RONCHÈSE (*J. Pharm. Chim.*, 1908, 28, 444—452; *Bull. Soc. chim.*, [iv], 3, 1135—1141).—Ten c.c. of urine are mixed with 10 c.c. of dilute solution of basic lead acetate (100 c.c. officinal solution and 150 c.c. of water), and 10 c.c. of the filtrate, which is now free from uric acid, are treated in the usual manner with sodium hypobromite. A check experiment is then made by means of 5 c.c. of a 2% urea solution, and the volumes of nitrogen evolved are compared. If the urine contains sugar, a judicious amount of dextrose should be added to the urea solution.

If ammonium salts are present, these evolve nitrogen, which would count as urea. In accurate investigations, it is therefore necessary to estimate the ammonia separately and to calculate the result into urea. The following method is recommended: 10 c.c. of urine are diluted to 100 c.c. with water free from carbon dioxide, and a few drops of phenolphthalein are added. *N*/10 sodium hydroxide is slowly added until the liquid turns a pale rose colour. Twenty c.c. of neutralised formaldehyde (1:1) are now added, and the solution is titrated with *N*/10 sodium hydroxide until the liquid turns pink. A correction is made by adding 0.1 c.c. to every 3 c.c. of alkali used. The sodium hydroxide represents the ammonia. L. DE K.

Estimation of Urea in Urine. STANLEY R. BENEDICT and FRANK GEPHART (*J. Amer. Chem. Soc.*, 1908, 30, 1760—1764).—The following process is recommended: five c.c. of urine are placed in a test-tube and mixed with 5 c.c. of dilute hydrochloric acid (1:4). The mouth of the tube is covered with a cap made of lead foil, and it is then placed in a small autoclave, which is heated for an hour and a half at 150—155°. When cold, the contents of the tube are transferred to a 800 c.c. Kjeldahl distilling flask, 400 c.c. of water and 20 c.c. of 10% sodium hydroxide are added, and the ammonia formed is distilled and titrated as usual. Allowance should be made for pre-existing ammonia. L. DE K.

Application of the Carbamino-reaction. V. HANS LIEBERMANN (*Zeitsch. physiol. Chem.*, 1908, 58, 84—91).—Various basic substances in solution were treated in the cold with lime-water and carbon dioxide alternately in the presence of phenolphthalein, the gas being passed into the solution until the indicator was only faintly coloured. The filtered liquid was afterwards warmed to 20° with excess of lime water (and in a few cases boiled), and the calcium carbonate thus precipitated was weighed and the nitrogen in the filtrate estimated. In this way, the ratio N:CO₂ and the degree of completeness of the

carbamino-reaction are ascertained. The ratios found were as follows : for piperazine 0.95, piperidine 0.93, coniine 1.56, tetrahydroquinoline 4.07, tryptophan 1.55, glucosamine 0.99, taurine 0.93. S. B. S.

Estimation of Vegetable Alkaloids by means of Mercuric Potassium Iodide [Mayer's Solution]. GUNNAR HEIKEL (*Chem. Zeit.*, 1908, **32**, 1149—1151, 1162—1163, 1186—1187, 1212—1213).—Mayer's reagent (6.775 grams of mercuric chloride and 25 grams of potassium iodide per litre) has been used for the estimation of alkaloids by simply adding it to the slightly acid solution so long as a precipitate is formed. The author has sensibly improved the method by adding a larger amount of the reagent than necessary, and then titrating the excess with potassium cyanide, the excess of which is, in turn, titrated with standard silver nitrate in presence of ammonia; the potassium iodide serves here as an indicator.

The author communicates a large number of experiments, showing the amount of Mayer's reagent required to precipitate 0.1 gram of the more important pharmaceutical alkaloids. The results, which in some cases depend somewhat on concentration and acidity, are not scientifically accurate, but sufficiently near the truth for pharmaceutical purposes.

When applying the process to drugs, these are, as a rule, extracted with chloroform in presence of ammonia. The solvent is then evaporated, and the residue taken up with water, acidified with sulphuric acid, and the acid solution is titrated as directed. In other cases they are simply treated with acid water. Plants are extracted with a solvent immiscible with water, and this is then shaken with acid water. For exact details of working in the assay of the various drugs and their preparations, the original paper should be consulted.

L. DE K.

Behaviour of Gelatin and Proteose to Bromine Water. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1908, **57**, 526—528).—The addition of bromine water to a solution of gelatin causes the formation of a sticky precipitate, which has been described as characteristic. A solution of proteose (or gelatose) behaves, however, in the same way.

W. D. H.

Diazo-reaction of Atoxyl. PAUL EHRLICH and ALFRED BERTHEIM (*Chem. Zeit.*, 1908, **32**, 1059).—The authors call attention to the fact that the reaction recently described by Covelli (*Abstr.*, 1908, ii, 1000) had been described in the literature previously; compare Ehrlich and Berthelm (*Abstr.*, 1907, i, 812); Blumenthal and Herschmann (*Abstr.*, 1908, ii, 613), and Berthelm (*Abstr.*, 1908, i, 591).

J. V. E. 3

General and Physical Chemistry.

Reflective Power of Ethyl Alcohol. HEINRICH RUBENS and ERIC LADENBURG (*Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 1140—1143).

—By means of a micro-radiometer the authors have measured the reflective power of ethyl alcohol for ultra-red radiation. In order to avoid errors resulting from the absorption of the radiation in the vapour above the liquid, this was cooled to a temperature of about -20° .

The experimental data indicate the existence of selective reflection, this being more pronounced than in similar experiments at 18° . The maxima on the curve representing the reflective power as a function of the wave-length are all found to be displaced towards the visible spectrum by a lowering of the temperature from 18° to -20° . Whether this is due to the diminution in the absorption of the alcohol vapour in contact with the liquid has not been established.

H. M. D.

Refraction and Dispersion of Krypton and Xenon and their Relation to those of Helium and Argon. CLIVE CUTHBERTSON and M. CUTHBERTSON (*Proc. Roy. Soc.*, 1908, A, 81, 440—448).—The measurements were made by a method previously described (Cuthbertson and Metcalfe, *Abstr.*, 1908, ii, 545). The values of $(\mu - 1) \cdot 10^6$ for the green mercury line ($\lambda = 5461$) are for krypton and neon respectively 428.74 and 705.49. The dispersion for krypton is given by the formula $\mu - 1 = 0.0004189(1 + 6.97/\lambda^2 \cdot 10^{11})$, and that for xenon by $\mu - 1 = 0.0006823(1 + 10.14/\lambda^2 \cdot 10^{11})$, both gases being at normal temperature and pressure.

When the refractivities for infinite wave-lengths of helium, neon, argon, krypton, and xenon are compared, the numbers are found to be very nearly in the ratio 1 : 2 : 8 : 12 : 20.

If the values of b in the equation $\mu - 1 = a(1 + b/\lambda^2)$ are plotted against the refractivities for infinite wave-lengths, a straight line can be drawn through the points representing helium, krypton, and xenon; the corresponding point for argon is also quite close. On the other hand, mercury does not fall into line with the other four monatomic elements in respect of the relationship between refractive and dispersive power.

H. M. D.

Spectroscopic Investigation of the Behaviour of Metallic Salts in Flames of Different Temperatures. HERBERT AUERBACH (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1909, 7, 30—39).—The apparatus used and details of the photographic method of registration are described. For the production of spectra corresponding with different temperatures, the Bunsen, ordinary blow-pipe, and oxygen blow-pipe flames have been employed. No experimental results are given in this part of the paper.

H. M. D.

Radiation and Temperature of the Flame of the Bunsen Burner. E. BAUER (*Compt. rend.*, 1908, 147, 1397—1400).—The absorption and emission of certain rays by illuminating gas flames has been measured. The radiation from a source traversed a considerable thickness (3—5 cms) of a homogeneous flame, it then passed through a hole in a screen, was reflected three times from a polished surface of fluorspar, and was then examined with a micro-radiometer. The absorption, which is due to the vapour of water, is selective; a flame which absorbs only 11% of the rays emitted by a solid substance giving a continuous spectrum, absorbs 28% of the radiation from another gas flame.

From the emission and absorption measurements with the rays emitted by a solid substance, and a knowledge of the emissive power of a black substance in the same position as the flame, the temperature of the flame a little above the blue interior cone has been calculated by application of Kirchhoff's law; it amounts to $1760 \pm 50^\circ$. G. S.

Extension of the Principal Series of the Sodium Spectrum. ROBERT W. WOOD (*Phil. Mag.*, 1908, [vi], 16, 945—947*).—The ultra-violet absorption spectrum of sodium vapour consists of a Balmer series of lines, of which the author has photographed thirty, this making the longest Balmer series known. In this series the *D*-lines appear as the third member, whilst the end is at λ 2411. The photographs were obtained by passing the light from a cadmium spark through a steel tube about one metre long containing sodium vapour at dull-red heat under nitrogen pressure of 15 cms. R. J. C.

Fraunhofer Lines of Thallium and an Error in Rowland's New Table of Standard Wave-Lengths. CARL FRITSCH (*Physikal. Zeitsch.*, 1908, 9, 900—901).—The author points out that Rowland's table of wave-lengths represents certain thallium lines as belonging to thorium. The spectral line measurements of thallium made by different observers are compared. H. M. D.

Re-determination of the Wave-Lengths of the Iron Lines used for Comparison Purposes. A. H. PFUND (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1909, 7, 1—16).—At the instance of the International Union for Co-operation in Solar Research, the author has re-determined the wave-lengths of certain iron lines by the interference method of Fabry and Perot. Details are given of the apparatus used and of the method of mounting, silvering, and polishing the plates of the interferometer. The measurements are tabulated and compared with the results obtained by the same method by Fabry and Buisson and by Eversheim. The independent series of measurements are in very good agreement. H. M. D.

Thermal and Chemical Absorption in Banded Spectra. JOHANNES STARK (*Physikal. Zeitsch.*, 1908, 9, 889—894).—The previous speculations of the author (compare Abstr., 1907, ii, 147, 417; 1908, ii, 138, 746, 911) are supplemented by a consideration of the relationships between coupled bands, of the nature of the double

* and *Physikal. Zeitsch.*, 1909, 10, 88—90.

and triple linkings in unsaturated compounds, of the so-called oxide spectra of the metals, and of the ultra-violet absorption of saturated valency electrons.

In the second part of the paper, application of the author's ideas is made to photochemical phenomena. Primary and secondary photochemical changes are distinguished. Primary changes are characterised by the fact that certain valency electrons absorb more energy in the form of light than that corresponding with the energy of combination of the electrons with the atomic or molecular remainders. Three general relationships which hold for primary photochemical changes are deduced from the author's hypothesis.

H. M. D.

Theory of Absorption in Gases. LÉON BLOCH (*Compt. rend.*, 1908, 147, 1284—1286).—According to Drude's theory of dispersion, the motion of the electrons is affected by friction, and the coefficient of friction, r , is assumed to be constant (independent of the wave-length). The author shows that, in the case of absorption in gases, r is a function of the wave-length. Employing the kinetic theory of gases, the formula obtained leads to the conclusion that r varies approximately as the square root of the absolute temperature, a deduction in agreement with recent work by J. Becquerel.

G. S.

Rotatory Power at Low Temperatures and the Relation between the Absorption of Light and Rotatory Polarisation in Crystals of Cinnabar. JEAN BECQUEREL (*Compt. rend.*, 1908, 147, 1281—1284).—Cotton (*Thèse*, 1896) has shown that there is a connexion between absorption of light and rotatory power in solution, and the author now shows by experiments with well-formed crystals of cinnabar that there is a similar relationship in active crystals.

The curve of rotatory dispersion at 18° and -188° , and the flutings in the spectrum at the same temperatures, are shown side by side on the same figure. The rotatory power increases rapidly near the absorbed region. On cooling to -188° , the yellow and a part of the red appear, and the great rotation appears no more in the orange, but is thrown back into the green, from which it is evident that the great rotatory dispersion is connected with the absorption.

Cinnabar possesses considerable magnetic rotatory power, and this property is being further investigated.

G. S.

Magnetic Rotatory Power of the Vapour of Calcium Fluoride and of Nitrous Oxide in the Neighbourhood of their Absorption Bands. A. DUFOUR (*Compt. rend.*, 1908, 147, 1471—1472).—In the case of calcium fluoride, the three bands $\lambda = 6037$, $\lambda = 6050.8$, and $\lambda = 6064.5$ were examined. The last shows the normal Zeeman effect, the other two the inverse phenomenon.

The nitrous oxide absorption bands $\lambda = 5854.9$ and $\lambda = 5846.8$ show the ordinary, whilst $\lambda = 5925.4$ and $\lambda = 5856.9$ exhibit the inverse, effect.

H. M. D.

Nitroquinol Dimethyl Ether and Theory of Solution. HUGO KAUFFMANN (*Ber.*, 1908, 41, 4396—4412).—Yellow nitroquinol di-

methyl ether yields coloured solutions in dissociating solvents, and practically colourless solutions in non-dissociating solvents (Abstr., 1907, i, 127). Hantzsch claims (Abstr., 1908, ii, 447) that the ordinary yellow preparation cannot be the true nitroquinol dimethyl ether; the latter is colourless, and existent in solutions in feebly dissociating or non-dissociating solvents. His claim is based on the assumptions that all true nitro-compounds are colourless, and that the molecular refraction of nitroquinol dimethyl ether in feebly dissociating solvents is only slightly greater than the calculated value, whilst in solutions in strongly dissociating solvents a pronounced exaltation of the molecular refraction is observed. The author points out that Hantzsch contradicts himself, since he states (Abstr., 1907, i, 513) that nitrobenzene shows absorption in the extreme violet, which is only another way of saying that nitrobenzene is not colourless. With regard to the second point, it is known that substances containing auxochromes in the benzene nucleus exhibit abnormally high molecular refractions. Therefore the true nitroquinol dimethyl ether must be that form existent in solutions in strongly dissociating solvents, that is to say, the yellow modification.

The author, however, rejects the theory of the existence of several modifications of nitroquinol dimethyl ether, and accounts for the varying colour of its solutions in different solvents by a novel conception. The outlines of the theory are as follows. Since the change of colour of a fluorescent substance in different solvents occurs, in general, without change of constitution (Abstr., 1904, ii, 528), the conception of constitution alone is insufficient. A constitutively unchangeable substance must have some capacity of change within its molecule, so that the molecule, under different conditions, can assume different states. The graphic representation of such states, which necessitates the theory of the divisibility of valencies, is called the conditioning formula. The substance has, in general, a single unchangeable constitutional formula and several conditioning formulæ. The constitutional formula is an ideal state, to which the conditioning formulæ approximate more or less according to the conditions.

Furthermore, the author assumes that the divided valencies represent lines of force. A line of force starting from an atom of a molecule may terminate either in another atom of the same molecule or in a different molecule, the latter case being important in the case of solutions. The molecules of a dissociating solvent have the power of attracting to themselves the lines of force issuing from the molecules of a solute. Non-dissociating solvents, on the contrary, tend to make the lines of force terminate in the molecule in which they originate. By this theory the author attempts to account for the change of the fluorescent colour of a substance in different solvents (Abstr., 1907, ii, 519).
C. S.

Triboluminescence. DÉsirÉ GERNEZ (*Ann. Chim. Phys.*, 1908, [viii], 15, 516—556).—A résumé of work already published (compare Abstr., 1905, ii, 365, 430, 431; 1908, ii, 748) together with a claim for priority against Trautz (Abstr., 1905, ii, 494, 662). Contrary to Tschugaeff's generalisation (Abstr., 1905, ii, 132), *d*-, *l*-, and *r*-erythritol

all exhibit triboluminescence (Bertrand, *Abstr.*, 1900, i, 424; Maquenne, *Abstr.*, 1902, i, 131).
M. A. W.

Disintegrating Action of Light and Optical Sensitisation. JOHANNES STARK (*Physikal. Zeitsch.*, 1908, 9, 894—900).—The disintegrating effect which ultra-violet light has been found to exert on gold-leaf exposed to its action is shown to be in accordance with theoretical requirements. An experiment is described which appears to show that positively charged atoms are emitted in consequence of the absorption of ultra-violet light. The action of sensitisers in promoting certain chemical changes is discussed in terms of the author's theory.
H. M. D.

Concerning the [Luminiferous] Ether. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1468—1471).—The author discusses the ether in relation to the atomic and electron theories.
T. H. P.

Action of Radium- and Röntgen-rays on the Colours of Precious Stones. CORNELIO DOELTER (*Monatsh.*, 1908, 29, 1145—1170).—A large number of observations are recorded relating to the changes in colour of precious stones and coloured glasses on exposure for different lengths of time to the action of radium- and Röntgen-rays. The colour changes are expressed in terms of the Radde scale. The two kinds of rays appear to act similarly on the coloured minerals. On account of the shorter periods of exposure in the case of the Röntgen-rays, a comparison of the activity of the two types of radiation is not possible. In certain cases the colour changes produced by the action of radium are reversed when the stones are heated to about 300° in oxygen or nitrogen.

The nature of the colouring substances is discussed. Amethyst, smoky quartz, rose quartz, and citrine are said to contain traces of iron thiocyanate, yellow diamonds, traces of iron and, possibly, cerium, ruby, traces of chromium and, possibly, iron. Chromium is also probably present as the chief colouring agent in yellow and green corundum and in certain sapphires.
H. M. D.

Decay of Radium Emanation when Dissolved in Water. JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1908, 6, 488—489).—A claim for priority (compare Moore, *Abstr.*, 1908, ii, 651).
W. A. D.

Radioactivity of the Atmosphere on Mountains. ALBERT GÖCKEL and TH. WULF (*Physikal. Zeitsch.*, 1908, 9, 907—911).—Measurements have been made of the induced activity collected on wires suspended for periods of twenty-four to one hundred hours at various points in the neighbourhood of the Matterhorn. The decay curves indicate that, at a height of about 3000 metres, the amount of induced thorium activity is relatively small, varying from 0.5% to 10%. The activity of collected rain-water was found to be of the same order of magnitude as that collected in Freiburg (Switzerland) at a height of 650 metres.

With a special type of electrometer, the ionisation due to very penetrating rays was examined. No influence of elevation on such ionisation could be detected, and the authors surmise that this penetrating type of radiation emanates from the earth's surface.

H. M. D.

Radioactivity of Italian Gaseous Emanations. RAFFAELLO NASINI and MARIO G. LEVI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 551—553).—The authors have measured the radioactivities of a number of gases of various Italian origins, of which they also give certain analytical data. The greatest radioactivity was exhibited by the gas, composed partly of hydrogen sulphide, from the thermal springs of Abano (Padua).

T. H. P.

Ionisation Phenomena caused by Rain-water. G. COSTANZO and C. NEGRO (*Jahrb. Radioaktiv. Elektronik*, 1908, 5, 395—402. Compare Abstr., 1908, ii, 551).—The activity of fresh rain-water, collected during March and April, 1908, was examined by bubbling air through it, and leading the gas into the ionisation chamber of an electroscope. In some cases the rate of discharge was greater when the electroscope was positively charged, in others when the charge was negative. If the rain-water is perfectly fresh, and especially if its fall is accompanied by atmospheric disturbances of an electrical nature, the negative ions are in excess.

H. M. D.

Radioactivity of Waters from Alange. JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fis. Quim.*, 1908, 6, 489).—The waters of Alange, which have great value in the treatment of nervous diseases, have a radioactivity of 1495·9 volts per hour litre.

W. A. D.

Radioactivity of Certain Springs in Upper Austria. MAX BAMBERGER (*Monatsh.*, 1908, 29, 1131—1140).—The radioactivity of spring-water emanating from the South Bohemian granite region in the neighbourhood of Schloss Tannbach has been found to be very high, 47—52 Mache units. The rate of decay of the induced activity indicates that the activity is due to disintegration products of radium.

H. M. D.

Radioactivity of Roumanian Mineral Waters. DRAGOMIR HURMUZESCU and N. PATRICIU (*Ann. Sci. Univ. Jassy*, 1908, 5, 159—165).—From measurements of the ionising power of the emanation obtained from various mineral waters, the authors have compared their radioactivities. These are of the same order of magnitude as the Swiss waters examined by Sury, Sarasin, Guye, and Micheli if the highly radioactive waters of Dissentis and Lavey-les-Bains are excepted.

H. M. D.

Radioactivity of Certain Spring-waters of the Semmering Province. MAX BAMBERGER (*Monatsh.*, 1908, 29, 1141—1144).—Numbers representing the radioactivity of spring-waters are recorded. The springs emanating from quartz-phyllite are the most radioactive, whilst those from limestone exhibit the property very feebly.

H. M. D.

Specific Radioactivity of Thorium and its Products. GEORGE C. ASHMAN (*Amer. J. Sci.*, 1909, 27, 65—72).—The specific activity of thorium has been deduced from experimental measurements of the activity of new and old thorium (1) freed from the easily separated products thorium-*X*, emanation, thorium-*A*, -*B*, and -*C*, (2) after a period sufficiently long for the disintegration products to have accumulated in the equilibrium quantities.

In order to separate thorium and radio-thorium from the other disintegration products, the authors have made use of *m*-nitrobenzoic acid. After four precipitations of the thorium at 80° and at intervals of two hours, the disintegration products are completely removed; the precipitated thorium *m*-nitrobenzoate is then heated over a Bunsen flame, and finally for ten minutes over the blow-pipe.

From the measurements specified above, the author finds that the specific activity of thorium is 119. This represents 11% of the total activity of the thorium when the equilibrium condition has been reached.

Of the remaining activity, 20% is due to radio-thorium, and 69% to thorium-*X* and its subsequent products. H. M. D.

Heat Development due to Radioactivity of Thorium Oxide. G. B. PEGRAM and H. WEBB (*Chem. Zentr.*, 1908, ii, 1851; from *Le Radium*, 1908, 5, 271—276).—By means of a thermo-couple the temperature difference has been measured between 4 kilos. of thorium oxide in a Dewar vessel supported in a partly evacuated metal cylinder which was surrounded with ice, and the ice jacket. A similar measurement was made when the thorium oxide was heated by passing a known current of electricity through a wire embedded in the mass. From these results, it is found that the liberation of heat per second per gram is equal to 1.11×10^{-8} watts, or 9.60×10^{-6} gram-calories per hour per gram. J. V. E.

Gaseous Ionisation and Pressure. T. H. LABY and G. W. C. KAYE (*Phil. Mag.*, 1908, [vi], 16, 879—889).—The authors have measured the ionisation produced by γ -rays of radium in air, hydrogen, and carbon dioxide at pressures from one to seventeen atmospheres. The γ -rays passed through 7 mm. of aluminium and 10 mm. of brass into a flat chamber containing an electrode and filled with the gas under investigation. The ionisation directly induced by the γ -rays is supposed to be small in amount and proportional to the pressure of the gas. The main effect is that of secondary β -rays from the aluminium electrode; this also varies as the pressure. Secondary β -rays excited in the gas, which would produce an ionisation proportional to the square of pressure, are not in evidence.

The amount of ionisation produced in the case of hydrogen was approximately proportional to the pressure. In air and carbon dioxide, the ionisation increased less rapidly than the pressure, particularly at high pressures. This phenomenon is attributable to a soft tertiary radiation produced in these gases by secondary β -rays. This would give a relatively larger effect at low pressures, since at higher pressures the gas would be more opaque to it and the range of the particles would be smaller. R. J. C.

Experimental Investigation of the Nature of γ -Rays. WILLIAM H. BRAGG and JOHN P. V. MADSEN (*Phil. Mag.*, 1908, [vi], 16, 918—939).—The authors adduce further experimental evidence in favour of the theory that γ -rays are material, and consist of β -particles combined with a positive charge (*Abstr.*, 1908, ii, 556).

The γ -rays from radium were purified as well as possible from β -rays by passing through a magnetic field and then allowed to impinge on plates of various elements. Measurements were made of ionisation on both sides of the plates, that is, of reflected secondary β -radiation and of emergent secondary β -radiation. The reflected secondary β -radiation depends very largely on the atomic weight of the material of the plate employed, but the emergent β -radiation, which is almost always greater, is of the same order for all the elements. The production of β -rays by hard γ -rays appears to follow a density law independent of atomic weights, but softer γ -rays are affected by atomic considerations in that heavier atoms are the more absorbent and produce more secondary β -radiation.

The speed and penetrating power of secondary β -radiation are governed by the corresponding properties of the primary γ -radiation. The γ -rays of radium produce secondary β -rays which closely resemble the primary β -rays of radium in speed.

It is argued that the energy of the secondary β -ray does not come from disintegrated atoms, but from the exciting primary γ -ray. The authors' theory, although it requires the existence of positive electrons, is held to be simpler and more complete than that advocated by J. J. Thomson. The theory is also applicable to X -rays. R. J. C.

Law of the Optimum of Cathodic Phosphorescence in Binary Systems. GEORGES URBAIN (*Compt. rend.*, 1908, 147, 1472—1474).—The discovery of the general relationship in question is not due to the author, but to Lecoq de Boisbaudran. If instead of referring to the entire phosphorescent spectrum, the component parts are taken into consideration, it is possible to give the law of the optimum a more precise form. According to this, if the relative proportions of the active substance and the diluent are varied, each phosphorescent band passes through a maximum. Although the maxima for different bands do not necessarily correspond with the same composition of the binary system, the proportion of the active component is always very small. H. M. D

Minimum Quantity of Electricity. N. L. MÜLLER (*Jahrb. Radioaktiv. Elektronik.*, 1908, 5, 402—408).—An explanation is given of the fact that the mass of the α -particle according to electromagnetic measurements is only 2, whereas if the α -particle be a helium atom it should be 4. If N is the number of ions in a gram, equivalent then $2 \times 96540/N$ is the quantity of electricity necessary for the separation of a molecule of hydrogen by electrolysis. This is supposed to be taken up by the hydrogen ions at the negative pole. Denoting the quantity by ϵ , the process of formation of a hydrogen molecule is represented by the equation $2H^+ + \epsilon = H_2\epsilon$. Other molecules can

be similarly formulated, and in the case of helium, the formula of the atom is $\text{He}\epsilon$, whereas that of the α -particle is He , and its mass is equal to 2. The direct measurements of ionic charges are discussed in terms of the author's hypothesis.

H. M. D.

Variation in the Electrical Conductivity at Constant Temperature of Mineral Waters Containing Radium. JOSÉ MUÑOZ DE CASTILLO and FAUSTINO DIAZ DE RADA (*Anal. Fis. Quim.*, 1908, 6, 485—488).—Measurements are given of the electrical conductivity and radioactivity of a number of natural Spanish mineral waters. The authors are collecting data which will enable them to discuss the relationship existing between the changes of conductivity and radioactivity of natural waters.

W. A. D.

Relation of the Charge to the Mass of the Electron. Comparison of the Values Deduced from the Zeeman Effect and from Recent Measurements with Cathode Rays. A. COTTON and P. WEISS (*Compt. rend.*, 1908, 147, 968—970).—From measurements of the distance between the side components of certain lines in the spectrum of zinc which become triplets in the magnetic field, the value $2 \times 1.767 \times 10^{-7}$ is obtained for e/m (e =electric charge, m =mass of electron) on the basis of the theory of Lorentz; a result practically double that obtained for the same ratio from measurements with slow cathode rays. From similar measurements on the helium spectrum, however, Lohmann (*Abstr.*, 1908, ii, 243) obtains $e/m = 1.77 \times 10^{-7}$, a value in good agreement with that obtained from observations on cathode rays.

G. S.

Electrical Resistance of the Alkali Metals, Gallium and Tellurium. ANTOINE GUNTZ and WITOLD BRONIEWSKI (*Compt. rend.*, 1908, 147, 1474—1477).—The metals were introduced into capillary U-tubes, the resistances being compared directly with that of mercury. Sodium, potassium, rubidium, and caesium were obtained from the chlorides by the action of calcium, and lithium by decomposition of the hydride. The specific resistances of these metals are recorded for a series of temperatures between -187° and the melting points of the metals. At 0° the values are caesium 19.30, rubidium 12.80, potassium 7.01, sodium 4.30, lithium 8.55.

Corresponding with the contraction which takes place on fusion, the specific resistance of gallium is greater in the solid than in the supercooled liquid condition. For the solid, the value at 0° is 53.4.

The specific resistance of tellurium at 0° is 0.102; it increases with the temperature, attains a maximum at about 50° , and then diminishes until the melting point is reached.

H. M. D.

E.M.F. of the Cadmium Normal Element at 0° . I. ERNST COHEN and HUGO R. KRUYT (*Zeitsch. physikal. Chem.*, 1909, 65, 359—370).—Jouaust (*Compt. rend.*, 1908, 147, 42) has stated that whilst the behaviour of cadmium elements made up with an amalgam containing 12.5% of cadmium by weight is regular down to 0° , the

E.M.F. of different cells containing a 10% cadmium amalgam shows deviations of several ten-thousandths, and these cells show certain other irregularities. The authors now show that there is a small, but probably real difference (since it is always in the same direction), not exceeding 0.2 millivolt, between cells made up with 10% and 12½% amalgams respectively, and consider that this small difference is due mainly to the difference in the concentration of the amalgams in the two cells, in accordance with the equilibrium relations discussed by Byl (Abstr., 1901, ii, 507). The differences, however, are not much greater than those observed with "identical" cells made up with the same amalgam, which may also amount to 0.2 millivolt. The statement of Jouaust (*loc. cit.*), that at 0° the use of a 12.5% amalgam is to be preferred, is therefore inaccurate.

Certain other of Jouaust's statements are criticised, but it is admitted that a further investigation of the electromotive behaviour of cadmium amalgams between 0° and 20° is desirable.

G. S.

Electrolytic Processes at the Surface of Electrodes. HANS G. MÖLLER (*Zeitsch. physikal. Chem.*, 1908, 65, 226—254).—According to Nernst, the phenomenon of supertension ("überspannung") is connected with the capacity of the electrode material to occlude gases. The author considers that the power of occluding gases is connected with the molecular forces between electrode and gas, and hence with surface tension phenomena. These theoretical deductions have been confirmed experimentally; it is shown that there is parallelism between the supertension and the surface tension between gas and electrolyte, and also between the supertension and the angle at the junction of gas and electrode.

The supertension at different electrodes has been determined by constructing curves representing the variation of strength of current with *E.M.F.*, and the precautions required to obtain accurate results are fully described. The angle, θ , between gas and electrode was read off directly by means of a microscope capable of turning on its axis, and a special method for obtaining conditions suitable for measurement is described. The relationship between supertension and the two capillarity factors mentioned above has been proved by experiments with mercury at temperatures between 0° and 10°, and also with other electrodes, the surfaces of which were of different degrees of roughness and in some cases were covered with a thin layer of fat.

The relation between θ and the supertension, π , is represented with great accuracy by the equation $\pi = (e^{a\theta} - 1)/b$, which holds for all temperatures and all electrodes under any conditions of surface. For hydrogen and *N*/10 sulphuric acid, the constant $a = 0.0264$ and $b = 9$.

It has not hitherto been possible to determine the absolute value of the surface tension at the junction of solid metals, but the curve representing the variation of the angle, θ , as a function of the polarisation must be parabolic and have a maximum at the same point as the electro-capillary curve. It is shown experimentally that

the maximum is the same for all the metals and electrolytes examined, provided the electrolyte contains metallic ions, but no complex ions, and that this value is at zero potential. If the metal is capable of forming complex salts, the maximum is displaced. The important result is thus established that the potential difference between electrode and electrolyte disappears when the surface tension at the electrode attains a maximum value; hence trustworthy results for absolute differences of potential are obtained by the use of the capillary electrometer. G. S.

[Oxide Theory of the Oxygen Electrode.] EMIL BOSE (*Zeitsch. Elektrochem.*, 1909, 15, 11—12).—Polemical in reply to Lorenz (this vol., ii, 15). T. E.

Electromotive Behaviour of Mixtures of Uranyl and Uranous Salts. ROBERT LUTHER and ARTHUR C. MICHIE (*Zeitsch. Elektrochem.*, 1908, 14, 826—829).—Uranous salts are strong reducing agents even in acid solutions; the oxidation by atmospheric oxygen is accelerated by iron salts, platinum black, and especially by copper salts. The difference of potential between a platinised platinum electrode and a solution of uranous and uranyl salts in sulphuric acid is given by $\epsilon = \epsilon_0 + RT/2F \log [\text{UO}_2^{++}][\text{H}^+]^4/[\text{U}^{+++}]$, where ϵ_0 is 0.419 volt more positive than the normal calomel electrode, or 0.696 volt more positive than the normal hydrogen electrode.

The *E.M.F.* of mercury-mercurous sulphate electrodes in 0.1*N* to 1.0*N*-sulphuric acid is very little affected by the strength of the acid. This is shown to be in quantitative agreement with Luther's views of the dissociation of sulphuric acid (*Abstr.*, 1907, ii, 610). T. E.

Minimum of Conductivity in the Titration of Acids. ALFRED THIEL (*Zeitsch. Elektrochem.*, 1909, 15, 1—4).—Bruni (*Abstr.*, 1908, ii, 935, 1012) pointed out that the equation by means of which the author calculated the dissociation constants of weak acids from the position of the minimum conductivity of the partly-neutralised solutions (*Abstr.*, 1908, i, 787) was based on incorrect assumptions. In the present paper, the author gives the correct equation for the case that the acid is titrated with 0.1*N* sodium hydroxide (the volume of the solution increasing). The assumptions made are the same as those made by Bruni, and the resulting equation becomes identical with his for the limiting case that the volume of the solution does not change during neutralisation. T. E.

Formation of Salts and Basicity of Acids. III. GIUSEPPE BRUNI and C. SANDONNINI (*Zeitsch. Elektrochem.*, 1908, 14, 823—825. Compare *Abstr.*, 1907, ii, 935, 1012).—The theoretical equation previously obtained indicates that when an acid, the conductivity of which is less than that of its neutral salt, is progressively neutralised, the conductivity must pass through a minimum which is displaced towards the salt end of the curve with increasing strength of acid and increasing dilution. The existence of this minimum is now proved for formic and acetic acids and *p*-nitrophenol. In all these cases it lies very close to the acid end of the curve. T. E.

Influence of Temperature on the Internal Energy and the Free Energy of Electrolytic Dissociation of Weak Acids and Bases. HARALD LUNDÉN (*J. Chim. phys.*, 1908, 6, 681—698).—The methods by which the heats of dissociation and of neutralisation may be calculated from the hydrolysis and dissociation constants are discussed. The relations between the heats of dissociation and neutralisation respectively and the absolute temperature T are best expressed by formulæ of the type $U=f(a, b, T)$, for example, $U=a+bT$ (U =internal energy; a and b are constants). The resulting formulæ are applied to calculate the changes of internal energy and of free energy obtainable in the electrolytic dissociation and neutralisation of a number of weak acids and bases. The temperature-coefficients of the internal energy, dU/dT , and of the free energy, dA/dT , and the inferior and superior limits of these coefficients have been obtained. From Nernst's theorem it is shown that dA/dT and dU/dT should have the same absolute value, but be of opposite sign, a deduction which is in moderate agreement with the facts. G. S.

Magnetic Properties of Simple Substances. P. PASCAL (*Compt. rend.*, 1908, 147, 1290—1292. Compare Abstr., 1908, ii, 756, 927).—It is shown that, for diamagnetic substances of the same valency and of analogous chemical properties, the atomic susceptibility, χ (the product of specific susceptibility and atomic weight), is an exponential function of the atomic weight, a ; hence the formula $\log_e \chi = a + \beta a$ applies, where a and β are constants for the same group, but vary, especially β , with the valency. The validity of the law is shown by observations on the halogen, sulphur, and phosphorus groups. It holds independently of the temperature. G. S.

Magnetic Dichroism of Calcite and Dolomite admixed with Liquids. GEORGES MESLIN (*Compt. rend.*, 1908, 147, 1277—1279).—Calcite and dolomite form, in association with a number of liquids, systems which show magnetic dichroism, but the sign of the effect is contrary throughout for the two substances. In both cases the change of sign takes place when the refractive index of the liquid exceeds 1.600; for calcite the change is from positive to negative at this point, and conversely for dolomite. G. S.

Magnetism of the Rare Earths. B. URBAIN and GUSTAV JANTSCH (*Compt. rend.*, 1908, 147, 1286—1288).—The magnetic susceptibility of the pure sesquioxides of a number of rare earths has been determined with the following results:

Element	Nd.	Sa.	Eu.	Gd.	Tb.	Dy.
Atomic weight ...	144.3	150.4	152.0	157.3	159.2	162.5
Magnetic power...	33.5	6.5	33.5	161.0	237.0	290.0

The relative numbers in the third line are referred to the value for cobalt sulphate heptahydrate = 39.7. The above and other results indicate that there is maximum of magnetic power in the cerium group, and a second in the yttrium group.

As the magnetic power differs so greatly for closely-allied elements, it may be used as a test for the composition of mixtures. G. S.

Measurement of Very Low Temperatures. XXII. The Thermo-element Gold-Silver at Liquid Hydrogen Temperatures. H. KAMERLINGH ONNES and J. CLAY (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 344—345).—The temperature-coefficient of the *E.M.F.* of the gold-silver thermo-element increases rapidly with falling temperature. The great sensitiveness of the element at the temperatures of liquid hydrogen renders it suitable for temperature measurements in this region. H. M. D.

New Model of the Calorimeter of N. A. Hesehus, and Determination by its means of the Specific Heat of Alloys of Tin and Bismuth. N. MARENIN [*J. Russ. Phys. Chem. Soc.*, 1908, 40, 393—398; (*Phys. Part*)].—This modification of Hesehus' calorimeter (*J. Phys.*, 1888, 489) allows of the weight of water in the calorimeter tube being determined by weighing this tube alone instead of the whole calorimeter. The author has measured for alloys of bismuth and tin containing from 0 to 100% of bismuth, (1) the temperatures of fusion; (2) the specific heats, which increase continuously with the content of bismuth, and (3) the densities, which diminish continuously as the percentage of bismuth increases. T. H. P.

Specific Heat of Solid Substances. MAX THIESEN (*Ber. Deut. physikal. Ges.*, 1908, 6, 947—952. Compare Abstr., 1908, ii, 653, 808; Grüneisen, Abstr., 1908, ii, 653).—A consideration of specific heat data for elements in the solid condition leads the author to conclude that the coefficient of expansion and the specific heat vary with the temperature quite differently. With rise of temperature, the coefficient of expansion increases the more rapidly. Although the formula given by the author can be used to calculate specific heat values for a wide range of temperatures, the empirical relationship pointed out by Grüneisen is incorrect.

The remainder of the paper is devoted to a consideration of Einstein's theory of the solid state of aggregation as furnishing a satisfactory basis for a theory of the specific heat of solids. H. M. D.

Plait Point Temperatures of the System Water-Phenol. A. KEESING (*Proc. K. Acad. Wetensch. Amsterdam*, 1908, 11, 394—397).—Measurements of critical temperatures for mixtures of water and phenol have been made by heating quartz tubes containing mixtures of known composition in the vapour of pure benzidine in contact with an atmosphere of nitrogen. A minimum critical temperature (357°) was found corresponding with 10% of phenol. The temperatures for pure water and phenol respectively are 364.7° and 419.2°. The curve connecting the critical temperatures for mixtures between 10 and 100% of phenol exhibits a point of inflexion. H. M. D.

Variation of Trouton's Constant in a given Homologous System. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1493—1501).—The author has collected or calculated the values of Trouton's constant for members of the following series: (1) elements; (2) inorganic compounds; (3) saturated hydrocarbons; (4) poly-

methylene compounds; (5) homologues of benzene; (6) ethers, and (7) esters.

The values for series (3), (4), and (5) show that the value of the constant diminishes as the molecular weight and boiling point rise. In the first two of these series, the constant exhibits a maximum value at b. p. 100—125°. With the ethers, too, the constant diminishes rapidly as the molecular weight increases.

T. H. P.

Melting Points. P. B. DALLIMORE (*Pharm. J.*, 1908, [iv], 27, 802).—A form of apparatus is described by means of which the m. p.'s of fatty acids, waxes, and similar substances can be readily determined. It consists of a glass U-tube, one arm of which is longer than the other and open at the top. The upper end of the shorter arm is bent at right angles, and drawn out to a fine point having a small aperture at the end. The tube is completely filled with the melted substance, and, when cold, is attached to a thermometer and heated in the usual way, the open end of the longer arm being slightly above the level of the liquid in the bath. As soon as the m. p. is reached, a drop of liquid is forced out of the aperture by the weight of the liquid in the longer arm.

E. G.

Hydrogen Polysulphides and Cryoscopy. EZIO PATERNÒ (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 627—633).—In criticising the conclusions drawn by Bruni and Borgo (*Abstr.*, 1908, ii, 102) concerning the formulæ of hydrogen polysulphides, the author points out that the cryoscopic constant of bromoform is variable and that no values obtained for the molecular weight of sulphur correspond exactly with the molecule S_8 (compare Orloff, *J. Russ. Phys. Chem. Soc.*, 1903, 35, 642). The calculation made by Bruni and Borgo of the apparent molecular weight when one of the molecules H_2S_5 , H_2S_6 , and H_2S_7 , or a mixture of them, exists in solution is faulty, since the same results are obtained in all cases where the relation between the numbers of hydrogen and sulphur atoms is constant, the total number of molecules also remaining unchanged. The uncertainty of the results obtained by these authors is confirmed by the work of Tanatar, Choina, and Kozireff (*Abstr.*, 1895, ii, 41), who found that the depressions of the freezing point of water caused by organic non-electrolytes are not altered sensibly by adding to the water 10 or 20% of methyl or ethyl alcohol, whilst with salts the addition of alcohol increases the depressions obtained in water alone.

The author has measured the freezing-point depressions of bromoform produced by varying quantities and proportions of sulphur and carbon disulphide. The mean difference between the experimental results and the calculated ones is 6.8%.

Further, Bloch and Höhn (*Abstr.*, 1908, ii, 579, 580) and Schenck and Falcke (*Abstr.*, 1908, ii, 762) have shown that crude hydrogen polysulphide is not a mixture of H_2S_5 , H_2S_6 , H_2S_7 , and H_2S_8 , but that it contains the two sulphides H_2S_2 and H_2S_3 .

The melting-point curves of mixtures of selenium and iodine obtained by Pellini and Pedrina (*Abstr.*, 1908, ii, 833) do not show

that these elements do not form a compound, but only that such compound decomposes before the eutectic temperature is reached.

Olivari's conclusions (this vol., ii, 37, 39) are also criticised.

T. H. P.

Law of Corresponding Boiling Points. ULRICH DÜHRING (*Zeitsch. physikal. Chem.*, 1909, 65, 338—340).—A claim for priority with reference to the discovery of the law in question, recently ascribed by Johnston (*Abstr.*, 1908, ii, 358) to Ramsay and Young.

G. S.

Relation between the Capillary Constants and the Latent Heat of Vaporisation of the Solvent. PAUL WALDEN (*Zeitsch. physikal. Chem.*, 1909, 65, 257—288. Compare this vol., ii, 122).—It is shown from the available data for over sixty liquids that there is a simple relationship between the heat of vaporisation, λ , and the specific cohesion, a^2 ($a^2 = rh$, where h is the height to which the liquid rises in a capillary tube of radius r mm.), both determined at the boiling point; for non-associated liquids, $\lambda/a^2 = 17.9$; for associated liquids, λ/a^2 is greater than 17.9. Conversely, the heat of vaporisation can be calculated from the above relationship when the specific cohesion at the boiling point is known, and a more complex formula is deduced, by which the value of λ at the boiling point can be calculated from the value of a^2 at lower temperatures.

When liquids with very divergent boiling points are compared, the relationship between a^2 and λ is represented more satisfactorily by means of the formula $\lambda/a^2 = 46.0/\log T_\sigma$, where T_σ is the boiling point of the liquid on the absolute scale. By combining the last formula with Van't Hoff's formula for the molecular elevation, E , of the boiling point, $E = 0.02T^2/W$, the relationship between specific cohesion at the boiling point and boiling-point constant is obtained in the form $E = 0.00043T_\sigma^2 \log T_\sigma / a^2$, a formula which permits of the calculation of E with considerable accuracy.

It is further shown that the molecular cohesion, Ma^2 , the molecular heat of vaporisation, $M\lambda$, and the boiling point on the absolute scale are additive in character. For compounds containing only hydrogen, oxygen (bivalent), nitrogen (trivalent), and carbon, the formula $Ma^2 = 11.5\Sigma n$, where Σn represents the sum of the valencies, holds within very wide limits. The formula is not valid for compounds containing the halogens on any of the usual assumptions as to their valency, nor does it hold for water, ammonia or methyl alcohol. The further relations $T_\sigma = 11.2\Sigma n$ and $M\lambda = 240\Sigma n$ are also shown to hold in many cases.

Finally, from the formula $\lambda/a^2 = \text{constant}$, the conclusion is drawn that the molecules of all non-associated liquids are approximately of the same diameter at their respective boiling points.

G. S.

Latent Heat of Evaporation of isoAmyl Ether. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1471—1474).—The mean specific heat of isoamyl ether between 24° and 170° is $0.5721 \pm 0.5\%$, the latent heat of evaporation, ρ , being 53.1 cal. with an accuracy of about 1% and Trouton's constant, K , 18.8. T. H. P.

Latent Heat of Evaporation and Specific Heat of Naphthalene. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1474—1477).—Taking the specific heat of naphthalene as 0.32 at 20° and 0.7 at 215°, the latent heat of evaporation is found to be 74.7 cal. and Trouton's constant, 19.3. The latter figure confirms the observation that, in an homologous series, Trouton's constant diminishes as the boiling point exceeds 100°. T. H. P.

Latent Heat of Vaporisation of Benzoin *iso*Butyl Ether. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1477—1480).—The latent heat of vaporisation of benzoin *isobutyl* ether is found to have the mean value 55.7 cal., the greatest deviation from this mean being 1.2%. From this value, Trouton's constant is calculated to be 19.3. The only substance having a high boiling point and a high Trouton constant (21.5) is mercury, which is not comparable with other substances, owing to the extreme simplicity of its molecular structure. T. H. P.

Latent Heat of Vaporisation of Acetic Anhydride and Determination of the Association of Liquids. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1480—1487).—The author shows that the value of the Ramsay-Shields constant for determining whether a liquid is associated is greatly diminished by the observations (1) that the magnitude of the constant changes with the molecular weight, and that (2) change of the constant with rise of temperature occurs even with non-associated compounds.

The author's measurements of the specific heat of acetic anhydride lead to the mean value $0.4551 \pm 0.33\%$ for the range of temperature 20—138°. The latent heat of vaporisation is found to be $92.6 \pm 0.5\%$ at 138°. Trouton's constant, calculated from these results, is 22.9. Acetic anhydride is hence associated, and is converted into simple molecules at the moment of boiling. T. H. P.

Lithium, Strontium, and Barium Oxides. ROBERT DE FORCRAND (*Ann. Chim. Phys.*, 1908, [viii], 15, 433—490).—A detailed account of work already published (compare Abstr., 1907, ii, 615, 683, 928; 1908, ii, 155, 493, 764). Using the corrected value for the heat of solution of strontium oxide (Abstr., 1908, ii, 765), the heat of formation of strontium oxide is 138.64 Cal., and not 137.6 Cal. as stated (Abstr., 1908, ii, 155). The heats of formation of the peroxides of calcium, strontium, and barium are 157.37, 153.07, and 145.58 Cal. respectively, and not 157.33, 152.10, and 145.71 Cal. as stated (*loc. cit.*). M. A. W.

Heat of Hydration. WILLEM P. JORISSEN (*Chem. Weekblad*, 1908, 5, 875—888).—A summary of the literature on heat of hydration, and a criticism of the results obtained. A. J. W.

Heats of Dissociation of some Electrolytes in Organic Solvents. PAUL DUROIT and H. DUPERTHUIS (*J. Chim. Phys.*, 1908, 6, 699—725).—The electrical conductivity, and hence the degree of ionisation, of sodium iodide in ethyl, propyl, *isobutyl*, and *isoamyl* alcohols,

and in acetone and pyridine, has been determined at intervals of 10° between 0° and 80° (in the case of acetone up to 40°), and similar measurements have been made with potassium iodide and sodium and potassium thiocyanates in pyridine. The dilutions employed were from 1000 to 20,000 litres per mol. of salt, within which limits Ostwald's dilution law applies in most cases, so that the degree of dissociation can be accurately determined. From the results, the heat of dissociation has been calculated by Van't Hoff's formula.

Contrary to Walden's statement (Abstr., 1907, ii, 437), the heat of dissociation of a salt has not the same value in different solvents; for sodium iodide as solute it is positive in ethyl alcohol, zero in acetone, and negative in the other alcohols and in pyridine. Further, the heat of ionisation also varies greatly with the temperature in most cases; in isoamyl alcohol it is -2008 cal. at 15° and $-16,760$ cal. at 75° . On the other hand, the heats of ionisation in pyridine of the four salts above mentioned are nearly equal and do not vary much with temperature.

The fact that for what is presumably the same reaction, $\text{NaI} = \text{Na}^+ + \text{I}^-$, the thermal effect in different solvents is very different, indicates that the process in question is not simple; it is probable that combination between ions and solvent is of importance. The differences between the authors' results and those of Walden are ascribed to the fact that the latter observer used erroneous values for the molecular conductivity at infinite dilution, obtained by extrapolation from relatively concentrated solutions.

G. S.

The Density of Liquids Below Zero. JEAN TIMMERMANS (*Bull. Soc. chim. Belg.*, 1908, 22, 427—439).—It has been shown previously (Abstr., 1908, ii, 85) that none of the liquids studied has a maximum density analogous to that of water at 4° . The original experiments, which were accurate to the extent of 1 in 1000, have now been repeated more exactly, the error not exceeding 1 in 10,000. The present paper relates to the apparatus and experimental methods employed. The measurements were made by means of the dilatometer. A series of the latter were employed in order to avoid capillary tubes of unwieldy length to cover the range of temperature considered, and were calibrated with an accuracy of 1 in 20,000. The apparent internal volume of the dilatometers at 0° was not altered by two hours' immersion in liquid air. The errors due to the meniscus were corrected in the case of mercury as calculated by Schalkwyk and by Göckel, and in the case of liquids which "wet" glass by assuming the surface of the liquid in the capillary to be hemispherical. This correction amounts to about $1/10,000$ th of the volume to be measured. With very volatile liquids a correction, amounting to about $1/10,000$ th of the total weight, had to be made for the weight of saturated vapour in the dilatometer above the surface of the liquid. The densities of the liquids at 0° compared with that of water at 4° were taken as standards, and were determined by means of an Ostwald-Perkin pycnometer. The apparatus for maintaining the dilatometer at constant and uniform temperatures below 0° consists of a tube to contain a pure liquid (for cooling the dilatometer), solidifying at a known temperature below 0° , surrounded by a Dewar

tube provided with a tubulure and stopcock, which again is surrounded by another Dewar vessel, the walls of the latter being silvered except over a small space left transparent for reading the volumes in the dilatometer. The outer vessel must be maintained (by means of liquid air or carbon dioxide) at least $15-20^{\circ}$ below the solidification point of the cooling liquid. Air is kept between the walls of the inner Dewar vessel until the cooling liquid (which must be kept continually stirred) solidifies (this should occur rapidly throughout the entire liquid) when it is pumped out until the internal pressure is $50-200$ mm., according to the difference of temperature of the inner tube and the outer Dewar vessel. This prevents further cooling of the cooling-bath, and enables the latter to be kept at a known constant and uniform temperature for some hours. Thus the volume of liquid in the dilatometer can be measured at fixed uniform temperatures below 0° . The temperatures are determined by a Callendar resistance thermometer in conjunction with a Callendar-Griffin bridge, by means of which resistances can be measured to $1/10,000$ th of an ohm. The exact evaluation of the temperature is made according to the calculations of Travers and Gwyer (*Abstr.*, 1905, ii, 372).

The sole systematic errors of any importance in the work are (1) that in the calibration of the dilatometers, equal to $1/20,000$ th of the density, (2) that in reducing the scale of the platinum resistance thermometer to the scale of the gas thermometer, equal to $1/10,000$ th of the density.

The results obtained for ethyl acetate show that the density of this liquid varies according to the expression $D_t = 0.92540 - 0.0011863t$, D_t being the density at $-t^{\circ}$, t the temperature interval below 0° , and 0.92540 the density at 0° . The greatest difference between the observed densities and those calculated by this formula is only 0.00014 .

E. H.

Expansion Coefficient, Specific Cohesion, Surface Tension, and Molecular Weight of Solvents. PAUL WALDEN (*Zeitsch. physikal. Chem.*, 1908, 65, 129—225).—The densities of a number of carefully purified liquids which have considerable solvent power have been determined at 0° , 25° , and 50° . From these results and the available experimental data on the density, specific cohesion, and surface tension of a large number of liquids, and the variation of these properties with the temperature, certain relationships are deduced between these properties themselves and between the physical properties and molecular weights of the solvents in question.

The general formula, $V_t = V_0/(1 - kt)$, proposed by Mendeléeff to represent the variation of the density of liquids with temperature, has been tested by application to the data for forty-nine different liquids, including some liquefied gases. It is valid for liquids boiling below 100° , but only moderately so for liquids boiling at higher temperatures; k varies for different liquids between 0.000178 and 0.00216 .

For non-associated substances, the "expansion modulus," k , is inversely proportional to the critical temperature, t_c , on the centigrade scale, and in many cases $kt_c = 0.34$. For certain liquefied gases and other liquids with low critical temperatures, the value of $kT_c =$

constant ≈ 0.49 , the critical temperature being measured on the absolute scale. There is also parallelism, but not proportionality, between the expansion modulus and the compressibility of liquids.

The data as to the surface tension, γ , for over fifty liquids are taken from the results of Ramsay, Guye, and others; those for the "specific cohesion," a^2 , are mostly calculated from the values of γ by means of the equation, $a^2 = 2\gamma/9.81d$, where d is the density. In some cases the γ values are calculated from the experimental values of a^2 by means of the same formula. The variations of the surface tension and the specific cohesion respectively with the temperature are represented through a wide range of temperature by the equations $\gamma_t = \gamma_0(1 - \beta t)$ and $a_t^2 = a_0^2(1 - k_1 t)$, where β and k_1 are constants for any one liquid, but vary with the nature of the liquid. It is shown that for non-associated liquids, $\beta t_c = \text{constant} = 1.16$, and that $k_1 t_c = \text{constant} = 0.94$. From these equations the critical temperature can be calculated when β or k_1 are known, and it is shown that the calculated and observed results are in good agreement. Other methods which have been suggested for calculating critical temperatures are discussed.

Further, the quotient of the latent heat of evaporation at the boiling point, λ_σ , by the specific cohesion at the same temperature is constant and $= 17.9$. Combining this with the mathematical expression for Trouton's rule, $M\lambda_\sigma/T_\sigma = 20.7$, where M is the molecular weight of the liquid, the equation $Ma_\sigma^2/T_\sigma = 1.16$ is obtained, and is shown to be valid for non-associated liquids (compare Kistiakowsky, Abstr., 1906, ii, 655). For associated liquids, this expression is no longer constant, but is smaller the more the liquid is associated. We have thus a new method for determining the molecular weight of liquids, which appears to give more consistent results than any other method so far suggested. In the first instance, the above equation only applies to observations at the boiling point, but a rather more complicated equation is derived which admits of the calculation of the molecular weight from capillary observations at any temperature.

When allowance is made for the fact that Trouton's rule is only valid over a limited range of temperature, a more accurate formula, $M = 0.435 T_\sigma \log T_\sigma / a_\sigma^2$, is obtained, and is applied to the determination of the molecular weight of liquefied gases and other liquids. Of the ten liquefied gases considered, only hydrogen chloride is considerably associated (association factor $= 1.32$). The association factor for cadmium is rather less than unity; it is therefore monatomic in the liquid state.

When, instead of the specific cohesion, the surface tension, γ , is used, the expression $M\lambda/V\gamma_\sigma = 3.64$ is obtained, where V is the molecular volume, and the other factors have the same significance as above. Combining this with Trouton's rule, we obtain $V\gamma_\sigma/T_\sigma = 5.67$. These expressions are shown to be valid for a large number of non-associated liquids, but for associated liquids the quotients are less than 3.64 and 5.67 respectively, and from the observed values the degree of association can be calculated.

According to Eötvös-Ramsay-Shields, the temperature-coefficient of

the "molecular surface energy" should be constant for non-associated liquids, that is, $d(\gamma V^{\frac{1}{3}})/dt = \text{constant} = 2.12$. The above considerations, however, lead to the conclusion that $d(\gamma V)/dt$ should be constant, and it is shown by application to twenty-four typical liquids that the latter expression varies less than the former; the mean value is 8.80. For associated liquids the value is less, and from the above equation the degree of association can be calculated as in the case of the Eötvös equation. The results obtained by the two methods are in satisfactory agreement. G. S.

Liquefaction and Compressibility of Gaseous Mixtures. A Case in which Combination Occurs. E. BRINER and E. CARDOSO (*J. Chim. Phys.*, 1908, 6, 641—680).—The gases were liquefied by means of liquid air or solid carbon dioxide and ether, and purified by fractional distillation. The compression was effected with a Cailletet pump, the compression tube contained a stirrer worked by a magnet, and the pressure was measured on a nitrogen manometer.

The compressibilities and vapour tensions of certain binary mixtures, and of the components separately, have been determined at different temperatures.

A mixture of sulphur dioxide and methyl ether in equivalent proportions liquefies with very little alteration of pressure, and the vapour-pressure curve of the system shows a minimum at the same composition, from which the conclusion is drawn that a compound, $\text{SO}_2 \cdot \text{Me}_2\text{O}$, exists. The critical temperature of a mixture of this composition is 152.5° , between those of the components, and the critical pressure 62 atmospheres. From the variation of the pressure of the binary mixture with temperature, it is calculated by means of Van't Hoff's equation that the heat given out by the reaction $\text{Me}_2\text{O}(\text{gas}) + \text{SO}_2(\text{gas}) = \text{Me}_2\text{O} \cdot \text{SO}_2(\text{solid})$ is 11.8 cal. between 50° and 100° and 8.7 cal. between 138° and 147° .

No evidence of combination has been obtained in the following binary systems: methyl ether and methane, methyl ether and carbon dioxide, and methyl ether and nitric oxide. G. S.

Relation between Surface Tension and Specific Volume of Non-associated Liquids. REGINALD O. HERZOG (*Zeitsch. Elektrochem.*, 1908, 14, 830—831).—By combining Avenarius' equation for the dependence of specific volume on temperature with Van der Waals' equation for surface tension and temperature, the author obtains $\log \gamma + \mu v = r$, where γ and v are surface tension and specific volume at the same temperature, and μ and r specific constants of the substance. The relation is shown to hold good for six liquids. The relation $\mu = 5.28$ times the critical density is also true. T. E.

Supertension and Viscosity. CHARLES MARIE (*Compt. rend.*, 1908, 147, 1400—1402).—The effect of variations in the viscosity of the electrolyte on the excess voltage required to liberate hydrogen at different electrodes dipping in *N*/1-sulphuric acid has been examined. When the supertension is small, the effect of increased viscosity is slight, thus 0.5% of gelatin raises the supertension at platinised

platinum electrodes at most by 0.001 volt, but for metals with high supertension the effect is much greater, thus 0.1% of gelatin raises the supertension at lead electrodes by 0.05 volt. G. S.

Viscosities and Limiting Conductivities. PAUL DUTOIT and H. DUPERTHUIS (*J. Chim. Phys.*, 1908, 6, 726—731).—Walden (Abstr., 1906, ii, 335) has shown that for tetraethylammonium iodide in organic solvents the product of the viscosity, η , of the solvent and the molecular conductivity at infinite dilution, μ_{∞} , is independent of the nature of the solvent and of the temperature; $\eta\mu_{\infty} = 0.7$ approximately. The authors have determined the viscosities at intervals of 10° between 0° and 40° (in some cases up to 80°) of the seven solvents already mentioned (see this vol., ii, 120), and show that Walden's rule is not of general validity. The product $\eta\mu_{\infty}$ is not the same for the different solvents, nor does it tend towards a fixed value as the temperature rises. At 0° the extreme values are 0.374 (in *isoamyl* alcohol) and 0.573 (in pyridine), and at 80° the extreme values are 0.225 and 0.559 (in the same solvents). Further, $\eta\mu_{\infty}$ varies with the temperature; in four of the solvents it diminishes, and in one it increases, with increase of temperature. The variations are considerable in some solvents; from 80° to 0°, $\eta\mu_{\infty}$ increases by 47% in *isoamyl* alcohol and by 25% in *isobutyl* alcohol. G. S.

Adsorption. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1908, 15, 196—216).—Determinations were made of the adsorption of acetone by charcoal, and the results were found to agree with the theory of Gibbs and Freundlich. The adsorbabilities of acetone in the presence of acetic acid, or acetic acid in the presence of acetone, by charcoal were also determined, and it was found that the simultaneous presence of two adsorbable substances diminished the adsorbability of either. The phenomenon of the diminution of adsorbability by the presence of a second adsorbable substance was not observed, however, in the case of proteins and certain dyes. In the case of the former substances, there is a further peculiarity, in that the adsorption process is not reversible. This was thought to be due to the conversion of the protein into an insoluble form, such as takes place on coagulation, but the same phenomenon takes place when albumoses are adsorbed, and it was experimentally shown that in this case the presence of acetone does not diminish its adsorbability by charcoal. The conclusion is drawn that the adsorption of proteins is not a simple mechanical process, but depends probably on the electrical properties of the surfaces. S. B. S.

Coefficient of Diffusion. BASIL W. CLACK (*Phil. Mag.*, 1908, [vi], 16, 863—879).—The author has endeavoured to elaborate an accurate method of measuring the diffusion coefficients of dissolved salts, and to determine to what extent diffusion depends on concentration.

The solutions under investigation were enclosed in a glass bulb into which a diffusion tube 4 cm. long was sealed in such a way that the end projected 2 cm. into the bulb. The bulb was suspended in

distilled water beneath the pan of a delicate balance, so that the weight of its contents could be measured automatically from time to time. As salt diffused out of the bulb, the solutions contracted, and water entered to make up for this contraction at nearly constant rates so long as the concentration was not appreciably diminished. A steady distribution of concentration being established in the diffusion tube, an equation could be deduced connecting the rate of loss of weight of the bulb with the coefficient of diffusion.

The results obtained are held to show that the method is capable of yielding accurate values when certain conditions of experiment are observed. The following diffusion coefficients at 0° are given: KNO_3 in 10% solution 0.844, in 5% solution 0.870; KCl in 20% solution 0.972, in 10% solution 0.954.

R. J. C.

Osmosis of the Alkali Haloids. FRANZ WIEMERS (*Ann. Physik*, 1908, [iv], 27, 1081—1098).—Measurements have been made of the relative changes in concentration which take place in solutions of the halogen salts of the alkali metals when the solutions are separated from water by a membrane of pig's bladder. The data are used to calculate the so-called endosmotic equivalent, the quantity of water which in a given time replaces unit quantity of the dissolved substance.

The endosmotic equivalent decreases as the molecular weight of the dissolved haloid salt increases. It is independent of the temperature, although the absolute magnitude of the two diffusion currents increases with rise of temperature in consequence of the greater velocity of the molecules. With increasing concentration of the solution, the diffusion currents increase in magnitude, but since the flow of water increases more rapidly than that of the salt solution, the endosmotic equivalent is greater the more concentrated the solution.

H. M. D.

Osmotic Pressures of Aqueous Solutions of Calcium Ferrocyanide. I. Concentrated Solutions. EARL OF BERKELEY, ERNALD G. J. HARTLEY, and C. V. BURTON (*Phil. Trans.*, 1908, A, 209, 177—203).—Porter's equation taking account of the effect of compressibility of solvent and solution on the relation of osmotic to vapour pressures (*Abstr.*, 1907, ii, 743; 1908, ii, 670), can be modified and applied to determinations of vapour pressure made in air at atmospheric pressure instead of under vacuum conditions. Whilst Porter's equation yields results differing from the authors' experiments by 2 or 3%, the modified equation is in close agreement with experiment. The authors have endeavoured to increase the accuracy of their vapour-pressure determinations in order to render the correction for compressibility significant.

Determinations were made at 0° of osmotic pressure, vapour pressure, and compressibility of concentrated solutions of calcium ferrocyanide. The purest salt, recrystallised to eliminate potassium, consisted of yellow crystals containing $11\text{H}_2\text{O}$.

In previous measurements of vapour pressure by the bubbling method, an unexplained loss of weight occurred in the whole apparatus

as well as in the particular bulb containing the solution. The complete elimination of rubber tubing from the apparatus and the substitution of mercury seals, although an advantage, was not entirely satisfactory, because a ponderable amount of mercury now volatilised. Finally, platinum-iridium connecting tubes with ground-in junctions were used throughout, and no appreciable source of error was found in the method so modified.

Determinations of osmotic pressure were carried out as previously described (Abstr., 1906, ii, 599). The amount of calcium ferrocyanide leaking through the copper ferrocyanide membrane was found to be practically nil.

A special form of piezometer was employed for compressibility determinations. The compressibility tube was made of Jena glass, the compression coefficient of which has been determined by Straubel to be 228×10^{-8} . A check experiment made by the authors gave the value 223×10^{-8} . Possible sources of error, particularly those due to temperature, were carefully guarded against.

The concordance of observed osmotic equilibrium pressures, and those calculated from vapour pressures and compressibilities by the modified Porter's equation, is held to indicate a satisfactory agreement between experiment and thermodynamic reasoning. R. J. C.

Contact Pyrogenetic Oxidation of Hydrogen and Carbon Monoxide by Air. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1590—1595).—The author has studied the oxidation of excess of hydrogen and of carbon monoxide by air in presence of copper or platinum gauze under such conditions that the contact material is heated by the oxidation process. The results are given in detail, and do not admit of condensation (compare following abstract).

T. H. P.

General Conditions of Contact Oxidations accompanied by Auto-heating of the Contact Layer. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1596—1603. Compare preceding abstract).—These contact oxidations are divided into two classes: (I) reversible reactions, such as $2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$, $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$, and $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + 2\text{Cl}_2$; (II) reactions which are not reversible under the experimental conditions, such as $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ and $4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$.

Class I.—In this case the velocity of flow of the mixed gases is without influence on the magnitude of $C^2.C_1/C_{11}^2$, which has the constant value 0.55, C and C_1 representing the initial concentrations of the hydrogen and oxygen respectively, and C_{11} the concentration of the water vapour. In contact with the heated layer of copper or platinum gauze, the gases occupy a volume V_m greater than the volume V they occupy after leaving this layer and cooling. If r is the ratio of the initial speed to the mean speed of the gases, and K and K_1 the concentrations of the hydrogen and oxygen respectively in the final gases, $(C^2.C_1/r^2)^{V_m} = (K^2.K_1)^V$. Inserting the values of $C^2.C_1/r^2$ and $K^2.K_1$ given by the four experiments previously described (see preceding abstract), the quotient V_m/V is found to be 6, 6.87, 5.87,

and 6.8° . If t° represents the fall of the temperature of the gases on leaving the heated contact layer, $V_m/V = 273/(273 - t)$, from which $t^\circ = 227^\circ, 233^\circ, 226^\circ$, and 230° ; using a contact layer 8—12 cm. in length, the actual difference of temperature between the heated and unheated parts was found to be approximately 230° .

Class II.—In this case, not only the concentrations, but also the speed with which the mixed gases meet the contact layer is of importance, and unless the velocity of flow reaches a certain value in each particular case, no heating of the contact layer takes place. For the oxidation of carbon monoxide and methyl and propyl alcohols, the constant, C^2C_1/V^2 , has the values 0.022 — 0.021 , 0.00103 , and 0.000103 respectively, C and C_1 being the initial volume concentrations of the carbon monoxide, etc., and of the oxygen respectively, and V the mean velocity of the gaseous mixture. From the equation $(C^2C_1/r^2)^x = (K^2K_1)^r$, it is calculated by means of the experimental numbers obtained (see preceding abstract) that $X/Y = 2.04, 2.21$, and 2.1 . It is found experimentally that the ratio of the absolute temperature of the heated portion of the contact layer to that of the cool portion, T_1/T_2 , has the approximate value 2, from which it is deduced that $T_1/T_2 = X/Y$. Replacing X and Y in the equation given above by T_1 and T_2 respectively, an expression is obtained showing that increase of r , decrease of V , and increase of T_1/T_2 , all cause increase of the reaction between carbon monoxide and oxygen. With methyl and propyl alcohols, the primary oxidation is accompanied by decomposition of the alcohol and oxidation of the decomposition products, whilst with ammonia part of the nitrogen originally formed is oxidised to oxides of nitrogen.

T. H. P.

Polyiodides. F. OLIVARI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 584—590).—The author has studied the influence of the solvent on the relation $x/y = \theta$ between the concentration x in gram-mols. of iodine dissolved and the concentration of an insoluble iodide (KI) passing into solution to form polyiodides (KI_{2n+1}).

The results show that all the alcohols, acids, esters, ketones, cyano- and nitro-derivatives, on which iodine has no chemical action, allow of the formation of polyiodides. The solubility of potassium iodide in presence of iodine increases approximately with the dielectric constant of the solvent.

With solvents having analogous chemical functions, the ratio θ , and also x , increase, and consequently the absorption of potassium iodide diminishes with increase of the molecular weight of the solvent, that is, with increase of its anomalous power and with decrease of its dielectric constant.

Comparison of the results obtained with solvents having different chemical functions shows that the absorption of potassium iodide depends on the anomalous property as well as on the dissociating power of the solvent. The solvents which increase the ratio θ , do so in the following order: acetic acid (9.7), ethyl acetate (6.11), ethyl alcohol (25.8), nitrobenzene (36.4), ethyl bromide (9), hydrocarbons (2), the numbers in brackets representing the respective dielectric constants. As regards anomalous power, the series $CO_2H, CO_2R, OH, NO_2, Br$,

Me is in very good agreement with the series given by Auwers (Abstr., 1903, ii, 268), considering that these groups are not united to the same radicle in the solvents investigated.

With different iodides and the same solvent, it is found that when the solutions of iodine are dilute, almost identical values of θ are given by the iodides of any one group of the periodic system. With concentrated solutions, however, deviations occur in a definite sense, which seems to indicate that they bear a relation to the electropositive character of the metal. Diminution of the latter character is accompanied by a diminution in the absorption of the iodide by a nitrobenzene solution of iodine.

T. H. P.

Kinetics of Alkylation. HEINRICH GOLDSCHMIDT (*Zeitsch Elektrochem.*, 1909, 15, 10—11).—The experiments of Acree and his pupils (Abstr., 1908, ii, 919) do not prove the existence of tautomeric forms in solution, as they are equally well explained by the supposition that the alkyl halide is added on to the anion of the salt in two different ways, the two complex ions yielding the O- and N-ethers respectively.

T. E.

Researches on the Formation of Esters. HEINRICH GOLDSCHMIDT [with M. ASRIEL, V. KOREN LUND, and OLAF UDBY] (*Zeitsch. Elektrochem.*, 1909, 15, 4—10).—Kailan (Abstr., 1908, ii, 936) finds that the rate of esterification of trichloroacetic acid without a catalyst is not in agreement with the theory of hydrogen ion catalysis. The author therefore gives a résumé of the unpublished results which he has obtained during the past few years. The rate of esterification of tri- and di-chloroacetic acids is increased slightly by the addition of a salt of the acid, that of formic acid is much diminished. With di- and tri-chloroacetic acids, the reaction is of the second order; with formic acid the second order constants rapidly diminish, but are constant in presence of a formate; the aromatic sulphinic acids give a reaction lying between the first and second orders. Probably in these cases the hydrogen ion catalysis is of secondary importance, some other reaction accounting for the main part of the ester formation.

The esterification of formic acid, using picric, trichloroacetic, trichlorobutyric, and dichloroacetic acids as catalysts, was studied in alcohol dried with calcium. The addition of the piperidine salt of the acid diminishes the rate of change, the effect being larger with the weaker acids. The catalytic action of hydrogen chloride is not affected by the addition of a chloride. The conductivity of the alcoholic solutions of the acids was also measured, and the catalytic action is found to be almost proportional to the conductivity of the solutions. The rates of esterification of formic acid by picric acid in different concentrations are also nearly proportional to the conductivities of the solutions. With weaker acids the agreement was not so good, possibly the non-dissociated complex of catalytic acid and alcohol reacts slowly with the acid to form the ester, the effect being superposed on that of the hydrogen ion. The addition of water to a solution of hydrogen chloride in absolute alcohol diminishes its

conductivity to a minimum; for all other acids the conductivity increases steadily. It follows from the theory of hydrogen ion catalysis that the ratio of the catalytic accelerations produced by two acids must be independent of the nature of the acid undergoing esterification. The ratio of the rates of esterification of acetic acid in presence of hydrochloric and picric acids is 13.5; for propionic acid it is 13.1; for *n*-butyric acid, 13.1; for phenylacetic acid, 13.8; and for phenylpropionic acid, 13.0. The ratio of the accelerations of hydrochloric and sulphosalicylic acids is also found to be the same with five acids.

The formation of isobutyl and methyl esters in presence of hydrochloric acid is studied. The equation obtained by the author and Udby (Abstr., 1907, ii, 852) applies in these cases as well as in that of the ethyl esters. The rates of esterification of acetic and phenylacetic acids are determined at different temperatures, and the temperature-coefficients found to be the same. All these results are in good agreement with the theory of hydrogen ion catalysis developed by the author (Abstr., 1907, ii, 852). The self-esterification of an acid, however, appears to be mainly due to some other reaction. T. E.

History of the Discovery of the Rules of the so-called "Steric Hindrance." FRIEDRICH KEHRMANN (*Ber.*, 1908, 41, 4357—4358).—A claim for priority in the statement of the phenomenon of steric hindrance. The author foreshadowed this in 1888 (Abstr., 1889, 243), and called attention (*inter alia*) to the difficulty of esterifying *o*-substituted carboxylic acids in 1890 (Abstr., 1890, 484), whilst V. Meyer's first paper on this subject was published in 1894 (Abstr., 1894, i, 243). J. C. C.

Physico-chemical Investigation of the Reactions between Egg-albumin and Acetic Acid. LUDWIK ZOJA (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 249—269).—On the addition of acetic acid to dialysed egg-albumin, the viscosity of the resulting solution increases with time, and under certain circumstances the end result is a solid jelly. The process of gelatinisation has been studied by measurements of viscosity, electrical conductivity, and density. The variation of the viscosity with time depends very much on the concentration of the acetic acid. Below 3.22 mols. per litre, the viscosity remains constant; with increasing acetic acid concentration the rate of alteration of the viscosity with time increases, attains a maximum at 7.01 mols. per litre, and then decreases as the acid concentration is further increased. On the other hand, the electrical conductivity does not change with time, and the curves which represent the dependence of the conductivity on the acetic acid concentration are closely similar to the corresponding curves for acetic acid-water mixtures. Both curves exhibit a maximum at about 3.2 mols. acid per litre.

The change of viscosity with time is supposed to be due to an action of hydrogen ions on the particles of the colloid. In agreement with this, it is found that the rate of gelatinisation is greater when the acetic acid is replaced by formic acid, and less when replaced by propionic acid.

Observations relating to the influence of calcium acetate indicate that the reaction is catalytically accelerated by calcium ions. The increase in viscosity takes place more rapidly at 25° than at higher or lower temperatures when the other conditions are maintained constant.

H. M. D.

Hydration in Solution as the cause of certain Solubility Influences. C. S. HUDSON (*Zeitsch. Elektrochem.*, 1908, 14, 821—823; *J. Amer. Chem. Soc.*, 1909, 31, 63—66).—The solubility of anhydrous sodium sulphate in water is diminished by the addition of carbamide, whilst that of Glauber's salt is increased. The author supposes that the solution contains molecules of the anhydrous salt and molecules of the hydrate; in presence of the solid anhydride, the concentration of the former is a , that of the latter is h . The total solubility of the anhydrous salt is therefore $s = a + h$. If p is the vapour pressure of the solution, $h/a = \text{const. } p^n$. The addition of a foreign substance to the solution diminishes p , and therefore diminishes h also, since a (in presence of the solid anhydrous salt) is constant. The solubility of the anhydrous salt is therefore diminished by the addition of a foreign substance to the solution. Precisely the same argument applied to the hydrated salt shows that its solubility must be increased.

T. E.

Theory of Colloidal Solutions. LUIGI ROLLA (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 650—654).—The author has carried out a series of experiments on metallic colloids with the object of determining the charge of the granules and the relation between charge and mass, making use of Stokes's formula. The colloids examined were Bredig's platinum and various preparations made by Zsigmondy's method.

Using a *P.D.* of 13 volts between electrodes 1 cm. apart, the time required to traverse uniformly a path of 0.125 mm. was found to be four seconds for the gold granules, and 4.3 seconds for those of platinum. The mobility or velocity for a field of 1 volt per cm. is hence 26.0×10^{-5} cms. per sec. for gold, and 24.0×10^{-5} cms. per sec. for platinum. Burton's measurements (*Abstr.*, 1906, ii, 275) gave the values 21.6×10^{-5} and 20.3×10^{-5} cms. per sec. for gold and platinum respectively. Electric transport measurements made on red, violet, and blue colloidal gold solutions, prepared according to Zsigmondy's method (*Abstr.*, 1898, ii, 522), show that the method of preparation does not influence the nature of the colloidal metallic solution obtained, the charge of the granules remaining practically constant.

The radii of the gold granules, measured by means of a hæmatometer, were found to be: red gold, 1.2×10^{-5} cms.; violet gold, 1.7×10^{-5} cms.; blue gold, 2.0×10^{-5} cms.

If the granules carrying a charge, e , move in an electric field of intensity, ϕ , they are subjected to an electric force, $e\phi$, and their velocity is given by $k\phi$, where k is their mobility. Owing to the very great dilution (0.00006 gram of gold per c.c.), the internal friction, η , will be sensibly the same as if the granules moved in pure water. According to Stokes's law, the velocity of spheres of radius r in a

medium having the internal friction η , under the influence of a force $f = e\phi$, is given by the expression: $v = e\phi/6\pi\eta r$, and since $v = k\phi$, $e = 6\pi\eta kr$. The experimental determinations give the value $\eta = 0.01782/(1 + at)$. The charge of Bredig's gold granules is hence $e = 12.19 \times 10^{-10}$ electrostatic units, the values for the other colloids being: Zsigmondy's red gold, 9.75×10^{-10} ; violet, 12.19×10^{-10} ; blue, 16.2×10^{-10} ; Bredig's colloidal platinum, 11.32×10^{-10} . The charges on the granules are hence of the same order of magnitude as the charges carried by the ions.

T. H. P.

Behaviour of Colloidal Suspensions with Immiscible Solvents. W. LASH MILLER and R. H. McPHERSON (*J. Physical Chem.*, 1908, 12, 706—716).—The experiments were undertaken to ascertain if colloidal suspensions distribute themselves between two immiscible solvents on shaking. No such distribution was observed in the case of two liquids; the colloid usually coagulated on shaking (compare Winkelblech, *Abstr.*, 1907, ii, 17).

More definite results were obtained with ternary systems which form two layers in the neighbourhood of the "plait point" (the point at which the layers become almost identical in composition). The binodal curve, tie-lines, and plait point have been determined directly at room temperature for a number of ternary systems, such as water-chloroform-alcohol, water-chloroform-acetone, and water-alcohol-ether, by a simple method. No distribution was observed with colloidal arsenious sulphide in the first two systems, but in the latter system and in certain other systems, distribution was observed in the neighbourhood of the plait point. It is, however, only for relatively clear solutions which approach true solutions in character that distribution has so far been obtained.

G. S.

Has the Crystallising Force any Influence on Properties in the Amorphous Condition. Latent Heat of Vaporisation of *p*-Toluidine. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1487—1492).—The latent heat of vaporisation of *o*-toluidine, m. p. -40° , b. p. 198° , is 95.1, and Trouton's constant, 21.6 (compare Luginin, *Abstr.*, 1903, ii, 7). The author's measurements of the latent heat of vaporisation of *p*-toluidine, m. p. 45° , b. p. 199.5° , give the value 91.8, Trouton's constant being consequently 20.6, the normal value. *p*-Toluidine is hence non-associated, and *o*-toluidine, associated. The author regards this difference as due to the difference in the crystallising powers of the two compounds. The crystallising power hence seems to be a molecular force, and to influence the properties of the compound in the amorphous condition.

The values of the Ramsay-Shields constant are different for the two toluidines, being 1.72 for the *p*-compound between 107° and 210.6° , and for the *o*-compound, 2.04 at 8.1 — 108.4° and 2.06 at 108.4 — 208.5° .

T. H. P.

Forms of Matter. II. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 282—304).—An account is given of methods which have been used in the preparation of crystalline substances in so-called

colloidal amorphous forms. According to the author's theory (crystallisation theory of colloids), the amorphous condition has no real existence; "amorphous" substances represent sponge-like formations consisting of extremely minute crystals. In a large number of cases it has been shown that crystalline substances can be obtained in "colloidal" form, and, conversely, "colloidal" substances in crystalline form, by suitable variation of the conditions under which separation from solution takes place.

The character of the precipitate, which separates from a solution as the result of a chemical change (for example, the double decomposition of two salts), depends on the rate of formation and the solubility of the solid phase, the degree of association of the components of the solution which react to form the insoluble substance, and on the viscosity of the liquid medium. The fact that the rate of formation of the solid and the association of the components of the solution both increase when the concentration of the solution increases, enables the process of crystallisation to be regulated by varying the concentration of the solution. Starting out from solutions just saturated with respect to the slightly soluble substance, and progressively increasing the concentration of the reacting solutions, it is possible to distinguish five concentration intervals, according to the crystalline character of the substance which separates out.

The character of the barium sulphate precipitate, which is obtained on mixing differently concentrated solutions of barium thiocyanate and manganous sulphate, is described and illustrated by photographs. The following intervals of concentration are distinguished. Between $N/20,000$ and $N/7000$ no precipitation takes place even when the solution is left for years. Between $N/7000$ and $N/600$ well-developed crystals separate out, whilst between $N/600$ and $0.75N$ the precipitate consists of star-shaped and needle-like aggregates. From $0.75N$ to $3N$, "amorphous" precipitates are obtained, distinguishable under the microscope as spherical granules, whilst between $3N$ and $7N$ "amorphous" precipitate, separate which cannot be differentiated either by the aid of the microscope or the ultra-microscope.

It is shown that the "amorphous" forms obtained in the fourth and fifth concentration intervals are actually crystalline. The minuteness of the crystals which result from these concentrated solutions is probably due for the most part to the very high velocity of formation.

The conditions for the preparation of a stable suspension of barium sulphate are considered, and it is shown that such a stable suspension can be obtained by mixing alcoholic solutions ($N/500$ — $N/10$) of barium thiocyanate and cobalt sulphate. This is due to the increase in the number of centres of crystallisation consequent upon the diminished solubility of the barium sulphate.

H. M. D.

[Forms of Matter.] MAX MÜNDE (Zeitsch. Chem. Ind. Kolloide, 1908, 3, 304—305).—A claim of priority in respect of P. P. von Weimarn's paper (preceding abstract). The author points out that he has previously demonstrated by microscopic observations that all forms of matter, organic and inorganic, are fundamentally identical.

H. M. D.

[Forms of Matter.] P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 305).—In reply to Münden (preceding abstract) the author states that the question of the identity of living and dead matter has not been considered by him. H. M. D.

Conservation of Weight. CONSTANTIN ZENGELIS (*Zeitsch. physikal. Chem.*, 1909, 65, 341—358. Compare Abstr., 1906, ii, 831).—It is shown by a number of different methods that many gases and vapours of solids can pass through glass even at the ordinary temperature.

In one set of experiments, substances such as stannic sulphide and iodic acid, were supported inside a glass beaker inverted on a glass plate, the junction between plate and beaker being closed by paraffin. On the outside of the beaker, at the same height as the material inside, a piece of silver foil was fixed, and the whole arrangement was surrounded by a large inverted beaker, also closed air-tight with paraffin. After some days, the silver foil showed evidence of the action of the solid, which must therefore have passed in the form of vapour through the glass. In another set of experiments, chlorine, bromine, and iodine were sealed up in separate flasks on the outside of which were fixed strips of silver foil, and the flasks were then enclosed in separate air-tight vessels. The silver outside the chlorine vessel showed signs of attack after fifty days, that of the bromine vessel in about the same time, but in the case of iodine there was distinct action in three days. The effect was much more rapid when the outer vessel was exhausted.

The rate of action is not proportional to the volatility of the substance, and, in some cases at least, is not markedly accelerated by a moderate rise of temperature. The effect is the more rapid the thinner the glass walls.

The author considers that Landolt's experiments, contrary to the latest views of Landolt himself (Abstr., 1908, ii, 366), afford evidence of a real loss of weight in certain chemical reactions, and that the loss of weight is due to the passage of vapours through the glass walls. The fact that there is no loss of weight when the inner surface of the vessel is coated with paraffin (Landolt) is in favour of this view.

G. S.

Are the Stoichiometric Laws Intelligible without the Atomic Hypothesis? FRANZ WALD (*Chem. Zeit.*, 1908, 32, 1249—1250, 1276—1279. Compare Abstr., 1908, ii, 367).—Polemical. A further reply to Kuhn (Abstr., 1908, ii, 826). W. H. G.

Combining Power of Metallic Atoms with Atoms of the Same Kind. LEOPOLD RÜGHEIMER (*Annalen*, 1908, 364, 51—63).—In a previous paper (compare Abstr., 1905, ii, 576), the author has pointed out that the tendency of atoms of metals to link together is very small even in non-ionised compounds; the only definite exception is tin triethyl, which, according to Ladenburg, has the formula Sn_2Et_6 (from vapour density determinations). The author has re-determined the molecular weight of this compound by the boiling-point method, ethyl ether being used as solvent. In the most dilute solution

the value found is not much greater than that corresponding with the formula SnEt_3 , but it increases rapidly with the concentration, so that the substance shows a considerable tendency to associate.

The remainder of the paper is occupied with a discussion on the nature of valency. G. S.

Physical and Chemical Properties as Functions of the Magnitude of the Granules (Number of Molecules in the Granule) of the Solid and Liquid Phases. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1434—1447).—The author gives a résumé of the literature on this subject, and shows that some of Pawloff's conclusions (*Abstr.*, 1908, ii, 927) are in entire disagreement with the results of previous investigators (compare also *Abstr.*, 1908, ii, 90, 263, 1023). T. H. P.

Method to Avoid Cracking Vacuum Vessels whilst Manipulating Liquid Air. ENRIQUE HAUSER (*Anal. Fis. Quim.*, 1908, 6, 428—429).—A tube of paper rolled several times on itself is introduced into the mouth of the vacuum vessel so as to fit it closely and to pass halfway to the bottom of the vessel and project an equal distance outside. The liquid air can then be poured out through this tube without undergoing violent ebullition in the neck and without risk of cracking the vacuum vessel. W. A. D.

Inorganic Chemistry.

Direct Determination of the Atomic Weight of Chlorine with reference to Oxygen. PHILIPPE A. GUYE and G. FLUSS (*J. Chim. Phys.*, 1908, 6, 732—768).—The atomic weight of chlorine with reference to oxygen has been determined by the complete analysis of nitrosyl chloride, NOCl.

Nitrosyl chloride was prepared according to Tilden's method (*Trans.*, 1874, 27, 634) by distilling a mixture of perfectly dry nitrosulphonic acid and sodium chloride, and purified by crystallisation and, finally, by fractional distillation. It has m. p. 61° and b. p. -5.6° . Contrary to the statement of Sudborough (*Trans.*, 1891, 59, 655), aluminium is not attacked by gaseous nitrosyl chloride in the cold; above 500° , however, interaction takes place, with formation of a white and a yellow substance, the former being aluminium chloride. Selenium and sulphur are changed to the lower chlorides, S_2Cl_2 and Se_2Cl_2 , by the action of gaseous nitrosyl chloride. Silver foil does not completely decompose the gas, but the latter is decomposed quantitatively by heating with finely-divided silver at $400-500^{\circ}$, the chlorine being completely retained by the silver, and nitric oxide liberated.

The fact last mentioned has been taken advantage of for the quantitative analysis of the gas; the nitric oxide is split up and the oxygen retained by heated copper, and finally the nitrogen is retained by heated calcium. The precautions taken to obtain accurate results are fully described.

As a mean of five experiments, the value $Cl = 35.468$ is obtained

from the ratio Cl : O, and $\text{Cl} = 35.471$ from the ratio Cl : NO ($\text{N} = 14.01$). The most probable value is $\text{Cl} = 35.466$, obtained from the first ratio, which compares with the value $\text{Cl} = 35.462$ obtained by Edgar ($\text{H} = 1.0076$). From the experiments, the value $\text{N} = 14.006$ is obtained for the atomic weight of nitrogen, in good agreement with the international value.

The investigation is being continued.

G. S.

The Deacon Process. KURT VOGEL VON FALCKENSTEIN (*Zeitsch. physikal. Chem.*, 1909, 65, 371—379. Compare Abstr., 1907, ii, 19, 538).—In the practical working of the Deacon process, 40% of hydrogen chloride and 60% of air are led through the apparatus heated at 430° . Under these conditions, 70—71% of the hydrogen chloride introduced is converted into chlorine, and it is shown theoretically that this mode of working is the most economical under ordinary conditions. Much better yields are obtained, however, as may be anticipated from theoretical considerations, when the issuing gas is freed from water by passing through sulphuric acid and then passed through a second Deacon tube, also at 430° ; in this way the yield is raised from 71% to 83—85%, and by repeating the process a third time, to 87—89%, only slightly less than the theoretical value. This method ought to prove economical on the technical scale; as a matter of fact, a British patent embodying the suggested improvement has been in existence since 1895.

G. S.

The Active Substance of Chlorates. H. KLOPSTOCK (*Chem. Zeit.*, 1908, 33, 21).—A sample of potassium chlorate, which according to the usual tests contained either active chlorine, potassium chlorite, or an obscure oxychlorine compound, was found to be contaminated with potassium bromate.

L. DE K.

Action of Heat on Iodic Anhydride. MARCEL GUICHARD (*Compt. rend.*, 1908, 147, 1306—1309 *).—As a preliminary to the determination of the atomic weight of iodine with direct reference to oxygen by analysis of iodic anhydride, the effect of heat on the latter has been investigated. When heated above 300° , iodine and oxygen are given off, and the undecomposed solid becomes brown. It is now shown that the brown colour is due to traces of iodine, which, along with oxygen, is retained very energetically by the solid; the brown colour is not modified by heating for some hours at 270° , nor by treating the solid with carbon disulphide, benzene, ether, or fuming nitric acid. The only substances capable of removing the colour are those which are capable of dissolving the anhydride and combining with the iodine, for example, an aqueous solution of potassium hydroxide.

G. S.

Production of Ozone with Rotating Anodes. FRANZ FISCHER and KURD BENDIXSOHN (*Zeitsch. anorg. Chem.*, 1909, 61, 13—39).—It has been shown previously (Fischer and Massenez, Abstr., 1907, ii, 162) that the best yields of ozone in the electrolysis of dilute sulphuric acid are obtained by the use of cooled platinum electrodes, the surface of which is divided into narrow strips by non-conducting material.

* and *Dull. Soc. chim.*, 1909, [iv], 5. 86—89.

Rotation may be employed instead of internal cooling, and several forms of apparatus are described, having an anode rotating about a horizontal axis. The anode may consist of thin platinum wires, or of platinum foil embedded in glass, the edge being exposed by grinding, so that the anode surface is a line only 0.1 mm. in breadth. The best form is a thin disk of foil, the edge only of which is exposed. Such an anode yields oxygen containing 23.4% by weight of ozone. Unlike the wire electrodes, the yield of such a disk is not improved by rotation, although rotation increases the life of the platinum by removing the warm acid from its surface. The greater efficiency is due only to the narrowness of the anode surface.

C. H. D.

Ozone Apparatus. GUSTAV MÜLLER (*Chem. Zeit.*, 1908, 32, 1228).—A modification of Berthelot's apparatus for submitting a slow current of oxygen to the silent electric discharge in the annular space between two surfaces of an electrolyte.

J. V. E.

Hydrogen Sulphide Generator. W. TH. CLOUS (*Chem. Weekblad*, 1908, 5, 889).—The generator consists of two tubulated aspirators, connected at the bottom by a stopcock and at the top by a tube bent twice at right angles. In the acid container, this tube ends just below the cork; in the sulphide container, it extends to the bottom. The acid container is fitted with a safety tube for introducing the acid, and the sulphide container with a glass stopcock for drawing off the gas.

A. J. W.

Compounds of Sulphur and Chlorine. ERNST BECKMANN [with F. JUNKER and THEODOR KLOPFER] (*Zeitsch. physikal. Chem.*, 1909, 65, 289—337).—There are three well-defined chlorides of sulphur. Sulphur monochloride, S_2Cl_2 , is a yellow liquid, b. p. 137—138°, m. p. -75° to -76°. It has very little tendency to give off chlorine, nor has it much tendency to unite with chlorine at the boiling point of the latter even in the presence of the dichloride, but combination takes place at higher temperatures.

Sulphur dichloride, SCl_2 , is a dark reddish brown liquid, b. p. 59°/760 mm., 22°/110 mm., and -24°/4 mm. It undergoes considerable decomposition when distilled at atmospheric pressure, but very little at lower pressures. It begins to solidify at -80°, and at -88° forms a tallow-like solid, orange-yellow in colour. It begins to fuse when the temperature reaches -78°; $D^{15} = 1.622$.

Sulphur tetrachloride, SCl_4 , is formed immediately when chlorine and sulphur dichloride are brought together at low temperatures. It is separated from mixtures of the composition S:4Cl to S:6Cl by freezing out, the excess of chlorine being removed by centrifugal action. It solidifies completely at -70°, but only fuses completely between -30° and -20°. It has considerable tendency to lose chlorine, and at room temperature is probably to a great extent split up into sulphur dichloride and chlorine. The fact that the dichloride and tetrachloride do not fuse at the temperature of solidification is ascribed to the formation of isomeric or polymerised compounds.

In liquid chlorine at its boiling-point, both S_2Cl_2 and SCl_2 have the

molecular weights corresponding with their formulæ, and the formula SCl_2 has also been confirmed by cryoscopic determinations in xylene, *p*-xylene, ethylene dibromide, acetic acid, and bromine.

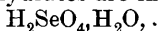
The freezing-point constant for S_2Cl_2 is 53·6. In this solvent sulphur dichloride dissolves as SCl_2 , sulphur as S_8 , but the tetrachloride is insoluble. The freezing-point constant for sulphur dioxide is 30·1. G. S.

Action of Sulphur Chloride (S_2Cl_2) on Metalloids and Metals. PAUL NICOLARDOT (*Compt. rend.*, 1908, 147, 1304—1306. Compare Abstr., 1908, ii, 1074).—Sulphur, selenium, white and even red phosphorus dissolve in sulphur chloride in the cold; in the latter case rapid effervescence occurs. Antimony is attacked in the cold, arsenic only on warming to 50°, and then only slightly, whilst carbon, silicon, and boron are not affected.

The majority of the metals, including the alkali and alkaline-earth metals, are not affected by sulphur chloride even at 136°. Silver, copper, and zinc are only slightly affected, but tin, aluminium mercury, and iron are attacked.

The action of sulphur chloride on iron has been studied in detail, the proportion of the products being determined by a special method of analysis. The main products are ferrous chloride and sulphide, in proportions depending on the conditions; practically no ferric chloride is formed. G. S.

Hydrates of Selenic Acid. ROBERT KREMAN and F. HOFMEIER (*Monatsh.*, 1908, 29, 1111—1118).—With the object of ascertaining the composition of the hydrates formed by selenic acid, the authors have determined the freezing points of various mixtures of selenic acid and water. Only two hydrates are indicated by the data:



melting at 26°, and $\text{H}_2\text{SeO}_4 \cdot 4\text{H}_2\text{O}$, melting at -51·7°. The eutectic data are recorded: H_2SeO_4 and $\text{H}_2\text{SeO}_4 \cdot \text{H}_2\text{O}$, +19° and 91·5% selenic acid; $\text{H}_2\text{SeO}_4 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{SeO}_4 \cdot 4\text{H}_2\text{O}$, -56° and 74·0% selenic acid; $\text{H}_2\text{SeO}_4 \cdot 4\text{H}_2\text{O}$ and H_2O , -83° and 43·0% selenic acid. Crystallisation of the tetra-hydrate is induced by the addition of the corresponding sulphuric acid hydrate, indicating that these are isomorphous.

H. M. D.

Synthesis of Ammonia by means of Peat. HERMANN WOLTERECK (*Compt. rend.*, 1908, 147, 1402—1403).—The results of further experiments on the synthesis of ammonia under the catalytic influence of peat are described (compare Abstr., 1908, ii, 174). After passing the gases over 50 grams of peat at 450° for four hours, the ammonia produced amounts to 2·6—3·1 per 100 of the material burned. After four hours the percentage of nitrogen in the residue is greater than that in the peat, but after six hours there is a diminution in the percentage of nitrogen present. G. S.

Silicon Hydrides. PAUL LEBEAU (*Compt. rend.*, 1909, 148, 13—45.* Compare Moissan and Smiles, Abstr., 1902, ii, 318, 560).—A large volume of mixed gases has been obtained by the action of

* and *Bull. Soc. chim.*, 1909, [iv], 5, 89—91.

hydrochloric acid on magnesium silicide. The first fraction yielded a gaseous product and a colourless liquid. The gas was again condensed, and, after repeated fractionation, the hydrides, SiH_4 and Si_2H_6 , were obtained pure. The latter hydride had the calculated density, less than that found by Moissan and Smiles, whose preparation was probably contaminated with a higher hydride; practically pure Si_2H_6 boils about -7° . The colourless liquid above-mentioned explodes violently in contact with oxygen, and burns with a bright flame; it is unsaturated, and the probable formula is Si_2H_4 . The spontaneous inflammability of the hydrides, SiH_4 and Si_2H_6 , is probably due to the one last mentioned. Finally, a small amount of solid which turned brown in air was observed in the apparatus; this may be a solid silicon hydride.

G. S.

Products of the Arc and Spark Electric Discharge in Liquid Argon. II. Experiments with Hydrogen, Titanium, Tin, Lead, Antimony, and Bismuth. FRANZ FISCHER and GEORG ILIOVICI (*Ber.*, 1908, 41, 4449—4457. Compare Abstr., 1908, ii, 1034).—Experiments are described with tubes fitted with "outside" electrodes, which show that argon must contain at least 4% of air before the spectrum lines due to admixed air appear. Further comparative experiments with argon (D 19.94) under 3.0, 0.3, and 0.03 mm. pressure in these tubes show that under the higher pressures the "red" argon spectrum appears, and the following lines, not observed by Travers, have been measured: λ 7600, 7465, 7380, 7235, 7130. At 0.03 mm. the red spectrum is no longer visible, the blue appearing.

Hydrogen, argon, and mixtures of these gases, when subjected to the silent electric discharge at the temperature of liquid air, undergo no change in volume, and therefore no alteration in molecular condition.

When titanium, tin, lead, antimony, and bismuth, elements from the fourth vertical column of the periodic system, are used as electrodes in the arc or spark discharge, nitrides in small quantities are obtained, which liberate nitrogen when heated in a vacuum, and give ammonium salts when treated with acids. This result is due to air introduced into the apparatus; the nitrogen, when removed by sparking with oxygen, left not a trace of argon behind.

W. R.

Acid Sulphates. III. JOH. D'ANS (*Zeitsch. anorg. Chem.*, 1909, 61, 91—95. Compare Abstr., 1906, ii, 351; 1907, ii, 459).—The solubility of sodium sulphate in water in presence of varying quantities of sulphuric acid has been further examined. The transformation temperature of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ into Na_2SO_4 is lowered by the addition of sulphuric acid, the lowest point reached being $16.67^\circ \pm 0.07^\circ$. At this temperature the three solid phases, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ — Na_2SO_4 — $\text{Na}_3\text{H}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, are in equilibrium with the solution. The transition point of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ is found to be $58.54^\circ \pm 0.05^\circ$, a temperature which is recommended as a thermometric fixed point. The isothermal at 25° was also determined.

C. H. D.

Dissociation of Sodium Hydrogen Carbonate. SOURY (*Compt. rend.*, 1908, 147, 1296—1299).—The phase rule indicates that, in order that there may be a definite gas pressure over sodium hydrogen carbonate at a definite temperature, four phases must be present, for example, vapour, saturated solution, and two solid carbonates in contact with the latter.

Experiments were made in which a mixture of 27.54 grams of sodium hydrogen carbonate and 5.4 grams of water were heated at 100°, and the pressure measured after removal of the carbon dioxide in successive portions. The total volume of carbon dioxide obtainable from the above mixture is 3660 c.c. The tension of the carbonic acid decreases at first as the carbon dioxide is progressively removed, but there are two periods of constant pressure: (1) from the removal of 260 to 1760 c.c. of the dioxide; (2) from 2560 to 3210 c.c. In the first case, the two solid phases are the hydrogen carbonate and a lower carbonate of the composition $3\text{Na}_2\text{O}, 4\text{CO}_2, 5\text{H}_2\text{O}$; at the second period of constant pressure the solid phases are in all probability the salt last mentioned and the normal carbonate, $\text{Na}_2\text{O}, \text{CO}_2, \text{H}_2\text{O}$.

The dissociation pressure has also been determined at different temperatures, and the results are represented graphically. G. S.

Synthesis of Silver Nitrate and Determination of the Atomic Weight of Sulphur. GUSTAVE D. HINRICHS (*Chem. Zentr.*, 1908, ii, 1410; from *Mon. Sci.*, 1908, [iv], 22, ii, 454—460).—Stas' synthesis of silver nitrate and Richard's determination of the atomic weight of sulphur are criticised and studied in the light of the author's method (*Abstr.*, 1907, ii, 945). From the investigation of Stas and Marignac and the correct placement of the errors, absolute atomic weights have been arrived at for silver at 108, nitrogen 14, and for oxygen 16. The opinion is held that matter is simple, and chemical elements are combinations of simple matter having commensurable atomic weights. J. V. E.

Atomic Weight of Silver. ANATOLE LEDUC (*Compt. rend.*, 1908, 147, 972—973).—An adverse criticism of a recent paper by Dubreuil (*Abstr.*, 1908, ii, 1035). G. S.

Atomic Weight of Silver. LOUIS DUBREUIL (*Compt. rend.*, 1908, 147, 1300—1302. Compare *Abstr.*, 1908, ii, 1035).—Polemical against Leduc (previous abstract). G. S.

True Atomic Weight of Silver. GUSTAVE D. HINRICHS (*Compt. rend.*, 1908, 147, 1302—1303. Compare previous abstracts).—In connexion with a recent paper by Dubreuil (*Abstr.*, 1908, ii, 1035), the author has given up his recently expressed view (*Abstr.*, 1908, ii, 573) that the atomic weight of silver is 107.875, and returns to his earlier opinion that it is exactly 108. G. S.

Atomic Weight of Silver. ANATOLE LEDUC (*Compt. rend.*, 1909, 148, 42—43).—Polemical against Dubreuil and Hinrichs (compare previous abstracts). G. S.

Warnerke's Modification of the Herschel Effect and the Preparation of the Substance of the Latent Image. A. P. H. TRIVELLI (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1908, 6, 438—442).—The film of an Agfa diapositive plate was removed, placed between two sheets of parchment paper, and subjected to high pressure by beating it with a hammer in a dark room. After this treatment, the film was found to be more easily developed than before, indicating that the α -silver subhaloid is insensitive to pressure.

On the basis of this observation, a method for the preparation of the α -subhaloid has been devised. Silver iodide, precipitated by an excess of potassium iodide and heated for a long time with ammonia, is mixed with a saturated solution of silver nitrate to absorb the free halogen and pounded in a mortar. The formation of the subhaloid is facilitated by heating at about 80° . The subhaloid so obtained is leaf-green in colour; the corresponding subbromide is a little lighter.

H. M. D.

Old and New Subhalides. LOTHAR WÖHLER and G. RODEWALD (*Zeitsch. anorg. Chem.*, 1909, 61, 54—90. Compare Wöhler and Kasarnowski, *Abstr.*, 1906, ii, 22).—The evidence for and against the existence of subhalides in coloured solid halides is discussed, and it is shown that this explanation of the colour is at least as probable as that of ultra-microscopic particles of metal. The present research is directed to the isolation and recognition of certain subhalides as chemical individuals.

Silver subfluoride, Ag_2F , is prepared in a pure state by the action of silver on a warm solution of silver fluoride, forms golden crystals, and is quite stable in dry air. It is insensitive towards even direct light, and thus differs markedly from other silver halides. A pressure of 20,000 atmospheres is also without influence. At 90° the solid in a dry state, or in contact with a saturated silver fluoride solution, decomposes into silver fluoride and silver. The heat of formation of Ag_2F is 26.3 Cal. Its formation from the fluoride is not, as Guntz supposed (*Abstr.*, 1890, 1055), endothermic, but exothermic (0.7 Cal.). Silver fluoride shows a great increase of solubility at 50° , due probably to a transition from the hydrate, $\text{AgF}\cdot 2\text{H}_2\text{O}$, to the anhydrous salt.

Calcium subchloride, observed incidentally by Borchers and Stockem (*Abstr.*, 1903, ii, 19), can only be prepared by heating calcium with dry calcium chloride in equivalent proportions in steel cylinders at 900 — 1000° for twenty-four hours, followed by rapid quenching in solid carbon dioxide and treatment with ethyl iodide, which allows of the separation of the subchloride and calcium by their density. The red crystals of CaCl , heated to 810° and allowed to cool slowly, show decomposition into chloride and metal. A small proportion of subchloride is sufficient to give a red colour to the chloride. The pure crystals have D_{20}^{20} 2.08.

Calcium subiodide, CaI , prepared by heating atomic proportions of calcium and iodine in a steel tube at 800° , quenching rapidly, and washing the mass with carbon disulphide, forms brown crystals, and,

like the subchloride, decomposes if cooled slowly from 800° , yielding calcium iodide and calcium.

Calcium subfluoride, CaF , is prepared by heating calcium with calcium fluoride above 1400° , the steel tube being protected by wrapping in platinum foil and coating with basic fire-clay. The product forms orange crystals, $D_{20}^{20} 2.305$, and is much less readily attacked by moisture than the subchloride or subiodide. All these compounds are stable only at high temperatures, decomposing into metallic calcium and the normal halide when cooled slowly. C. H. D.

Formation of Fulminating Silver. A. SIEVERTS (*Zeitsch. angew. Chem.*, 1909, 22, 6—7).—A warning as to the danger incurred in working with ammoniacal silver solutions. Ten grams of silver nitrate were converted into oxide by potassium hydroxide, and the precipitate was digested at 40° with 45 c.c. of 6.7% ammonia for ten minutes. On the surface of the liquid a white crust had formed, and a heavy, black powder was noticed at the bottom of the utensil. In order to facilitate solution, this was stirred with a glass rod, when a violent explosion took place, doing much damage, and seriously wounding the operator. Even clear solutions may give rise to explosions.

L. DE K.

Crystalline Form of Calcium Carbonate Precipitated from Concentrated Solutions. EMIL HATSCHKE (*Chem. Zeit.*, 1909, 33, 49).—From concentrated solutions of calcium chloride and with various reagents, it is found that at all temperatures from 15° to the boiling point the precipitate consists almost exclusively of calcite. At temperatures below 15° , the carbonate is precipitated in granules, which, even when kept for some time under the mother liquor, do not become crystalline.

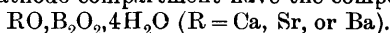
L. DE K.

Experiments Showing the Formation of Nitrides of Barium, Strontium, Calcium, and Aluminium. H. RUSSELL ELLIS (*Chem. News*, 1909, 99, 4).—When the oxides of these metals are mixed with magnesium powder and ignited on an iron tray, the magnesium replaces the other metal, which, as soon as it is set free, combines with the oxygen and nitrogen of the air. With barium oxide, calcium oxide, and strontium oxide, the product obtained was quite yellow, and, when moistened with water, smelt very strongly of ammonia; with aluminium oxide, the product was black, but also smelt strongly of ammonia when water was added. The presence of carbonate, hydroxide, and peroxide with the oxides of the alkaline-earth metals increases the violence of the reaction and hinders nitride formation. Calcium oxide, if carbonate is present, gives neither nitride, carbide, nor cyanide; barium and strontium oxides containing appreciable quantities of carbonates yield nitride, cyanide, carbide, and possibly cyanamide. Excess of magnesium powder, as a rule, produces a larger yield of nitride, but never more than that which could be produced from the metal obtained from the oxide. The conclusion is drawn that the nitride produced is not that of magnesium, because when magnesium burns in air, either alone or admixed with the oxide of a metal not

forming a nitride, less than 1% of nitride is obtained. Moreover, magnesium nitride readily burns, so that if great development of heat takes place, it could not exist. Estimations of nitrogen contained in the product from igniting the following mixtures gave: ($\text{BaO} + \text{Mg}$), 24.4% Ba_3N_2 ; ($\text{BaO} + 2\text{Mg}$), 43.3% Ba_3N_2 ; ($\text{SrO} + \text{Mg}$), 33.7% Sr_3N_2 ; ($\text{SrO} + 2\text{Mg}$), 53.8% Sr_3N_2 ; ($\text{CaO} + \text{Mg}$), 33.6% Ca_3N_2 ; ($\text{CaO} + 2\text{Mg}$), 31.5% Ca_3N_2 ; ($\text{Al}_2\text{O}_3 + 3\text{Mg}$), 11.1% AlN . J. V. E.

Certain Electrolytic Borates. MARIO G. LEVI and S. CASTELLANI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 613—617).—The authors have applied the electrolytic method formerly employed (*Gazzetta*, 1907, 37, ii, 562) for the preparation of borates of sodium to those of other metals. In the electrolytic cell employed, the metallic salt solution containing the platinum anode was separated by a diaphragm from the boric acid solution, in which the platinum cathode was placed.

With calcium, strontium, and barium salts, the crystalline cathode deposit and the first portions of the white, flocculent material precipitated in the cathode compartment have the composition



In the case of calcium salts, the later deposits in the cathode chamber consist of the pyroborate, CaB_4O_7 , but with strontium and barium salts these deposits have indefinite compositions, as also do the precipitates obtained by the addition of alcohol to the cathode liquid. With magnesium salts, the cathode deposit seems to consist of the borate, MgB_2O_4 , mixed with a large proportion of magnesium oxide; precipitation of the cathode solution by means of alcohol yields the borate, $3\text{MgO}, 4\text{B}_2\text{O}_3$.

With salts of copper, cadmium, mercury, lead, iron, and nickel, no definite borates were formed. T. H. P.

Magnesium-Silicon Alloys. RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1909, 61, 46—53).—Molten alloys of magnesium and silicon readily pass through magnesia vessels, and strongly attack porcelain; it is therefore necessary to melt them in carbon tubes in an atmosphere of hydrogen, the porcelain tube enclosing the thermocouple being protected with a layer of carbon.

The freezing-point curve falls from the freezing point of silicon to a eutectic point at 950° and 42% of magnesium, rises to a maximum at 1102° and 63.2% Mg, corresponding with the compound Mg_2Si , falls to a second eutectic point at 645° and 96% Mg, and again rises to the freezing point of magnesium. Solid solutions are not formed.

The compound Mg_2Si forms glistening, hard, light blue crystals, slowly attacked by concentrated sulphuric and nitric acids, rapidly by dilute acids, with evolution of hydrogen. Hydrochloric acid attacks it violently, with evolution of silicon hydride.

The microscopic examination of the alloys confirms the above conclusions. C. H. D.

Compounds of Magnesium and Sodium Sulphates. A. S. GINSBERG (*Zeitsch. anorg. Chem.*, 1909, 61, 122—136).—The

determinations of the freezing-point diagrams of the systems K_2SO_4 - $MgSO_4$ and Na_2SO_4 - $MgSO_4$ by the author (*Ber. St. Petersburg Polytech. Inst.*, 1906, 6) have been confirmed as regards the first system by Nacken (*Abstr.*, 1908, ii, 692), but the second system gave somewhat different results. A re-examination of mixtures of sodium and magnesium sulphates has shown that the equilibrium is very complicated. The freezing-point curve has a eutectic point at 44.2 mol. % $MgSO_4$ and 670° , and a break at 71.3 mol. % and 814° . α -Sodium sulphate forms solid solutions containing up to 35.8 mol. % $MgSO_4$. The compound $Na_2SO_4 \cdot 3MgSO_4$ melts with decomposition at 814° . Magnesium sulphate does not form solid solutions. The existence of two other compounds, $Na_2SO_4 \cdot MgSO_4$ and $3Na_2SO_4 \cdot MgSO_4$,

formed only in the solid state, is also indicated. These compounds are identical with anhydrous blödite and vanthoffite respectively, the former existing in α -, β -, and γ -modifications. Sodium sulphate only forms two modifications, the transition point being at 232° .

C. H. D.

Gases Occluded in a Complex Brass, containing Manganese, which showed Numerous Flaws. G. GUILLEMIN and B. DELACHANAL (*Compt. rend.*, 1908, 147, 1309—1311).—The specimen of brass in question contained 60.15% of copper, 34.76% of zinc, 2.34% of manganese, and small amounts of tin, lead, iron, and aluminium, and was full of small holes due to escaping gas. Fifty grams of it were heated in a porcelain tube up to 1000° , and the gas given off, which amounted to 3.5 times the volume of the alloy, collected and analysed. It contained 79.1% of hydrogen, 3.9% of methane, 8.9% of carbon monoxide, and 8.1% of carbon dioxide.

G. S.

Variations in the Structure of Coinage Bronze during Working. FEDERICO GIOLITTI and ERNESTO PANNAIN (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 668—670).—The authors have made a metallographic study of the bronze used for Italian coinage, which contains 3.82% of tin, 95.80% of copper, and 0.38% of impurities (about 0.2% of lead). The polished surfaces of the specimens were treated repeatedly with hot 0.24% nitric acid, each such treatment being followed by gentle polishing with chromic oxide.

The cooled ingots, before treatment, consist of solid solutions, α , of heterogeneous concentration, among which are scattered crystals of the solid solution, β . According to the equilibrium diagrams of alloys of copper and tin (compare Giolitti and Tavanti, *Abstr.*, 1908, ii, 946), bronze containing about 4% of tin should consist entirely of the α -mixed crystals, whilst in reality the above structure is nearer to that given by an alloy containing more than 8% of tin. The presence of the β -crystals is explained by the velocity with which the alloy cools. This velocity is not sufficiently slow to allow the first α -crystals, rich in copper, to react with the liquid, which becomes less and less rich in copper, and is in equilibrium with the crystals separating at continually lowering temperature, so as to give

homogeneous mixed crystals. Nor is the velocity sufficiently rapid to prevent, at 790° , the reaction between the borders of the mixed crystals, rich in tin, and the residual liquid giving rise to the β -mixed crystals. After re-heating for half an-hour at about 800° and tempering in cold water, the heterogeneous masses of α -crystals are transformed into homogeneous crystals with a lamellar structure, among which are still seen the β -crystals. After flattening in the cold, both the α - and β -crystals are elongated in the direction of the flattening. Subsequent re-heating and tempering are accompanied by the appearance of α -crystals having a rectilinear outline, these and also the β -crystals being elongated by further flattening, whilst successive re-heating and tempering bring back the former crystalline structure, which undergoes only slight deformation during the final flattening. It is noteworthy that the β -crystals, formed during the initial cooling of the alloy, are preserved through all the various treatments to which the ingot is subjected.

T. H. P.

New Apparatus for the Distillation of Mercury. JOHANNES WETZEL

(*Chem. Zeit.*, 1908, 32, 1228).—Mercury

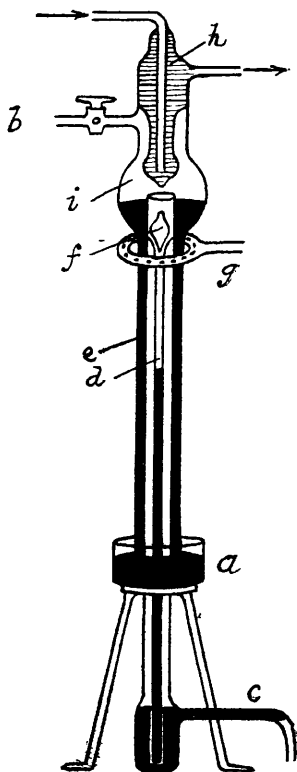
to be purified is placed in *a*, the bent tube *c* is placed in a dish containing pure mercury, and *b* is connected to a water-pump. By this means mercury is

made to rise in both inner tube, *d*, and outer tube, *e*, until the mercury in *e* enters the bulbous enlargement, *i*, and is within about 2 cms. of the mouth of tube *d*. Water is made to circulate through the condensing head, *h*, and the mercury in *i* is heated by means of a gas ring, *g*. After about thirty minutes,

b is closed, and mercury vapour condensing on the cold surface of *h* drops on to a float, *f*. When sufficient mercury has collected to lift the float, it falls down tube *d*, assisting to more completely evacuate the distillation bulb, *i*. By this arrangement, *i* may be almost com-

pletely evacuated, and the purified mercury obtained at *c*. Mercury boils at 155° when in the highest vacuum, so that if the apparatus described is made of Jena glass, there is little risk of it cracking. Indicative of the rapidity of distillation, it is mentioned that in ten hours nearly 23 kilos. of mercury may be obtained, showing a great increase over Kasten's method, generally employed, which gives in the same time only about $2\frac{1}{2}$ kilos. of mercury.

J. V. E.



Use of the Colour Thermoscope. III. [Silver-Mercury Iodide.] H. REBENSTORFF (*Chem. Zentr.*, 1908, ii, 1803; from *Zeitsch. phys.-Chem. Unter.*, 1908, 21, 291—304. Compare Lüttke, *ibid.*, 10).—As a result of many physical and chemical experiments, it has been ascertained that a liberation of heat accompanies the transformation of yellow silver-mercury iodide at 45° into the orange form. Both modifications of this substance are found to exist in contact with one another for quite a considerable time at 33—45°. J. V. E

Distribution of Scandium. WLADIMIR I. VERNADSKY (*Bull. Acad. Sci. St. Petersburg*, [vi], 1908, 1273—1274. Compare Eberhard, *Abstr.*, 1908, ii, 862).—A criticism of Eberhard's conclusions regarding the mineralogical distribution and formation of the scandium compounds found in the crust of the earth. Z. K.

Aluminium. Analysis of Aluminium Powder. ÉMILE KOHN-ABREST (*Compt. rend.*, 1908, 147, 1293—1296).—The proportion of aluminium in commercial aluminium powder has been estimated by its reducing action on ferric sulphate, as previously described (*Abstr.*, 1904, ii, 844), and also by measurement of the hydrogen given off when a known weight of it is treated with excess of hydrochloric acid. From a complete analysis, it is further shown that the specimen contains 95.93% of total aluminium as well as iron, silicon, carbon, nitrogen, and 2.29% of oxygen, the latter being obtained by difference. From the results of the two first methods of estimation, corrected for the action of the impurities on the reagents, it is shown that the specimen contains 92.5% of aluminium as metal. The amount of oxide present, deduced from this observation, is 5.72%, in excellent agreement with the direct determination. It is not certain that the oxide present is Al_2O_3 . G. S.

Alum [Correction]. ROBERT MARC (*Zeitsch. anorg. Chem.*, 1908, 60, 459).—The results described in the previous paper (this vol., ii, 47) are untrustworthy, owing to the fact, which had previously escaped notice, that Merck's alum is contaminated with rubidium and caesium. G. S.

The Decomposition of Felspar by Water. W. FUNK (*Zeitsch. angew. Chem.*, 1909, 22, 145—146).—Finely-powdered felspar forms a colloidal suspension with water, chemical decomposition taking place at the same time, as shown by the alkaline reaction of the water. The attack on coarser particles may be shown by staining with methylene-blue and washing, when only the partly decomposed outer zone of each particle is found to be stained. Carbon dioxide hastens the attack, but lessens the tendency to form colloidal suspensions. Fused felspar is more rapidly attacked than the natural mineral. C. H. D.

Variation of the Composition of Colloids formed in a Solution of Ferric Chloride according to the Conditions of Hydrolysis. LEOPOLD MICHEL (*Compt. rend.*, 1908, 147, 1288—1290. Compare Malfitano and Michel, *Abstr.* 1908, ii, 1042).—Further

experiments on the variation in the composition of the colloidal particles with the conditions of hydrolysis of ferric chloride are described. The proportion of chlorine in the particles is usually greater the more slowly the solutions are warmed; it is the smaller the higher the temperature employed in hydrolysis and the less concentrated the solution. The effect of the addition of hydrochloric acid is to diminish both the quantity of colloid formed and the proportion of chlorine in it. G. S.

Hydrates and Acid Salts of Ferrous Sulphate. FRANK B. KENRICK (*J. Physical Chem.*, 1908, 12, 693—705).—The composition of a number of ferrous sulphates and their range of existence in contact with sulphuric acid solutions at room temperature have been determined by solubility measurements in the usual way, and the results are represented in tables and diagrams. The composition of the solid phases could not be obtained directly, owing to the difficulty of separating them from the liquid phase, but this has been effected by a combination of two methods of indirect analysis, which are fully described.

The more important solid phases are as follows: $\text{FeO} \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$, minute, granular crystals, is stable in contact with solutions from $\text{SO}_3 \cdot 2 \cdot 186 \text{H}_2\text{O}$ to $\text{SO}_3 \cdot 7 \cdot 93 \text{H}_2\text{O}$, above which the heptahydrate is formed. $2\text{FeO} \cdot 3\text{SO}_3 \cdot 2\text{H}_2\text{O}$ (composition somewhat doubtful) forms small, colourless, hexagonal crystals, and is stable between the limits of $\text{SO}_3 \cdot 1 \cdot 637 \text{H}_2\text{O}$ to $\text{SO}_3 \cdot 2 \cdot 186 \text{H}_2\text{O}$. $\text{FeO} \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$ occurs in well-formed crystals, and is stable in contact with solutions from $\text{SO}_3 \cdot 1 \cdot 342 \text{H}_2\text{O}$ to $\text{SO}_3 \cdot 1 \cdot 595 \text{H}_2\text{O}$. $\text{Fe}_2\text{O}_4 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$, slender needles, is stable in contact with solutions from $\text{SO}_3 \cdot 1 \cdot 122 \text{H}_2\text{O}$ to $\text{SO}_3 \cdot 1 \cdot 342 \text{H}_2\text{O}$. The solubility of all the compounds in the liquid phases is very small, the tetra- and hepta-hydrates excepted. G. S.

Action of Hydrogen Peroxide on Metallic Sulphides.

J. FERRER y HERNÁNDEZ (*Anal. Fis. Quim.*, 1908, 6, 476—484).—Precipitated nickel sulphide decomposes hydrogen peroxide solution (3%) containing a trace of acid, nickel sulphate being formed; hydrogen peroxide solution rendered alkaline with sodium or potassium hydroxide does not, however, change nickel sulphide. Ammoniacal hydrogen peroxide rapidly dissolves nickel sulphide, giving a deep blue solution containing a complex ion.

Cobalt sulphide behaves like nickel sulphide with hydrogen peroxide containing a trace of acid; in presence of sodium or potassium hydroxide, however, it is oxidised to cobaltic hydroxide.

Ferrous sulphide is oxidised by hydrogen peroxide (acid), giving ferric sulphate or products formed by the hydrolysis of the latter. Manganese sulphide is, under similar conditions, converted into the sulphate, but, in presence of alkalis, manganese hydroxide and sulphur are formed. Zinc sulphide is oxidised by hydrogen peroxide containing a trace of acid to zinc sulphate; in presence of alkali, soluble zinc oxides are formed. W. A. D.

Borotungstic Acids. HIPPOLYTE COPAUX (*Compt. rend.*, 1908, 147, 973—976. Compare Klein, *Abstr.*, 1883, 23, 786; 1884, 559, 1266).—Two complex borotungstic acids have been prepared as follows. To one part of normal sodium tungstate and 1.5 parts of boric acid sufficient water is added to form a clear solution at the boiling point. After some time a precipitate separates. The mother liquors are concentrated, more boric acid added, a further precipitate is rejected, and to the mother liquors, which now contain complex borotungstic acids, ether and 2 to 3 volumes of sulphuric acid are added and the mixture shaken. The resulting oil is decomposed by cold water, and on evaporation in a vacuum the complex acid, $B_2O_3 \cdot 28WO_3 \cdot 6H_2O + 56H_2O$ separates in hexagonal crystals. From the same solution the other acid is obtained as the insoluble barium salt by adding barium carbonate; the barium salt is decomposed by sulphuric acid, and the acid $B_2O_3 \cdot 24WO_3 \cdot 5H_2O + 61H_2O$ obtained in octahedral crystals by evaporation.

The acid occurring in hexagonal crystals is hexabasic, and not very stable; the other acid is more stable, and is isomeric with silicotungstic acid, $Si_2O_4 \cdot 24WO_3 \cdot 4H_2O + 62H_2O$, although the formulæ do not correspond, and the borotungstic acid, unlike the latter, is pentabasic.
G. S.

Preparation of Urano-uranic Oxide and a Standard of Radioactivity. HERBERT N. MCCOY and GEORGE C. ASHMAN (*Amer. J. Sci.*, 1908, [iv], 26, 521—530).—Pure urano-uranic oxide, U_3O_8 , can readily be prepared by heating any higher or lower oxide of uranium for some time in air at 700°.

Uniform films of the oxide, 7 cms. in diameter and weighing 0.6 to 0.8 gram, have been prepared in flat, circular tin dishes or copper plates as previously described (McCoy and Ross, *Abstr.*, 1908, ii, 80); the thickness of the film is such that the α -ray activity is definite and constant, and the films are therefore suitable standards of radioactivity.

The α -ray saturation current for such a standard film is 5.79×10^{-13} amp. per $cm.^2$; from this result it is calculated that the total α -ray ionisation current of 1 gram of uranium is 4.61×10^{-10} amperes.
G. S.

Molecular Weight of Uranium Tetrachloride in Boiling Bismuth Chloride Solution. LEOPOLD RUGHEIMER and L. GONDER (*Annalen*, 1908, 364, 45—50).—The molecular weight of uranium tetrachloride in boiling bismuth chloride solution, as determined by the special method already described, is 373, as compared with the calculated value, 380.3, for the formula UCl_4 .
G. S.

Reduction of Uranyl Chloride. WILLIAM ECHSNER DE CONINCK (*Compt. rend.*, 1908, 147, 1477—1478).—The author has made experiments to ascertain whether the reduction of uranyl chloride by hydrogen at a red heat can be used as a method for the determination of the atomic weight of chlorine. The results are not sufficiently concordant for the purpose.
H. M. D.

Alloys of Silicon with Tin, Lead, and Thallium. S. TAMARU (*Zeitsch. anorg. Chem.*, 1909, 61, 40—45).—Liquid silicon and tin are miscible in all proportions, and, on cooling, pure silicon separates, the eutectic being practically pure tin. The freezing-point curve falls very slowly until about 80% Sn is reached. and then very rapidly.

Silicon is not miscible to an appreciable extent with either lead or thallium in the liquid state. C. H. D.

Preparation of Chloride of Thorium. CAMILLE MATIGNON (*Compt. rend.*, 1908, 147, 1292—1293 *).—The author considers that the use of a mixture of chlorine and sulphur chloride (S_2Cl_2) as a reagent for the preparation of anhydrous chlorides, such as that of thorium, from the corresponding oxides, already recommended (Abstr., 1904, ii, 340) is preferable to the employment of carbonyl chloride, recently used by Chauvenet (this vol., ii, 53).

The value +53.8 Cal. has been obtained for the heat of solution of thorium chloride (1 mol. in 2700 mols. of water) at 18°, as compared with +56.75 Cal. obtained by Chauvenet (*loc. cit.*). G. S.

Spitting of the Acid Vanadates of Univalent Metals. WILHELM PRANDTL and HANS MURSCHHAUSER (*Zeitsch. anorg. Chem.*, 1908, 60, 441—445).—In a previous paper (Abstr., 1908, ii, 46) the composition of the vanadylvanadates, $xM_2O, (y-z)V_2O_5, zV_2O_4$, present in the solid state after the evolution of oxygen from certain alkali acid vanadates on solidification was determined, and it was shown that the volume of oxygen given off from the potassium and lithium vanadates was less than the calculated amounts, a result ascribed to the incompleteness of the respective reactions. To test this view, the vanadylvanadates in question have been repeatedly fused and allowed to resolidify in an atmosphere free from oxygen. After 50 fusions, the amount of oxygen given off from the potassium compound corresponds with the formula for this compound previously given, but even after 100 fusions the oxygen obtained from the lithium compound is less than that corresponding with the composition previously given, $4Li_2O, V_2O_4, 7V_2O_5$, and it must therefore be assumed that the compound present has the formula $6Li_2O, V_2O_4, 11V_2O_5$. G. S.

Action of Antimony Trichloride on Nickel: Formation of NiSb. ÉMILE VIGOUROUX (*Compt. rend.*, 1908, 147, 976—978. Compare Lossen, Abstr., 1906, ii, 361).—When nickel is heated in a tube at 800° and antimony trichloride passed over it, a vigorous reaction takes place, and nickel chloride and nickel antimonide are formed. The former is removed by treatment with water, and the heating in antimony trichloride repeated, until finally only the antimonide, NiSb, remains as a crystalline powder. When the heating is carried out at higher temperatures, the residues become progressively poorer in antimony.

The compound NiSb has also been prepared by direct combination of the elements.

Nickel antimonide, NiSb, occurs in lustrous, reddish-violet crystals, which are non-magnetic and have $D^{20} = 7.70$. It fuses at 1100° and

* and *Bull. Soc. chim.*, 1909, [iv], 5, 92—93.

decomposes at 1400°. It is vigorously acted on by chlorine and by oxygen when heated to dull redness. It is not affected by concentrated hydrochloric acid, but is decomposed by warm concentrated sulphuric acid and by warm nitric acid. It is scarcely affected even by fused alkalis.

G. S.

Bismuthous Compounds. III. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1909, 61, 119—121).—The freezing-point determinations of Eggink (Abstr., 1908, ii, 1043) indicate the existence of BiCl and BiBr only, and are thus in disagreement with the results of Herz and Guttman (Abstr., 1908, ii, 199), which showed maxima corresponding with the formulæ BiCl₂ and BiBr₃. Both series of experiments gave concordant figures, and the cause of the difference is unexplained.

C. H. D.

Dichloropalladous Acid. ITALO BELLUCCI and PIETRO DE CESARIS (*Gazzetta*, 1908, 38, ii, 602—614).—The addition of a silver salt to an aqueous solution of palladous chloride results in the precipitation, not of silver chloride, but of a compound corresponding with the formula PdCl₂(OH·Ag)₂. The conclusion is hence drawn that the aqueous palladous chloride solution contains an acid, termed

dichloropalladous acid, dissociated thus: $\text{PdCl}_2 \begin{matrix} \swarrow \overline{\text{OH}} \\ \searrow \text{OH} \end{matrix} + 2\text{H}^+$. The

silver salt, and also the lead and thallium salts, of dichloropalladous acids are obtained as amorphous precipitates having the formulæ [PdCl₂(OH)₂]₂Ag₂, [PdCl₂(OH)₂]₂Pb, Pb(OH)₂, and [PdCl₂(OH)₂]₂Tl₂ respectively. The silver salt is hydrolysed slowly by hot water, and the other two salts more rapidly.

T. H. P.

Pulverisation [Volatilisation] of Iridium in Water Vapour and Carbon Dioxide. Experiments to Determine the Density of Carbon Dioxide by the Method of Diffusion. FRIEDRICH EMICH (*Monatsh.*, 1908, 29, 1077—1085).—The author's attempts to measure the dissociation of carbon dioxide at high temperatures by observing the rate of diffusion of the gas through an aperture in an iridium tube have not been successful, because of the change in the aperture consequent on pulverisation of the metal.

The rate of pulverisation of electrically-heated strips of iridium in water vapour and carbon dioxide has been determined at a series of temperatures and under different gas pressures. The velocity of the process, which is supposed to be due to the formation of a volatile oxide, IrO₄, increases rapidly with the temperature. In the case of water vapour the velocity increases when the pressure is reduced from 1 to 0.1 atmosphere. On the other hand, for carbon dioxide the velocity increases when the pressure is reduced to 0.5 or 0.25 atmosphere, and then increases on further reduction of the pressure.

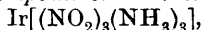
At 1900° the rate of pulverisation in carbon dioxide is almost twice as large as in water vapour, whilst at 2100° very little difference can be observed. This is said to be in agreement with the data relative to the dissociation of the two gases.

H. M. D.

Complex Iridium Compounds. ALFRED WERNER and O. DE VRIES (*Annalen*, 1908, 364, 77—127).—The preparation and properties of a number of iridium compounds, mainly chloronitrito-, amino-nitrito-, and chloroammino-compounds, are described.

Sodium iridiotetranitritodichloride, $[\text{IrCl}_2(\text{NO}_2)_4]\text{Na}_3 \cdot 2\text{H}_2\text{O}$ (salt *A*), one of the salts intermediate between $[\text{IrCl}_6]\text{M}_3$ and $[\text{Ir}(\text{NO}_2)_6]\text{M}_3$, examples of which are already known, has been prepared as follows: 5 grams of sodium iridichloride, $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$, are heated at 80—90° with 80 c.c. of water, 40 grams of sodium nitrite added gradually, and the solution warmed until it becomes yellowish-red and transparent. After a time, a salt, *A*, separates in well-formed, orange crystals, solubility 1 in 0.87 parts of water at 25°. From the mother liquors other products have been obtained, but not yet fully investigated. Salt *A*, in smaller yield, is also obtained by the action of sodium nitrite on ammonium iridichloride. Salt *A* has been obtained in the anhydrous form by crystallisation from dilute alcohol; it occurs in small, pale yellow crystals. The corresponding *potassium* salt, $[\text{IrCl}_2(\text{NO}_2)_4]\text{K}_3$, is obtained by repeated crystallisation from solutions containing salt *A* and excess of potassium nitrate; it forms small, light yellow crystals, and is less soluble than the sodium salt. By double decomposition between salt *A* and ammonium chloride, a yellow, crystalline precipitate was obtained, which has not been fully investigated; it is not the corresponding ammonium salt. The *lead* salt, in an impure form, was also obtained by double decomposition.

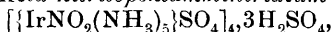
Nitritoamminiridium Compounds.—*Trinitritotriamminiridium*,



is obtained in thin, lustrous, colourless scales by heating 1 gram of salt *A* with 4 c.c. of 27% ammonia for eighteen hours in a sealed tube at 135—140°; the solution is evaporated, and the salt crystallised repeatedly. It is only freed from chloride with great difficulty, most satisfactorily by boiling with sodium nitrite. It is not affected by boiling hydrochloric acid (1 : 1), sulphuric acid (1 : 5), or concentrated nitric acid, but is decomposed when heated with concentrated sulphuric acid to 85°. One part of the compound dissolves in 2570 parts of water at 25°; the aqueous solution is practically a non-conductor.

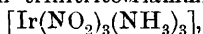
Dinitritotetramminiridium chloride, $[\text{Ir}(\text{NO}_2)_2(\text{NH}_3)_4]\text{Cl}$, is obtained by heating 5 grams of salt *A* with 20 c.c. of 27% ammonia for eighteen hours at 170°, and evaporating the product on a water-bath. The leaflets which first separate are contaminated with nitrite, and the salt is obtained pure by dissolving in water and crystallising repeatedly in the presence of hydrochloric acid; solubility 1 in 16.8 parts of water at 55°. Its behaviour towards the mineral acids is, in most cases, similar to that of the salt last mentioned. The following compounds are prepared from the chloride by double decomposition, generally with alkali salts. The *bromide*, $[\text{Ir}(\text{NO}_2)_2(\text{NH}_3)_4]\text{Br} \cdot \text{H}_2\text{O}$, occurs in colourless rods or prisms; the anhydrous bromide, obtained by recrystallisation in the presence of hydrobromic acid, in colourless prisms. The *iodide* occurs in colourless leaflets, crystals, or prisms; the *sulphate*, $[\text{Ir}(\text{NO}_2)_2(\text{NH}_3)_4]_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, in prisms or needles, which become anhydrous on heating to 120°. The solubility is about 1 in 400 of water at room temperature.

Nitritopentamminiridium chloride, $[\text{IrNO}_2(\text{NH}_3)_5]\text{Cl}_2$, can also be obtained by the action of ammonia on salt *A*, but in better yield by the action of silver nitrite on the aquopentammine chloride (compare Palmaer, Abstr., 1896, ii, 179; 1897, ii, 44); it forms small, colourless crystals, readily soluble in water. It is scarcely affected by boiling with nitric acid or aqua regia, or by moderately strong hydrochloric acid. The *iodide* and the *sulphate* are both anhydrous, and form colourless needles. *Acid nitritopentamminiridium sulphate*,



obtained by the action of concentrated sulphuric acid on the chloride, forms colourless, transparent needles. The *nitrite*, obtained by inter-action of the chloride and silver nitrite, also forms colourless crystals.

Chloroamminiridium Compounds.—The compound $[\text{IrCl}_3(\text{NH}_3)_3]$ appears to be formed when trinitritotriamminiridium,



is heated with ammonium chloride and hydrochloric acid to 180° , but attempts to obtain it pure were unsuccessful.

Dichlorotetramminiridium chloride, $[\text{IrCl}_2(\text{NH}_3)_4]\text{Cl} \cdot \text{H}_2\text{O}$, is obtained by heating together 1 gram dinitritotetrammine chloride, 1 gram ammonium chloride, and 15 c.c. of concentrated hydrochloric acid for nineteen hours at 140° . It occurs in light yellow needles and prisms, which are finally purified by repeated crystallisation from water. It is not affected by boiling hydrochloric acid; on heating with silver nitrite, even the intra-radicle chlorine reacts. It does not lose all its water even on prolonged heating at $125\text{--}130^\circ$. The corresponding *bromide*, yellow needles, crystallises with $1\text{H}_2\text{O}$, which it loses at 80° ; the *sulphate*, yellow scales, has also $1\text{H}_2\text{O}$, which it retains at 120° ; the *iodide*, yellow needles, is anhydrous. By the action of iridium chloride and of potassium iridium chloride on dichlorotetramminiridium chloride, sparingly soluble precipitates are obtained, but no pure salt has been isolated. The dichlorotetrammine compounds just described appear to be identical with those obtained by Palmaer (*loc. cit.*) by the action of ammonia on iridium chloride.

G. S.

Mineralogical Chemistry.

Fossil Coals. EDUARD DONATH (*Chem. Zeit.*, 1908, **32**, 1271—1273).—The extract obtained by treating coal from Rossitz, near Brünn, with carbon disulphide or chloroform is found to contain anthracene, chrysene, and probably also carbazole, indene, and polymerised coumarones. The view put forward previously (*Zeitsch. angew. Chem.*, 1906, **19**, 657), namely, that the formation of coal is accompanied by a process of distillation under pressure, and that coal consists of small quantities of a variety of pitch with the solid carbon material, thus receives support. W. H. G.

Influence of Centrifugal Force on the Optical and Other Properties of Naphtha. MICHAEL A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1583—1588).—The author has made experiments to ascertain whether the rotation of the earth has any effect on the properties of naphtha. A closed tube containing a sample of Grosny naphtha, $D^{15} 0.8791$, having a carbonisation constant of 3/32%, was spun for two hours in a centrifuge revolving 3000 times per minute, after which it was found to have the carbonisation constant 1/8% and $D^{15} 0.8768$.

Evidently a considerable part of the products of carbonisation had settled on the conical bottom of the tube. So that, whilst natural filtration of naphtha produces a differentiation of naphtha in a vertical direction, an analogous process in a horizontal direction may be brought about by centrifugal force. The author considers that such action has some bearing on the formation of asphalte, and may explain why asphaltes having a venous character are met with in some parts of the earth.

T. H. P.

Rinneite. H. E. BOECKE (*Chem. Zeit.*, 1908, 32, 1228).—An anhydrous mineral, having the composition $\text{FeCl}_2, 3\text{KCl}, \text{NaCl}$, has been found in considerable quantities at the Nordhausen Works. It crystallises in the hexagonal system; it decomposes when exposed to the air, but is stable under petroleum, and when a hot saturated aqueous solution is allowed to cool, potassium chloride separates out.

J. V. E.

Analysis of Plumosite from Felsöbánya. JOSEF LOCZKA (*Ann. Musei Nat. Hungarici*, 1908, 6, 586—590).—The material consists of a felted aggregate of dark steel-grey fibres with entangled quartz crystals. Neither the colour nor the lustre is affected by a 25% solution of sodium hydroxide, proving the absence of stibnite (which under these conditions quickly loses its lustre and becomes red); with a 30% solution, the material acquires a coloured tarnish, although still retaining its lustre. It is not acted on by an 8% solution of potassium sulphide. Analysis gave:

S.	Sb.	Pb.	Cu.	Fe(Mn,Zn).*	Insol.	Total.
21.59	35.80	39.38	trace	2.87	0.50	100.14

* Mn about 0.12, Zn about 0.10 per cent.

No iron-pyrites could be detected. The formula is deduced as $4\text{PbS}, \text{FeS}, 3\text{Sb}_2\text{S}_3$ [but the figures agree still more closely with the jamesonite formula, $7(\text{Pb}_4, \text{Fe}_1)\text{S}, 4\text{Sb}_2\text{S}_3$ (*Abstr.*, 1907, ii, 700)].

L. J. S.

A Group of Manganates, comprising Hollandite, Psilomelane, and Coronadite. L. LEIGH FERMOR (*Rec. Geol. Survey India*, 1908, 36, 295—300).—Hollandite (*Abstr.*, 1907, ii, 701) has recently been described as a manganate of manganese, barium, and iron corresponding with the hypothetical acid, H_4MnO_6 , an acid suggested by Laspeyres, in 1876, to explain the composition of psilomelane. It is

here pointed out that the new mineral coronadite (Abstr., 1905, ii, 96) may also be referred to the same acid, the formula being $\text{Mn}_{21}\text{Pb}_6\text{R}''_5(\text{MnO}_5)_{16}$. These three minerals therefore form a group of manganates.

L. J. S.

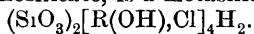
Whewellite from Schlan, Bohemia. FRANTIŠEK SLAVÍK (*Bull. Intern. Acad. Sci. Bohême*, 1908, 13, 9 pp.).—A crystallographic description is given of some large (up to 37 mm. across) twinned crystals of whewellite, found with crystals of ankerite and barytes in a fault-breccia in the Theodor coal mine near Schlan. The individual crystals have D 2·223, 2·222, 2·229. Analysis by J. Milbauer agrees with the formula $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$:

CaO.	C ₂ O ₃ .	H ₂ O.	Total.
38·46	49·65	12·12	100·25

L. J. S.

Study of Hydrated Silicates. FERRUCCIO ZAMBONINI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 148).—The author has examined about thirty hydrated silicates with reference to the condition of the water present, the main results being as follows.

Thaumasite contains only water of crystallisation, and is to be regarded as $\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$. Pyrosmalite, regarded up to the present as an orthosilicate, is a metasilicate,



Ekmanite is not allied to pyrosmalite, but is an altered chlorite. Calamine contains only $\frac{1}{2}$ a mol. of water of constitution, its probable formula, considering its crystallographic relations with bertrandite, being $\text{Zn}_2(\text{ZnOH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$. Cordierite has no water of constitution. Diopase is not an acid orthosilicate, but a metasilicate with dissolved water. Katapleite does not contain water of constitution, and is the sodium salt of a zircon-silicic acid; the same is the case with elpidite. The water present in steenstrupite and epistolite is not water of constitution. Sepiolite, which is regarded as a meta- or an ortho-silicate, contains absorbed water, and must be given the formula $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot n\text{H}_2\text{O}$. The minerals collected together under the name of deweylite have, so far as the water present is concerned, properties analogous to those of sepiolite, but must be distinguished as deweylite, $\text{Mg}_4\text{Si}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$, and pseudodeweylite, $\text{Mg}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$.

T. H. P.

Optical Characters of Minerals of the Amphibole Group and their Relation to the Chemical Composition. STEFAN KREUTZ (*Sitzungsber. K. Akad. Wiss. Wien.*, 1908, 117, Abt. I, 877—972).—Detailed determinations were made of the optical constants of a number of minerals of the amphibole group; analyses are given of the following: I, grünerite from La Mallière, dep. Var.; II, tremolite from Switzerland; III, actinolite from Zillerthal; IV, richterite from Långban, Sweden; V, hornblende from Russell, New York; VI, pargasite from Pargas, Finland; VII and VIII, basaltic hornblende from Lukow, Bohemia.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	F.	Total, less O for F. Sp. gr.
I.	47.17	—	1.00	1.12	43.40	0.08	1.90	2.61	0.07	0.47	2.22	0.07	100.08 3.518
II.	58.22	—	1.37	0.04	0.61	0.04	12.95	23.97	0.04	0.24	2.17	0.17	99.75 2.980
III.	56.38	—	1.23	0.15	5.26	0.30	12.41	21.74	0.22	0.43	1.96	0.09	100.18 3.044
IV.	56.01	—	0.14	2.14	—	5.81	8.29	20.99	0.47	3.69	1.94	0.18	99.59 3.044
V.	54.75	—	2.23	0.85	1.49	0.15	11.36	22.54	1.10	2.40	2.16	0.85	99.50 3.033
VI.	48.38	0.05	10.83	0.76	1.56	0.04	12.24	20.78	1.38	2.69	0.91	1.82	100.68 3.095
VII.	39.60	2.50	18.51	5.50	2.26	0.74	12.57	14.11	1.87	2.58	0.26	0.10	100.63* —
VIII.	39.90	2.90	17.03	4.14	4.00	0.23	12.70	14.39	2.19	2.51	0.48	—	100.47 —

* CO₂, 0.07.

No definite relation can be traced between the chemical composition and the optical characters of the amphiboles except in tremolite-actinolite. The strength of the double refraction, for instance, does not vary progressively with the percentage of iron; and even in the colour of the material there is no such relation, for the highly ferruginous grunerite is pale yellow, whilst others containing less iron are dark green, and glaucophane is blue or violet. The amphiboles are therefore not to be considered as mixtures of simple salts, such as FeSiO₃, Al₂Si₃O₉, etc., but are complex compounds as suggested by Tschermak's double salts. L. J. S.

Composition of the Sand from the Eruption of Vesuvius, April, 1906. GIULIO PARIS (*Chem. Zentr.*, 1908, ii, 1287; from *Staz. sperim. agrar. ital.*, 1908, 41, 321—328).—Sand collected two days after the eruption had the following percentage composition:

Cl.	SO ₃ .	SiO ₂ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	NiO.
41.45	12.67	0.25	4.05	3.58	2.5	7.48	27.51	0.46

and the acidity, calculated as hydrochloric acid, was 7.68%. Casoria (*Ann. R. Scuola Super. Agric. Portici*, 1907, 7) considered from his analysis that it contains a new nickel mineral:

SiO ₂ .	NiO.	MgO.	Co, Fe, Al, Ca.	Water.	Volatile.
35.014	44.75	4.528	trace	4.528	9.81

together with a small quantity of magnesium hydroxy-oxide and another silicate of the composition:

SiO ₂ .	NiO.	MgO.	Co, Fe.	Water.
39.756	19.348	26.808	trace	13.888

The ash that fell in the Province of Avellino had D 1.215, and contained an average of 0.6% phosphoric acid and 10% of alkali, of which latter 50% was soluble in acids. Some specimens contained varying quantities of nitrogenous substances which liberated ammonia when heated with soda-lime. J. V. E.

Composition of the Ash and Lapilli from the Eruption of Vesuvius, April, 1906. NAPOLEONE PASSERINI (*Staz. sper. agrar. ital.*, 1907, 40, 40—53).—A sample of ash (1) and lapilli (2) were found to have the following composition:

	K ₂ O.	Na ₂ O.	MgO.	CaO.	FeO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	TiO ₂ .	SiO ₂ .	Cl.
I.	5.43	3.54	4.76	10.80	4.01	4.41	17.84	0.66	0.17	1.02	46.72	0.34
II.	2.52	3.54	3.28	16.92	4.81	4.71	13.64	0.63	0.10	1.31	47.60	0.16

The acidity is only slight, and is mainly due to volatile acids

(hydrochloric and sulphurous), which soon disperse if the ash is left exposed to air and not ploughed in.

The ashes resemble qualitatively those examined by Vauquelin and by Lavini in 1822 and 1829 respectively. The proportions of the different constituents vary, however, considerably (compare Lacroix, *Abstr.*, 1906, ii, 555). N. H. J. M.

Lavas of the Last Eruption of Vulcano, Lipari Islands. ALFRED LACROIX (*Compt. rend.*, 1908, 147, 1451—1456).—During any one period of eruption the magmas of Mt. Pelée, of Vesuvius, and of Etna have in each case proved to be almost constant in chemical composition. From the various published descriptions of the products of the 1888—1889 eruption of Vulcano, this would, however, not appear to hold good; but two analyses now given of trachyte with anorthoclase, augite, and olivine are practically identical. Analyses are also given of microsanidinite occurring as enclosures in the trachyte, of glassy rhyolite, and of leucite-tephrite from Vulcanello.

L. J. S.

Investigations on the Eruptive Basic Rocks of Northern Sardinia. AURELIO SERRA (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 597—602).—The rocks of the Fenosu district of Northern Sardinia have a felspar basis, which exhibits inclusions of augite, hypersthene, magnetite, biotite, apatite, and ilmenite. The following is the chemical composition of the rock:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	TiO ₂ .	P ₂ O ₅ .	CaO.
48·72	22·56	1·08	3·74	0·77	0·50	0·50	10·00
MgO.	K ₂ O.	Na ₂ O.	H ₂ O (at 110°).	H ₂ O (at red heat).	Total.		
2·68	2·05	4·65	0·84	1·88	99·87		

In the region of S'Adde de S'Ulmer, the rock, which is dark grey, contains large crystals of felspar (labradorite), smaller crystals of augite, together with magnetite, biotite, apatite, and hypersthene, and has the following composition:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	TiO ₂ .	P ₂ O ₅ .	CaO.
52·13	20·55	5·13	1·86	0·71	0·40	0·27	9·22
MgO.	K ₂ O.	Na ₂ O.	H ₂ O (at 100°).	H ₂ O (at red heat).	Total.		
2·07	2·90	3·35	0·40	1·22	100·21		

The two rocks belong to the same eruptive magma. T. H. P.

Rocks from Central Borneo. J. SCHMUTZER (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 398—415).—Detailed descriptions and analyses, by M. Dittrich, are given of (I) glassy amphibole-dacite; (II) ditto; (III) biotite-amphibole-andesite; (IV) aplitic microgranite: the first three rocks being from the Müller Mtns., and the last from Mt. Kēlam.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.	66·16	0·50	15·39	1·25	1·72	0·90	3·47	3·94	2·00	4·94	100·27
II.	65·72	0·48	15·06	1·35	1·80	1·57	4·18	4·24	1·07	4·46	99·93
III.	62·78	0·56	17·16	1·96	2·31	2·32	4·84	4·11	2·15	1·12	99·58*
IV.	72·44	trace	16·51	0·24	0·52	0·05	2·47	4·54	2·13	1·26	100·16

* Including P₂O₅, 0·15; MnO, 0·06; BaO, 0·04.

L. J. S.

Meteoric Iron. WALTER FRAENKEL and GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1908, **60**, 416—435).—A typical specimen of meteoric iron contains three structure elements: (1) bars of kamacite, formed of hexahedral crystals containing about 6% of nickel; (2) taenite, the crystals of which contain about 33% of nickel; (3) plessite, a mixture of taenite and kamacite. From this structure it would appear that there is a break in the solubility of nickel in iron from 6 to 33% of nickel, but these metals form a continuous series of mixed crystals under ordinary conditions. The authors attempt to account for the differences in the structure of ordinary nickel-iron ores and meteoric nickel-iron of the same composition.

Osmond and Cartaud (Abstr., 1904, ii, 135) have suggested a hypothetical diagram for meteoric iron, according to which the latter is more stable than ordinary nickel-iron alloys. The authors now show, however, that when meteoric iron is heated without access of air, the kamacite first changes into granular crystals, and then the taenite begins to disappear, doubtless owing to the diffusion of the nickel into the altered kamacite. The change in the γ field is slow at 700°, but rapid at 1400°. The change in question takes place even in the α field; after heating meteoric iron for two hundred hours at 420°, granulation of the kamacite is observed, although not with the same certainty as at higher temperatures. It is shown indirectly, however, that the change must take place, and hence that meteoric nickel-iron is unstable at the ordinary temperature.

In order to find whether heated meteoric iron corresponds in properties with ordinary nickel-iron alloys, the magnetic properties of the two substances have been compared. When heated, meteoric iron loses its magnetic properties at about the same temperature as the ordinary alloy of the same composition, but as different pieces of meteoric iron from the same large piece not previously heated lose their magnetic properties at very different temperatures, this result is not conclusive.

Attempts to prepare meteoric iron artificially, or to account for its structure, did not lead to any definite result. It is probable that the iron in kamacite has not crystallised at first in the ordinary (γ) form.

The paper is illustrated with 16 photomicrographs.

G. S.

Physiological Chemistry.

Ionic Equilibrium in the Animal Organism. II. The Influence of Carbon Dioxide on the Division of Electrolytes between the Blood-corpuses and Plasma. KARL SPIRO and LAWRENCE J. HENDERSON (*Biochem. Zeitsch.*, 1908, 15, 114—122).—The explanation of Zuntz's observation that the passage of carbon

dioxide into blood increases the alkalinity of the plasma, as determined by titration, has been ascribed to the selective action of the living membrane. The phenomenon can, however, be explained as a purely physico-chemical process. If a dialysed globulin solution is mixed with sodium hydrogen carbonate, a solution of the hydrogen carbonate placed in a dialyser inside the former solution, and carbon dioxide be led into both liquids, the alkalinity of the inner liquid increases. This can be explained by assuming that the following reaction takes place: $\text{Na-globulin} + \text{H}_2\text{CO}_3 = \text{NaHCO}_3 + \text{H-globulin}$. This increase of sodium salt increases the osmotic pressure of the inner liquid, to compensate for which, water passes out from inside and the carbonate passes to the inside, and thus increases the alkalinity. In the case of blood, a similar reaction takes place between the proteins and carbon dioxide when the latter is passed through. In the corpuscles, the protein content is higher than in the plasma, and a reaction then takes place between potassium phosphate and carbonic acid, leading to the formation of potassium monophosphate and potassium hydrogen carbonate. As a result, the osmotic pressure of the corpuscles becomes greater than that of the serum. Water will therefore have a tendency to pass from the corpuscles to the plasma, and as the cell walls are not permeable to the cations, the system will be "neutralised" by a wandering of anions, chlorine ions passing into the cells and OH^+ and HCO_3^- ions into the plasma. A plasma will therefore be obtained with smaller chlorine content, and greater alkalinity. S. B. S.

Coagulation of Blood. JOHN MELLANBY (*J. Physiol.*, 1908, 38, 28—112).—Many of the experiments recorded do not support Morawitz's views on the causes of blood-coagulation. Fibrinogen is always associated with prothrombin, and therefore solutions of this substance may be coagulated by kinase and calcium chloride, or by fibrin-ferment. The residual fluid after coagulation contains fibrin-ferment generated from the prothrombin by kinase and calcium chloride; if, however, fibrin-ferment is used as the coagulant, the residual fluid contains prothrombin, but no ferment. The action of calcium is considered to be specific. Salts which inhibit coagulation may precipitate calcium salts, and those which do not precipitate calcium salts may restrain coagulation by holding fibrin in solution, or by depressing the action of calcium and kinase on prothrombin. Plasma and serum contain a large amount of anti-fibrin ferment, but not an anti-kinase; the former is very susceptible to the action of alcohol. Serum usually contains no prothrombin. The activity of Schmidt's fibrin-ferment depends mainly on the presence of kinase and calcium salts in it. Gamgee's ferment solution is one of fibrin-ferment dissolved out by sodium chloride solution from the fibrin which had adsorbed it. Serum-globulin (in the author's sense) is probably derived from the decomposition of fibrinogen under the influence of fibrin-ferment. Serous fluids contain the same substances, but in smaller quantity than the bird's plasma which was employed in most of the present experiments; they therefore coagulate on the addition either of kinase (prepared from testis) or of fibrin-ferment. W. D. H.

Hæmagglutination and Hæmolysis. M. VON EISLER (*Centr. Bakt. Par.*, 1909, 48, ii, 679—681).—Polemical against von Liebermann; the views put forward by this author (*Abstr.*, 1908, ii, 865) are different from those originally propounded by him, but very similar to those of Landsteiner. G. B.

Seromucoid. HUBERT W. BYWATERS (*Biochem. Zeitsch.*, 1909, 15, 322—343).—Blood was coagulated in slightly acid solution by means of steam. The filtrate from the coagulum was concentrated, and the solution thereby obtained submitted to dialysis. It was then filtered, and, after further concentration, acidified with acetic acid and thrown into three times the volume of alcohol. The crude seromucoid obtained in this way is pigmented, and the author describes a method of purification by means of sulphur dioxide. In properties, seromucoid is similar to ovomucoid, but differs from the latter by the intensity with which it gives Hopkins and Coles' glyoxylic acid reaction and by the fact that no scission of sulphur takes place when treated with concentrated alkali hydroxide. It gives most of the other characteristic protein reactions. It contains 47·6% C, 6·8% H, 11·6% N, and 1·75% S. There is 25% carbohydrate in the molecule; this was isolated as a hydrolysis product in the form of glycosamine. The quantity of seromucoid in the blood is small; a method is described for its quantitative estimation; it increases after a meal rich in carbohydrates—in the case of dogs from about 0·3 to 0·9 gram per litre of blood. In spite of its small quantity, the carbohydrate it contains accounts for about 10% of the total circulating in the blood, and the results obtained justify Pavy's hypothesis that, after carbohydrate ingestion, a part enters the circulation in combination with proteins. Seromucoid was also isolated from the mucous membrane of the intestine. S. B. S.

The So-called "Albumose" in Normal Blood. HUBERT W. BYWATERS (*Biochem. Zeitsch.*, 1909, 15, 344—349).—The author criticises the methods by which previous observers have arrived at the conclusion that albumoses exist in the blood. He concludes that albumoses are absent, and that what has been regarded as albumose is in reality seromucoid. S. B. S.

Prolonged Existence of Adrenaline in Blood. D. E. JACKSON (*Amer. J. Physiol.*, 1909, 23, 226—245).—If the blood of a dog poisoned with adrenaline is injected into another or the same animal, it produces a rise of blood-pressure, provided the rise of pressure in the first dog still persists. But if the blood-pressure in the first dog has regained its normal level, which is usually in about a minute after the injection, the blood of that dog will no longer produce a rise of pressure when injected into a second animal. W. D. H.

The Effect on Blood-Pressure of *l*-, *d*-, and *dl*-Suprarenine (Adrenaline). EMIL ABDERHALDEN and FRANZ MÜLLER. **The Resolution of *dl*-Suprarenine into its Components.** FRANZ FLÄCHER (*Zeitsch. physiol. Chem.*, 1908, 58, 185—188, 189—194).—In

the first paper, Cushny's statement that *l*-adrenaline has a powerful effect on blood-pressure, that *d*-adrenaline has a feeble effect, and that *dl* adrenaline has an intermediate effect, is confirmed. In the second paper, the methods are described for the resolution of synthetic *dl*-adrenaline into its optically active components. The methods used consisted in the growth of the mould *Penicillium glaucum*, and in the fractional precipitation of salts. Under the latter head, the tartrates gave the best results. The naturally-occurring *l*-adrenaline gives a crystallisable tartrate. The rotatory powers of the two substances are $[\alpha]_D^{19.6} - 51.40^\circ$ and $[\alpha]_D^{19.8} + 51.88^\circ$ respectively. W. D. H.

Influence of Quinine on Phagocytosis. TH. GRÜNSPAN (*Centr. Bakt. Par.*, 1908, i, 48, 444—450).—Weak (less than 0.002%) solutions of quinine have no appreciable influence on phagocytosis *in vivo*; a 0.002% solution increases it, and a 0.1% solution diminishes it. Egg-albumin leads to no increase of phagocytic activity. The intracellular *Staphylococci* appear to be living as judged by their staining reactions. Further work is in progress, as some of the results are regarded as questionable. W. D. H.

Phagocytosis. HEINRICH BECHHOLD (*Chem. Zentr.*, 1908, ii, 1269—1270; from *Munch. med. Woch.*, 1908, 55, 1777—1798).—The inhibiting action of sodium hydroxide on the phenomenon is lessened by the presence of serum, and still more so by the unaltered blood. Relatively large quantities of lactic acid do not act in this way, even although they produce microscopic alterations of the phagocytes; oxygen and carbon dioxide have no effect, and carbon monoxide has no inhibitory effect. Various colloidal materials were investigated, but they were unable to influence phagocytosis as serum does; the colloidal properties of serum *per se* therefore play no part in the phenomenon. The action of pepsin and pancreatin is stimulated by lactic acid. W. D. H.

Salivary Secretion. IV. Influence of Non-electrolytes. A. JAPPELLI (*Zeitsch. Biol.*, 1908, 51, 435—459).—Strongly hypertonic solutions of non-electrolytes injected into the blood-stream raise the osmotic pressure of the blood, and also, after a short time, increase the concentration of the electrolytes in that fluid. The organism appears to have the power to maintain the osmotic pressure, and also the proportion between electrolytes and non-electrolytes, at a constant level. The physico-chemical properties of the submaxillary saliva obtained by stimulation of the chorda tympani nerve appear to be independent of the osmotic concentration of the blood, but they are influenced by such electrolytes and non-electrolytes as are permeable through the secreting cells. Dextrose is not permeable, sucrose and lactose only slightly so; these substances hardly alter the saliva at all, although, owing to the greater amount of salts which pass into the blood from the tissues when they are present, they do so indirectly, leading to the production of a saliva rich in salt. An excess of sodium ions in the blood, however, inhibits salivary activity. W. D. H.

Action of Peroxides on the Digestive Organs. TOGAMI (*Chem. Zentr.*, 1908, ii, 1275; from *Berl. klin. Woch.*, 1908, 45, 1528—1532).—The three substances investigated, hydrogen peroxide, magnesium peroxide, and sodium percarbonate, favour gastric secretion.

Hydrogen peroxide (0.1 to 1%) has no effect on the action of ptyalin, pepsin, trypsin, or amylpsin. The other two substances have also no effect, but magnesium chloride favours the action of diastatic ferments, in virtue of the chlorine ion.

Concentrated solutions of hydrogen peroxide produce profuse secretion of mucus, but dilute solutions have no effect on the gastric mucous membrane.

W. D. H.

Action of Hydrochloric Acid on the Secretion of Ferments of the Stomach and Pancreas. R. EHLMANN and R. LEDERER (*Chem. Zentr.*, 1908, ii, 1274; from *Berl. klin. Woch.*, 1908, 45, 1450—1452).—In opposition to the statements of earlier investigators, the administration of hydrochloric acid either with or after a test meal produces no increase in the secretion of pepsin. The amount of trypsin secreted by the pancreas is also lessened, and Pawloff's view that hydrochloric acid acts as a specific stimulus for pancreatic secretion is regarded as incorrect.

W. D. H.

The Influence of Acids on the Calcium Metabolism of Herbivora. E. GRANSTRÖM (*Zeitsch. physiol. Chem.*, 1908, 58, 195—213).—Rabbits were fed on various diets (cream, wheat), and hydrochloric acid or phosphoric acid added to the food. The effect on calcium excretion in urine and faeces was investigated; both during inanition and after feeding, the calcium in the urine is increased by acid; the amount in the faeces falls except in two cases of phosphoric acid feeding, but the influence of this acid on the faeces is far from clear. Suggestions are made regarding the therapeutic uses of acids in man.

W. D. H.

Carbohydrate Metabolism. JOHAN E. JOHANSSON (*Chem. Zentr.*, 1908, ii, 1373; from *Scand. Arch. Physiol.*, 1908, 21, 1—34).—In men, carbohydrate food produces an increase in the output of carbon-dioxide, but the amount varies considerably; in doses beyond 150 grams no further increase occurs. Lævulose causes twice as great an increase in carbon dioxide excretion as the same amount of dextrose. Conditions affecting the output which were investigated are (1) previous state of hunger or not; this largely depends on the amount of glycogen storage; and (2) adiabatic condition: here the results are very inconstant.

W. D. H.

Rôle of Inorganic Phosphorus in Nutrition. EDWIN B. HART, ELMER V. MCCOLLUM, and J. G. FULLER (*Amer. J. Physiol.*, 1909, 23, 246—277).—A number of young pigs were fed on normal diets, on diets containing a minimal amount of phosphates, and on diets containing an excess of these salts. In some experiments, nuclein, lecithin, and phytin were used, but these did not give any better results than inorganic phosphates. A low phosphorus intake is

prejudicial to growth; increase of phosphorus chiefly leads to skeletal growth. There is no evidence of the synthesis of nuclein and other organic phosphorus compounds from inorganic phosphates.

W. D. H.

Changes of Phosphatic Nutrients in the Human Body. E. KOCH (*Bied. Zentr.*, 1908, 37, 858; from *St. Petersburg Med. Woch.*, 1906, 400—402).—In general, inorganic and non-protein phosphorus is not utilised. It is possible, however, that inorganic phosphorus may be utilised if organic phosphorus is excluded from food for a long time.

N. H. J. M.

The Importance of Chlorides in the Life Processes of the Organism. HERMANN FRIEDRICH GRUNWALD (*Zentr. physiol.*, 1908, 22, No. 16, reprint).—Rabbits were fed on a chlorine free diet, and then excreted urine which was almost chlorine-free. After administration of diuretin, however, large quantities, 1 gram or more, of sodium chloride were excreted. After four or five doses, the animals exhibited characteristic symptoms of poisoning—weakness, shivering, paresis of the hind limbs, and gradually increasing paralysis, terminating in death in four or five days. The chlorine in the blood sank to a half or even a third of the normal, and in the latter stages of the poisoning, re-administration of chlorine was ineffective in saving the animal. Control animals which had received 1 gram of sodium chloride with the diuretin kept perfectly healthy. The toxic symptoms are therefore due to loss of chlorine, to which von Wyss has ascribed the effects of sodium bromide poisoning, which produces similar symptoms.

S. B. S.

Influence of High Body-temperature on the Decomposition of Sugar in the Animal Body. HERMANN HOHLWEG and F. VOIT (*Zeitsch. Biol.*, 1908, 51, 491—510).—An elevation of the body-temperature to over 40° by artificial means (warm chamber) leads to an increase in the metabolism of protein, and an increased excretion of nitrogen. This may be lessened or prevented if a sufficient amount of carbohydrate is also administered. Respiratory ventilation is enormously increased, and the excess of combustion falls on the sugar. This occurs also if the sugar is given subcutaneously, and even if sugars (such as sucrose) which are burnt with difficulty under normal conditions are chosen.

W. H. D.

Chemistry of the Brain. A. RIELÄNDER (*Chem. Zentr.*, 1908, ii, 1371; from *Zentr. Physiol.*, 1908, 22, 377—380).—The basic constituents precipitable by phosphotungstic acid were investigated after hydrolysis by hydrochloric acid. Histidine, arginine, lysine, and choline were obtained; also bases with a heavier molecule than choline.

W. H. D.

Chemico-physical Investigations on the Crystalline Lens. FILIPPO BORTAZZI and NOÈ SCALINCI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 566—571. Compare this vol., ii, 71).—When the

crystalline lens of a dog or rabbit is suspended in dry air, it loses in weight rapidly for four to six hours and then slowly. Notwithstanding the great loss in weight, which amounts to 30·42—49·25% in four hours, the lens does not become opaque, but only wrinkles, so that the opacity of the lens is not due to desiccation alone. When the desiccated lens is immersed in water vapour, it increases in weight very slowly, the original weight of the lens not being attained even after eighty to ninety hours; in some cases, a slight loss in weight occurs during the first few hours of immersion in water vapour. When the desiccated lens is immersed in water, the increase in weight is rapid during the first two hours, after which time the water is only taken up very gradually.

T. H. P.

Physiology of Glands. X. The Liver in Different Nutritive Conditions. LEON ASHER and PAUL BOEHM (*Zeitsch. Biol.*, 1908, 51, 409—434).—Feeding on protein, proteoses, and amino-acids (alanine and aspartic acid) increases the size of the liver cells; the most marked effect was obtained with proteoses. Feeding with fat causes the appearance of fat globules in the cells. Feeding with the proteins, and especially with proteoses, leads, not only to an increase in the size of the cells, but to appearances which are figured, showing they have been stimulated to activity. Alanine and aspartic acid do not seem to act as stimuli in the same way. The view that proteoses are absorbed in part as such is supported.

W. D. H.

Salts of Muscle. FUMIHIKO URANO (*Zeitsch. Biol.*, 1908, 51, 483—490. Compare Abstr., 1907, ii, 978).—Some analytical figures are given of the total ash and proportion of sodium and potassium in the frog's sartorius before and after washing with sugar solution; this method gives the proportion of salts in the muscles themselves as distinguished from that due to the adherent blood and lymph. A discussion of Overton's views on the osmotic properties of muscle is also given.

W. D. H.

Physiological Function of the Arborescent Glands of the Female Generative Apparatus in the Cockroach. L. BORDAS (*Compt. rend.*, 1908, 147, 1495—1497).—The larger of the above glands secretes a milky fluid containing large numbers of minute octahedra of calcium carbonate, which serve to form the walls of the ootheca.

G. B.

Protein Bases of the Sperm and Ovaries of the Tunny Fish and their Products of Hydrolysis. SERAFINO DEZANI (*Giorn. R. Accad. Med. Torino*, 1908, 14, reprint).—The dried sperm of the tunny fish, after removal of the fat, was found to contain 15·87% of nitrogen, of which 20—22% is dissolved by 2% sulphuric acid in the form of a base answering to the reactions of that isolated by Ulpiani (Abstr., 1903, i, 215). On hydrolysing the base, 49·74% of the nitrogen present was accounted for as follows: 6·79% as ammonia, 3·86% as histidine, 37·02% as arginine, and 2·07% as lysine. The composition of the base present in the sperm of the tunny fish hence

differs from the mean composition of the protamines in its small proportion of arginine and its large proportion of ammonia. Excepting as regards the arginine, which is always present to the extent of less than 30% in the histones, the base resembles in composition rather the latter than the protamines.

The sperm also contains a nucleic acid, which was obtained as a gelatinous, white mass, turning brownish-yellow on drying in a vacuum, and containing N 14.10% and P 3.10%; this proportion of phosphorus is lower than in any other nucleic acid known.

The dried ovaries of the tunny fish, after removal of the fat, contained 13.65% of nitrogen. Dilute sulphuric acid dissolved 4.46% of the total nitrogen in the form of a base, which was obtained as an amorphous, white powder, becoming oily in the air. The base dissolves sparingly in cold water and more readily in hot water, especially if acidified with sulphuric acid; it gives the biuret reaction, and Millon's reaction after the lapse of some time, and is precipitated by concentrated ammonia, picric acid, phosphotungstic acid, and platinum chloride solutions. 16.71% of its nitrogen is present as basic nitrogen, 2.23% as histidine, 0.95% as arginine, and 13.53% as lysine. The molecule of this base has a more complex composition than that of the base present in the sperm, a fact in accord with Kossel's hypothesis, according to which the male sexual cells, with their purely fecundating function, contain the more simple proteins, whilst the female cells, which have to supply nutriment to the new individuals, contain more complex protein substances.

The ovaries contain a nucleic acid, which was separated as a white powder, slightly soluble in hot water, giving an acid solution, with which lead acetate or copper acetate gives an abundant precipitate. The acid contains 13.31% of nitrogen and 9.36% of phosphorus, and is hence a true nucleic acid.

T. H. P.

Influence of Sugars on the Secretion of Milk. GIOVANNI PIANTONI (*Chem. Zentr.*, 1908, ii, 1784—1785; from *Arch. Farm. sper.*, 1908, 7, 329—336).—The subcutaneous injection of small quantities of mono- and di-saccharides in a goat produced an increase in the amount of milk secreted without altering its composition. Larger quantities lessened the secretion and the amount of sugar and fat in it, causing also polyuria and the passage of lactose into the urine; this was intensified by repeating the injection daily. Polysaccharides do not have this action.

W. D. H.

The Variability of Milk. The Influence of the Addition of Various Salts to Fodder on the Composition and Quantity of the Milk. GEORG VON WENDT (*Chem. Zentr.*, 1908, ii, 1881; from *Skand. Arch. Physiol.*, 1908, 21, 89—145).—Sodium chloride, chalk, sodium phosphate, magnesium bromide, and calcium glycerophosphate when added to fodder do not influence in any definite way the composition of milk. Calcium hydrogen phosphate often increases the quantity of milk, and generally, to a slight extent, the calcium. The variability in the composition of the milk of cows of different breeds and in different periods of lactation is generally about the same. The

protein content as lactation proceeds, in contrast to the other constituents, does not diminish. The phosphorus, nitrogen, and caseinogen contents are the least variable; then come calcium, fat, and lactose; then chlorine, whilst potassium and albumin are the most variable constituents.

S. B. S.

Ionic Equilibrium in the Animal Organism. I. The Equilibrium of Acids and Bases in the Urine. LAWRENCE J. HENDERSON and KARL SPIRO (*Biochem. Zeitsch.*, 1908, 15, 105—113).—The ionisation constant of the two acids, β -hydroxybutyric acid and acetoacetic acid, which occur under pathological conditions in the urine, was determined. This was done by ascertaining the relative amount of salt and free acid which was present when a certain tint of an indicator was attained, and comparing it with the amount of free acid and salt present in another acid of which the ionisation constant is known when it gives under the same conditions the same tint. From the equation $(H)^+ = C(HA)/NaA$, where C = ionisation constant divided by the grade of dissociation of the salt, and HA and NaA the quantities of acid and salt present, it is possible to calculate the relative quantities of acid and salt present with different hydrogen ions. These concentrations in urine and blood have been determined under various normal and pathological conditions. As a result it was shown that in blood, even in acidosis, all, or almost all, the hydroxybutyric acid is combined as salt, whereas in urine a considerable quantity is free. The acidity of the urine prevents a large loss of alkali from the body of carnivora, and the kidneys possess the capacity of holding back about half the alkali when it exists in the form of salts of those acids which occur in diabetes.

S. B. S.

The Physiological Basis of Radium Emanation Therapeutics. F. NAGELSCHMIDT and F. L. KOHLRAUSCH (*Biochem. Zeitsch.*, 1908, 15, 123—163).—The radioactivity of urine and faeces of patients after ingestion of radioactive solutions was determined, also that of the liver, bile, and blood of rabbits. The following conclusions were arrived at: The radium emanation is a gas, which can be resorbed by the lungs, stomach, and alimentary canal, but not under ordinary conditions by the skin. The greatest part of this gas leaves the system within a relatively short space of time, chiefly in the expired air; a small quantity can be detected in the faeces, and also minute traces in the liver and bile, probably existing here as residual activity. The blood showed no radioactivity, but it is possible that the gas is evolved from this fluid only in a vacuum. The therapeutic significance of these results is discussed.

S. B. S.

Elimination of Radium Bromide [in the Organism]. A. JABOIN and BEAUDOIN (*J. Pharm. Chim.*, 1909, [vi], 29, 15—23).—The elimination of radium by the animal organism was studied; 0.05 mg. of radium bromide given in solution to a rabbit by the mouth was wholly eliminated in four days.

G. B.

Lecithin, Choline, and Formic Acid. GIUSEPPE FRANCHINI (*Chem. Zentr.*, 1908, ii, 1785; from *Arch. Farm. sper.*, 1908, 7, 371—399).—In rabbits fed on lecithin, the amount of this substance increases in

the liver and muscles, but not in the brain; this goes on for two weeks after the administration of lecithin ceases. Small quantities of glycerophosphoric acid pass into the urine, also formic acid, but not choline. In the faeces, the amount of lecithin increases; glycerophosphoric acid increases in the liver and muscles. W. D. H.

Elimination of Nitrogen after the Administration of Glycine, Asparagine, and Glycyl-glycine Anhydride. PHOEBUS A. LEVENE and P. A. KOHN (*Amer. J. Physiol.*, 1909, 23, 324—343).—This is a contribution to the attempts now being made to determine the rôle played by individual cleavage products of the protein molecule. If glycine is given, the increase of excreted nitrogen begins earlier than when protein is administered; all the glycine nitrogen is removed as urea within twenty-four hours. Asparagine more nearly approaches protein in its behaviour, where nitrogen retention may last seventy-two hours. Asparagine also is not so rapidly absorbed as glycine. On the hypothesis that the slow excretion was due to the $\text{CO}\cdot\text{NH}_2$ group in asparagine, glycyl-glycine anhydride, which contains two $\text{CO}\cdot\text{NH}$ groups, should be eliminated more slowly still; the experiment was frustrated by the death of the dog, but there was no evidence that there was any change into glycine or urea. W. D. H.

The Effect of Muscular Work on the Excretion of Endogenous Purines. ERNEST L. KENNAWAY (*J. Physiol.*, 1908, 38, 1—27).—During unaccustomed muscular work, the output of uric acid is lessened, whilst that of purine bases is increased, the total output of purine substances being about normal. A greatly increased output of uric acid follows the work. If the work is repeated, the changes noted show a progressive diminution, but they reappear when another kind of muscular exercise is taken up. The increase in purine bases is attributed to defective oxidation, but is not modified by inhalation of oxygen. The output of these bases exhibits diurnal variations similar to, but less marked than, those which occur in connexion with uric acid. The amount of the latter tends to vary inversely, and that of the bases directly, with the volume of the urine. The experiments are considered to support Leathes' contention that muscular work leads to an increased formation of uric acid. W. D. H.

The Purine Substances Normally Excreted in Man (when neither Tea nor Coffee have been taken). The late MARTIN KRÜGER (*Biochem. Zeitsch.*, 1909, 15, 361—364).—In the urine of a patient who entirely abstained from tea and coffee, the three known methyl derivatives of xanthine usually found in urine, *l*-methylxanthine, heteroxanthine, and paraxanthine, were absent. Guanine was also absent, but xanthine, adenine, and epiguanine were present. Hypoxanthine was absent, and this fact is accounted for by the circumstance that a modified method of isolating the bases was employed, which is described in detail, in which a change of adenine into hypoxanthine does not take place. The results account for the origin of the methylated purine derivatives in urine. S. B. S.

The Excretion and Detection of Atoxyl in the Urine. GEORG LOCKEMANN and MARTIN PAUCKE (*Chem. Zentr.*, 1908, ii, 1542—1543; from *Deutsch. med. Woch.*, 1908, 34, No. 34).—Gadamer's statement (*Apoth. Zeit.*, 22, 566) that atoxyl is not decomposed by hydrogen sulphide is only correct in a limited degree. If the gas is passed through the heated solution acidified with hydrochloric acid, arsenic is precipitated quantitatively. In the presence of strong hydrochloric acid at 0°, hydrogen sulphide also produces a precipitate, which is probably *p*-aminophenylarsenic sulphide, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsS}_2$, or a similar compound. Also in neutral hot solutions, hydrogen sulphide causes a precipitate. If the atoxyl compound is warmed with sulphur dioxide until all the latter is driven off, hydrogen sulphide then causes a yellow precipitate at the ordinary temperature.

Atoxyl preparations are very inconstant in composition; this is not only due to variations in water of crystallisation, but to other compounds mixed with the atoxyl. Atoxyl can be detected by Ehrlich and Berthelm's reaction (*Abstr.*, 1907, i, 812) either in water or in urine. In water 1 mg. in 100 c.c. can be detected; the delicacy of the test in urine is less.

After subcutaneous injection, atoxyl is rapidly excreted in the urine almost wholly unchanged. If the injections are repeated, traces are found for a week afterwards; a small amount of cleavage occurs in the body, as shown by the presence of "free" arsenic in traces in the urine. Later, a certain amount is taken up and bound in the organism, and finally excreted with keratin.

W. D. H.

The Diazo-reaction of Normal Urine. R. ENGELAND (*Chem. Zentr.*, 1908, ii, 1273—1274; from *Münch. med. Woch.*, 1908, 55, 1643—1645).—The statement of Penzoldt and Petri (*Berl. klin. Woch.*, 1883; *Zeitsch. klin. Med.*, 1884) that normal urine gives Ehrlich's diazo-reaction is confirmed. It is attributed to substances, such as histidine, which contain an imino-azo-nucleus, and the absence of the reaction in many normal urines is attributed to the presence of such substances as creatinine, which unite with imino-azo-compounds. In certain pathological conditions, the excretion of the last-named substances is increased.

W. D. H.

A Simple Apparatus for the Cryoscopy of Urine. ERWIN RUPP (*Chem. Zentr.*, 1908, ii, 1536—1537; from *Apoth. Zeit.*, 1908, 23, 714).—A form of apparatus suitable for rapid freezing-point estimations with urine.

W. D. H.

Hydrochloric Acid Content of Gastric Juice in Anchylostomiasis, with Special Reference to its Relationship to Anæmia and Appetite. TANZO YOSHIDA (*Chem. Zentr.*, 1908, ii, 1950; from *Arch. Schiffs. Tropenhyg.*, 1908, 12, 683—697).—The acidity of the gastric juice in Japanese and also in Chinese varies between 45 and 49 degrees of acidity with 0.09—0.17% HCl. In anchylostomiasis these figures remain normal; the juice was rarely subchlorhydric, and still more rarely hyperchlorhydric. The proportion of free hydrogen chloride decreases when anæmia becomes more intense, and the appetite in anchylostomiasis is closely connected with this.

G. B.

Experimental Glycosuria. IV. Cause of the Hyperglycæmia Produced by Asphyxia. JOHN J. R. MACLEOD (*Amer. J. Physiol.*, 1909, 23, 278—302).—Hyperglycæmia lasts some time after asphyxiation. The source of the sugar is the hepatic glycogen, for after extirpation of the liver, hyperglycæmia does not occur. The same is true for the hyperglycæmia produced by curare. The asphyxial (and curare) blood acts directly on the liver cells, for the usual results take place after the hepatic nerves are cut. The substance in the blood considered to be responsible for the action is carbon dioxide, and not loss of oxygen.

W. D. H.

Toxicology of Nickel Carbonyl. H. W. ARMIT (*J. Hygiene*, 1909, 8, 565—600).—The lethal dose of nickel varies according to the animal employed and the method of administration. In the form of nickel carbonyl the conditions for rapid absorption are most favourable, and rabbits die after 3—4 mg. per kilo. of body-weight, and cats after 8.5 mg.

When the gas is breathed, nickel, probably as hydrated basic carbonate, is deposited on the respiratory surface, from which it is taken up by the lymph and blood. It is thus carried to the tissues and deposited there, especially in the brain and adrenals. The histological appearances produced are figured; there is endothelial degeneration, fatty degeneration of the vessel walls and adrenals, and possibly a primary action on the brain cells. Hæmorrhages and other secondary results follow. Nickel is excreted by the kidneys and intestine. Iron-carbonyl produces very similar results, but the fatal dose is larger; cobalt occupies an intermediate position in toxicity. No treatment was found to avert death.

W. D. H.

Chemical Constitution and Physiological Activity of Acids. JACQUES LOEB (*Biochem. Zeitsch.*, 1909, 15, 254—271).—The physiological activity was determined by ascertaining the strengths of various acids necessary to produce a fertilisation membrane in the eggs of sea-urchins. A number of eggs were immersed in solutions of the acids of varying strengths in sodium chloride solution isotonic with sea-water for definite intervals, then transferred back again to sea-water, and the percentage of eggs which had formed membranes determined in each case. It was found in the case of the fatty monobasic acids that the larger number of carbon atoms they contained the more active were they as membrane producers. The hydroxy-acids were less active than the corresponding unsubstituted acids; the polybasic acids were less active than the monobasic. The mineral acids were also less active than organic acids. The conclusion is drawn that the first action of the acids is to penetrate the cell-membranes, and this is a function of the undissociated acid as a whole, and not of the hydrogen ions. The hydrogen ions appear, however, to inhibit the formation of the membrane, as this takes place only after the eggs are transferred back to sea-water after immersion in the acid.

S. B. S.

Is Phenolphthalein Split in the Body? C. FLEIG (*Chem. Zentr.*, 1908, ii, 1374; from *Bull. Sci. Pharmacol.*, 1908, 15, 381—384. Compare Abstr., 1908, ii, 313).—Various organs of the dog were perfused with a solution of phenolphthalein. The amount was the same after as before perfusion, except in the case of the kidney, where it was slightly lessened.
W. D. H.

Influence of the Asymmetric Carbon Atom in Pharmacology. The Action of *d*-, *r*-, and *l*-Camphor on the Chloral-poisoned Frog's Heart. JUHO HÄMÄLÄINEN (*Chem. Zentr.*, 1908, ii, 1451; from *Skand. Arch. Physiol.*, 1908, 21, 64—79).—The three modifications of camphor have no action on the normal frog's heart. They, however, stimulate the heart's action after this has been lessened by chloral. The action of the three kinds of camphor is pretty equal, but that of the *l*-variety is least.
W. D. H.

Chemical Examination and Physiological Action of Nutmeg. FREDERICK B. POWER and ARTHUR H. SALWAY (*Amer. J. Pharm.*, 1908, 80, 563—580).—The narcotic action of nutmeg is generally attributed to myristicin, but owing to the fact that the action of nutmeg itself is much more pronounced than that of an equivalent quantity of pure myristicin, it was considered desirable to make a complete investigation in order to ascertain if other substances are present which contribute to the effect.

The essential and expressed oils of nutmeg have already been studied (*Trans.*, 1907, 91, 2037; 1908, 93, 1653). An examination of the "press-cake" has revealed the presence of the following substances which were not identified in either of the oils: dextrose, tannic acid, colouring matters, resins, and a very small quantity of ipuranol (*Trans.*, 1908, 93, 907; Abstr., 1908, ii, 725).

The results of a physiological investigation have shown that the narcotic property of nutmeg is undoubtedly due to myristicin, but have indicated that this substance when associated with the other constituents is in a more favourable condition for absorption than when it is in a pure state.
E. G.

Absorption, Excretion, and Destruction of Strophanthine. ROBERT A. HATCHER (*Amer. J. Physiol.*, 1909, 23, 303—323).—The absorption of strophanthine is rapid even from ligatured loops of intestine. Absorption when the drug is given by the mouth (in man and dog) is, however, comparatively slow, and with small doses, excretion keeps pace with it, so that a large dose has to be given to produce toxic effects. The amount destroyed in the alimentary canal is small. It can, in the rat, be detected subsequently in all the tissues. The oral administration of strophanthine is regarded as therapeutically irrational.
W. D. H.

Influence of Iodothyryn, Spermine, and Adrenaline on Oxidation Processes, and on the Toxicity of the Urine. A. J. JUSCHTSCHENKO (*Biochem. Zeitsch.*, 1909, 15, 365—452).—In mental diseases the toxicity of the urine varies, being sometimes

increased, sometimes lessened. It is stated that similar variations are produced in animals, accompanied by changes in gaseous metabolism, by the administration of iodothyron, spermine, and adrenaline, or by the extirpation, partial or complete, of the glands which produce these substances. W. D. H.

Behaviour of "Bromoglidin" in the Organism. HEINRICH BORUTTAU (*Chem. Zentr.*, 1908, ii, 1742; from *Deutsch. med. Woch.*, 1908, 34, 1883—1884).—The bromine of "bromoglidin" is secreted in a similar manner to the bromine of potassium bromide, except that secretion is increased. The physiological action appears also to be greater than is indicated by the bromine content.

J. V. E.

Effect of Magnesium on Some of the Toxic Effects of Eserine. DON R. JOSEPH (*Amer. J. Physiol.*, 1909, 23, 215—225).—Although magnesium salts have no influence on eserine myosis, they have a certain value as an antidote in eserine poisoning; thus they abolish the muscular tremor produced by eserine.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Aeration on the Formation of Volatile Products in Alcoholic Fermentation. E. KAYSER and A. DEMOLON (*Compt. rend.*, 1909, 148, 103—105. Compare Abstr., 1907, ii, 714; 1908, i, 317; Trillat, Abstr., 1908, ii, 615).—The authors have compared the action of the champagne yeast No. 3 with that of a yeast (the yeast of bananas No. 221) of a definitely aerobic character on malt extract (containing 15.76% of sugar) with reference to the quantities of volatile acids, esters, aldehydes, and higher alcohols formed. Comparative experiments were made (*a*) in long-necked flasks completely filled in order to avoid contact with the air; (*b*) in shallow vessels two-thirds full and exposing a large surface of liquid to the air. The results are given in tabular form. At the end of one month the quantities of sugar decomposed, and of yeast, volatile acids, esters, and aldehydes formed, by the banana yeast were considerably greater (two to five times) in the shallow vessels than in the flasks, whilst the alcohol content was found to be greater in the unexposed liquid. On the other hand, similar experiments with the champagne yeast showed that exposure to the air had very slight effect on the amounts of sugar decomposed, and yeast formed, decreased those of volatile acids and esters to less than half, doubled the amount of higher alcohols, and enormously increased the proportion of aldehydes.

At the end of six months the effect of exposure to air on the action

of the banana yeast is still to increase the amount of sugar decomposed and of yeast formed, although to a smaller extent than after one month, but to largely decrease the amounts of volatile acids and esters. Only traces of aldehyde are found in either exposed or unexposed liquids.

After six months, comparison of the exposed with the unexposed liquids fermented with the champagne yeast shows that the weights of yeast, aldehydes, and higher alcohols are greater, and that of esters is less, in the former than in the latter. Addition of mercuric chloride to the liquid fermented by the champagne yeast in a shallow vessel for six months reduces the amounts of yeast and aldehydes formed, but increases those of esters, ethyl alcohol, and higher alcohols, probably by protecting these from oxidation. E. H.

Influence of Inorganic Salts, particularly of Stannous Chloride, on Fermentation. G. GIMEL (*Compt. rend.*, 1908, 147, 1324—1326).—Kayser and Marchand have shown that small traces of manganese favour alcoholic fermentation. The author now finds that the effect of stannous chloride on various species of yeast is even more marked, a culture containing one part in 10,000 producing 4% more alcohol than the control. G. B.

Denitrification. MASANIELLO CINGOLANI (*Chem. Zentr.*, 1908, ii, 19, 1626; from *Staz. sperim. agrar. ital.*, 1908, 41, 530—540).—Five grams of fresh faeces (from a calf) were placed in 100 c.c. of a 0.3% solution of sodium nitrate, and two organisms which cause denitrification were isolated. Both were cocci, and they are termed *Bacillus porticensis denitrificans*- α and - β . The latter attacks nitrates, reducing them to nitrites, but it has no further action; the former reduces nitrites to ammonia and then to free nitrogen, but has no action on nitrates. Ammonia is said to be an intermediate product; when ammonium nitrate is used in place of sodium nitrate, the reaction is much accelerated. E. J. R.

Sewage Purification. W. MAIR (*J. Hygiene*, 1909, 8, 609—654).—An experimental discussion of the methods of sewage purification, especially in relation to the part played by bacteria. In the contact beds, a considerable proportion of the organic nitrogen disappears as gas as a result of alternate nitrification and denitrification. The amount of nitrate in the effluent is a direct measure of the degree of aeration to which the sewage has been exposed in the percolating beds. If the nitrate disappears from a contact bed, it is a sign that the bed is being overworked; the denitrifying process being allowed to proceed too far. So long as nitrate is present, cultures of the *Bacillus hyponitrosus* have no putrefactive odour. W. D. H.

Standardisation of Disinfectants. Emulsified Disinfectants. HARRIETTE CHICK and CHARLES J. MARTIN (*J. Hygiene*, 1909, 8, 654—697, 698—703. Compare Watson, *Abstr.*, 1908, ii, 976).—In any method of standardisation, it is necessary that the tests be carried out under constant conditions of temperature, culture medium,

number of bacteria per unit volume, and duration of observation. A logarithmic relation exists between concentration of the disinfectant and velocity of disinfection. In the case of metallic salts, traces of the disinfectant carried over with the test sample must be neutralised by sulphide; in the case of mercuric chloride, an excess of sulphide is necessary to decompose a compound formed between the salt and the substance of the bacterium.

Some disinfectants are more efficient against one species of bacterium, others against another. In the case of spores, metallic salts are most efficient. As a rule, virulent species are more difficult to kill than non-virulent ones. In the process of standardisation, it is therefore necessary to fix on a particular organism in the test. *Bacillus typhosus* is the best to employ, but a non-virulent strain should be selected in order to minimise danger to those engaged in the test.

The presence of 10% of blood-serum reduces the efficiency of 1% of phenol by about 12%. The effect on emulsified disinfectants is somewhat greater. The presence of finely particulate matter affects the germicidal value of emulsified disinfectants containing the higher phenols to a much greater extent than it does solutions of phenol. The removal of an emulsion of the higher phenols by bacteria, by finely divided animal charcoal, by dust, etc., obeys in all cases the same quantitative laws. Finer emulsions are more seriously reduced in value by particulate matter than coarser ones.

The removal of an emulsion of higher phenols by bacteria is in the first instance a process of adsorption; disinfectants of this class possess superior efficiency, because owing to this adsorption the bacteria rapidly become surrounded by the disinfectant in much greater concentration than exists throughout the liquid. W. D. H.

Degradation of Sugar during the Respiratory Process.

P. BOYSEN JENSEN (*Ber. Deut. bot. Ges.*, 1908, 26a, 666—667).—Alcoholic fermentation is identical with the intramolecular respiration of seeds, and the latter process is the starting point for normal respiration. In alcoholic fermentation, dihydroxyacetone is formed as an intermediate product; if hydroxylamine hydrochloride is added during fermentation, the oxime is formed in small quantity, and after the end of the fermentation, dihydroxyacetone can be isolated as its phenylmethylosazone. Dihydroxyacetone, prepared by Fenton and Jackson's method, yields, on fermentation, alcohol and carbon dioxide. Zymase consists, therefore, of two separate enzymes: *dextrase* and *dihydroxyacetonease*.

In a glycerol solution of dextrose, the second of these is inhibited, so that dihydroxyacetone is the end product. Dihydroxyacetone is also decomposed by oxydase, yielding carbon dioxide and water, but not alcohol. The fact that oxydase attacks neither sugar nor alcohol leads to the hypothesis that in the normal respiration of plants, dihydroxyacetone is the immediate precursor of the carbon dioxide and water; in intramolecular respiration, that is, in an atmosphere deprived of oxygen, it yields carbon dioxide and alcohol. The process of normal respiration can therefore be imitated by adding oxydase to

a fermenting dextrose, the degradation of the latter then taking place as follows: $C_6H_6O_6 \rightarrow OH \cdot CH_2 \cdot CO \cdot CH_2 \cdot OH \rightarrow CO_2 + H_2O$.

G. B.

The Rôle of Zymases in the Respiratory Processes of Seed-plants. S. KOSTYTSCHOFF (*Biochem. Zeitsch.* 1908, 15, 164—195).—It has been shown by various observers that anaerobic respiration of pea-seeds is in all essential respects identical with the process of typical alcoholic fermentation. Experiments were carried out to throw further light on the mechanism of the reaction, by determining the amount of alcohol and carbon dioxide produced by pea-seeds and wheat embryos in the presence and absence of air, and in the presence of sugar, and also in the intermediate products formed from the latter by yeast fermentation. It was shown that the assumption that the alcoholic fermentation of seed-plants is independent of the oxygen respiration will not hold, in that such powerful excitants of alcoholic fermentation as pea-seeds produce, with full aeration, no alcohol. Furthermore, alcohol does not appear to be a normal intermediate product of sugar utilisation, for although pea-seeds will when aerated consume slowly the alcohol previously produced in absence of air, the consumption is not accompanied by an increased output of carbon dioxide. Wheat-seeds and embryos do not possess this capacity for alcohol consumption at all. On the other hand, dextrose causes an increased production of carbon dioxide. Solutions containing the intermediate products of fermentation (produced, for example, by the action of zymase in the presence of phosphates) cause an even larger carbon dioxide output than sugar itself. The greater part of the primary products of the zymase action appear to be immediately oxidised further without production of alcohol. The presence of the latter substance in certain seeds is to be explained on the assumption that these primary products do not all undergo immediate oxidation; in this case they are converted into carbon dioxide and alcohol, which latter must be regarded as a by-product only, of the respiratory processes.

S. B. S.

Phosphorus and the Formation of Amino-acids in Higher Plants. FRANCESCO SCURTI (*Chem. Zentr.*, 1908, ii, 16, 1370; from *Staz. sperim. agrar. ital.*, 1908, 41, 456—470).—The non-protein nitrogen compounds in plants are made up of the same substances as are found in germinating seeds and in young seedlings. Phosphorus is known to play an important part in protein formation, and the author considers that it may function in the formation of amino-acids.

E. J. R

Occurrence and Rôle of Zinc in Plants. MAURICE JAVILLIER (*Chem. Zentr.*, 1908, ii, 1828; from *Bull. Sci. Pharm.*, 1908, 15, 559—565).—Besides certain well-defined varieties growing on soils which are rich in zinc, most plants contain appreciable quantities of this metal, which is especially found in Conifers. The growth of yeast is favoured by small quantities of zinc, although the optimum concentration of the metal is greater than in the case of *Aspergillus*.

Zinc can also act favourably on the growth of Phanerogams, for example, cereals. G. B.

The Chemical Processes of Ripening. The Ripening of Oranges. Presence of Asparagine and Glutamine in the Juice. FRANCESCO SCURTI and G. DE PLATO (*Chem. Zentr.*, 1908, ii, 16, 1370; from *Staz. sperim. agrar. ital.*, 1908, 41, 435—455).—The authors draw the following conclusions from their experiments: (1) The acidity of oranges is due to citric and malic acids, the quantity of which increases in the earlier stages, but falls off afterwards. In this respect oranges resemble other acid fruits. (2) The sugars present are dextrose, lævulose, and sucrose; the two first steadily increase during ripening, whilst the sucrose decreases. There is more lævulose than dextrose. In sweet and in bitter oranges there is more reducing sugar than sucrose, but not in common Italian oranges. No relationship could be discovered between acidity and the amount of sucrose present. (3) The total nitrogenous matter decreases, but the loss falls entirely on the proteins precipitated by basic lead acetate and not on the other nitrogen compounds, which remain constant in amount. These non-protein compounds consist chiefly of asparagine and glutamine it is significant that these two, which are constantly associated with germination and assimilation, should also be present during ripening.

E. J. R.

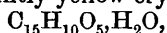
The First Stages in the Development of Perennial Plants compared with those of Annuals. GUSTAVE ANDRÉ (*Compt. rend.*, 1908, 47, 1485—1487).—During the first two years of the life of a perennial plant, the root is much more developed, relative to the shoot, than is the case in annual plants, and contains a larger proportion of phosphates than the root of the latter. G. B.

Constituents of the Fruit of *Rhamnus cathartica*. NICOLAI A. WALJASCHKO and N. KRASOWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1502—1509).—Discussion of previous work on this subject (see Tschirch and Pedersen, *Abstr.*, 1898, i, 599; Hesse, *Abstr.*, 1900, i, 40; Tschirch and Polacco, *Abstr.*, 1900, i, 681) and of the results obtained by Krasowsky (see following abstract). T. H. P.

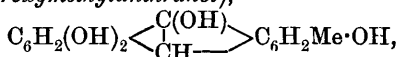
Berries of *Rhamnus cathartica* and the Methods of Separating the Substances Contained Therein. N. KRASOWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1510—1569. Compare Tschirch and Polacco, *Abstr.*, 1900, i, 681).—After describing in detail the methods used for extracting the various constituents from the berries and purifying them, the author discusses separately each of these constituents, which are as follows.

(1) Quercetin, apparently identical with that obtained from quercitrin. (2) Rhamnetin. (3) Xanthorhamnin (compare Tanret and Tanret, *Abstr.*, 1900, i, 185), which is hydrolysed by dilute sulphuric acid, giving rhamnetin, galactose, and rhamnose (2 mols.): $C_{34}H_{42}O_{20} + 3H_2O = C_{15}H_9O_7 + C_6H_{12}O_6 + 2C_6H_{12}O_5$. The only difference between the product described by Tanret and Tanret (*loc. cit.*) and that obtained

by the author is that the former gives golden-yellow crystals, whilst the latter separates in faintly yellow crystals. (4) Emodin,



m. p. 254—255°, which is a trihydroxymethylanthraquinone, and closely resembles frangula-emodin (compare Oesterle, Abstr., 1900, i, 304). (5) *Rhamnoxanthin*, $C_{21}H_{20}O_9 \cdot H_2O$, which is reduced to methylanthracene by zinc dust in an atmosphere of hydrogen, and readily undergoes transformation into emodin when crystallised repeatedly from alcohol. *Tetra-acetylramnoxanthin*, $C_{21}H_{16}O_9Ac_4$, crystallises from acetic acid in microscopic, pale yellow needles, m. p. 146—149°. Rhamnoxanthin is a glucoside, and is resolved into emodin and methylpentose on hydrolysis with dilute hydrochloric acid: $C_{21}H_{20}O_9 + H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_5$. (6) *Jesterin*, $C_{26}H_{30}O_{13} \cdot \frac{1}{2}H_2O$, m. p. 205—218°, which is a glucoside yielding emodinanthranol, hexose, and pentose on hydrolysis: $C_{26}H_{30}O_{13} + 2H_2O = C_{15}H_{12}O_4 + C_6H_{12}O_6 + C_5H_{10}O_5$. (7) *Rhamnocathartin*, $C_{27}H_{30}O_{14}$, which is hydrolysed by alkali, giving rhamnoxanthin and an unknown hexose, $C_{27}H_{30}O_{14} + H_2O = C_{21}H_{20}O_9 + C_6H_{12}O_6$, and by acid, giving emodin, rhamnose, and hexose, thus: $C_{27}H_{30}O_{14} + 2H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_5 + C_6H_{12}O_6$. (8) *Emodinanthranol* (*trihydroxymethylanthranol*),



which separates from ethyl acetate in faintly yellow crystals, m. p. 280°; its *tetra-acetyl* derivative, $C_{15}H_8O_4Ac_4$, crystallises from alcohol in pale yellow plates, m. p. 197°. In alkaline solution, emodinanthranol is oxidised by the oxygen of the air, yielding emodin,

$C_6H_2(OH)_2 \begin{array}{c} \text{CO} \\ | \\ \text{CO} \end{array} \text{---} C_6H_2Me \cdot OH$, reduction of which by means of tin and hydrochloric acid yields emodinanthranol. (9) Rhamnonigrin or a mixture of rhamnonigrins, which were not characterised. (10) Succinic acid.

The berries of *Rhamnus cathartica* contain dextrose in the free state, and galactose, rhamnose, and pentose only in the form of glucosides. T. H. P.

Chemistry of the Higher Fungi. II. *Polyporus ignarius*.

JULIUS ZELLNER (*Monatsh.*, 1908, 29, 1171—1187. Compare Abstr., 1908, ii, 216).—The constituents of *Polyporus* closely resemble those of *Trametes suaveolens* previously examined (*loc. cit.*), in accordance with the fact that these closely-related fungi are parasitic on the same host (willow). The ash (with much calcium sulphate), ergosterols, fats, resins, soluble proteins and volatile substances, dextrin-like carbohydrates (which are abundantly present), and ferments are all very similar. The constituents of the cell wall, however, are different, and, unlike *Trametes*, *Polyporus* contains mannitol and tannins, but no mycose. G. B.

Presence of Urea in Certain Higher Fungi. A. GORIS and M. MASCRÉ (*Compt. rend.*, 1908, 147, 1488—1489).—Young specimens of *Psolliota campestris* contain urea to the extent of 2.75%, and mature ones, 4.3% of their dry weight (compare Abstr., 1903, ii, 567). G. B.

Some Mannas and Related Products. ALFRED EBERT (*Chem. Zentr.*, 1908, ii, 1874—1875; from *Zeitsch. Allg. Oesterr. Apoth. Ver.*, 1908, 46, 427—429, 439—440, 447—450, 459—460, 467—470, 479—481, 491—492, 503—504, 515—516, 529—530).—This gives the proximate composition of a number of Persian and Australian mannas. The figures given below are expressed in percentages of the crude materials, except where otherwise stated.

“Trehala,” derived from the larval cocoons of a beetle living on the stems and flowering heads of *Echinops persicus*, contains moisture 11.1, ash 2.6, trehalose 17.5, gum (yielding mucic acid on oxidation) 27.1, and tannin and residue 44.5; of the residue, 71% consists of a starch giving a reddish-brown colour with iodine.

“Terendschabin” is exuded from the leaves and thorns of *Alhagi maurorum*; it consists of moisture 5.2, ash 9.4, chlorophyll with some gum 0.5, sucrose 42.0, a gum (yielding oxalic acid on oxidation) 20.3, and residue 32.0.

“Bide-khecht,” derived from the leaves of *Salix fragilis*, contains moisture 4.1, ash 25.4, dextrose 17.5, sucrose 50.1, matter soluble in water 13.3, and insoluble matter 19.2. The sample was adulterated with wheat-flour and gypsum.

“Gueze-elefi,” from *Quercus vallonica*, contains moisture 7.5, ash 5.4, sucrose 53.2, dextrose 19.0, gum (yielding mucic acid on oxidation) 10.3, and insoluble residue 10.0.

“Schir-Khist,” the manna from *Cotoneaster nummularia*, contains moisture 15.9, ash 2.2, dextrose 37.5, sucrose 12.9, gum (yielding mucic acid) 24.2, and insoluble residue 9.5.

“Eucalyptus manna,” from *E. Gunnii*, var. *rubida*, contains moisture 9.7, ash 6.8, melitose 68.5, dextrose 20.9, sucrose 2.1, gum (yielding mucic acid) 3.2 and insoluble residue 4.3. A specimen from *E. pulverulenta*, S., consists of melitose 21.4, lævulose 16.2, sucrose 60.0, and insoluble residue 1.0.

Tabasheer, a siliceous deposit from bamboo culms, especially *Bambusa stricta* R., contains sucrose 4.2, gum (yielding mucic acid) 2.6, and inorganic residue about 90 (compare Ince, Abstr., 1897, ii, 278).

T. A. H.

Mode of Combination of Mineral and Organic Acids in Wine. ANTONIO QUARTAROLI (*Bied. Zentr.*, 1908, 37, 862; from *Staz. sper. agrar. ital.*, 1906, 39, 993).—The mineral acids of wine are in the form of salts unless present in very large amounts. Addition of mineral acids can be detected by determining the electrical conductivity, which is distinctly increased by adding potassium hydroxide to wine containing neither mineral nor free organic acid. When organic acids have been liberated by addition of mineral acid, the conductivity is diminished by adding potassium hydroxide. Addition of 1 gram of sulphuric acid per litre can be detected in this manner.

N. H. J. M.

Amounts of Nutrients Utilised by Sugar-beet in the First Year, and their Relation to the Amount of Sugar in the Roots. KARL ANDRLÍK and JOSEF URBAN (*Zeitsch. Zuckerind. Böhm.*, 1909, 33, 221—240. Compare Abstr., 1908, ii, 1066).—For

a yield of 400 quintals per hectare of roots, it was found that the indispensable amounts of phosphoric acid, nitrogen, and potash were 65.1, 139.8, and 168.6 kilos. respectively. The amount of phosphoric acid is thus approximately the mean of the amounts found by Hoffmann (71.4) and by Willfarth (62.0 kilos.), whilst the amount of nitrogen is lower, and that of potash higher, than those given by Hoffmann and Willfarth; the yield of sugar in Bohemia was, however, also higher than the yields obtained in Germany.

At present the most favourable relations of the different nutrients are $N=2.15$ and $K_2O=2.59$ to 1 part P_2O_5 . When, by selection, roots are obtained containing higher amounts of sugar, it will be necessary to ascertain whether these amounts still hold good.

N. H. J. M.

Influence of Some Calcium Compounds on the Manurial Value of Ammonium Sulphate and Calcium Cyanamide.

ALEXANDER STEBUTT (*Bied. Zentr.*, 1908, 37, 805—806; from *Fuhling's Landw. Zeit.*, 1907, 56, 669).—Pot experiments in which mustard was grown in loam, containing 0.09% of calcium carbonate, and manured with ammonium sulphate and calcium cyanamide in conjunction with calcium oxide, carbonate, and sulphate respectively. The conclusion is drawn that, under normal conditions, the calcium compounds are without effect on the action of the two nitrogenous manures.

N. H. J. M.

Is Dicyanodiamide Poisonous to Crops? OSCAR LOEW (*Chem. Zeit.*, 1909, 33, 21—22. Compare Abstr., 1908, ii, 775).—Pot experiments with barley in garden soil with mineral manures and with $N=0.75$ gram in the form of dicyanodiamide (1 and 2) and as ammonium sulphate (3). The soil of (1) was heated at 100° for one hour. A fourth pot was without nitrogen.

The highest amount of dry matter (43.2 grams) was obtained in the pot which had ammonium sulphate. Dicyanodiamide in heated soil gave the next highest amount (31.3 grams), then the pot which had no nitrogen (24.8 grams), and last, dicyanodiamide in non-sterilised soil. The conclusion is drawn that dicyanodiamide is directly utilised by plants under sterilised conditions, but that in unsterilised soil it is converted by microbes into substances injurious to plants.

N. H. J. M.

Phosphoric Acid with Different Citric Acid Solubility as Manure for Meadows. HANNO SVOBODA (*Chem. Zentr.*, 1908, ii, 1893; from *Zeits. Landw. Versuchswes. Oesterr.*, 1908, 11, 733—774).—Whilst the rapidity of action of phosphate manures depends on a high percentage of phosphoric acid soluble in citric acid, the value of the manure depends mainly on the amount of total phosphoric acid.

N. H. J. M.

The Causes which Determine the Replacement of Potassium of Leucite in Soils. LUIGI BERNARDINI (*Chem. Zentr.*, 1908, ii, 1285; from *Staz. sperim. agrar. ital.*, 1908, 41, 304—320).—The leucite used contained when dried at 110° : SiO_2 , 56.89; Al_2O_3 + Fe_2O_3 , 24.08; K_2O , 15.63; Na_2O , 1.77; CaO , 1.11; MgO , traces.

The solubility was determined in hydrochloric acid, 5% acetic acid, water, a solution of carbon dioxide in water, and in a number of salt solutions including sodium chloride, nitrate and sulphate, ammonium chloride, nitrate, sulphate and carbonate, calcium chloride, nitrate, sulphate and dihydrogen phosphate, and magnesium chloride, nitrate and sulphate. Sodium and ammonium salts caused a good deal of potassium to go into solution; magnesium and calcium salts, on the other hand, had only a slight solvent power. The author considers that double decomposition takes place, the potassium of the leucite being replaced by sodium or ammonium. Ammonia produced in the soil by bacterial processes would therefore react with leucite, forming an insoluble ammonium leucite, whilst at the same time a soluble potassium compound is formed which is available for plants. The ammonia can no longer be washed away by rain, but may still be nitrified.

E. J. R.

Humus-Silicic Acid. HJALMAR VON FEILITZEN (*Bied. Zentr.*, 1908, 37, 793—794; from *Svenska Mosskulturforening Tidskr.*, 1907; and *Wiener landw. Zeit.*, 1907, No. 43).—The manure, which is prepared from peat, has the following composition: water, 10.12; organic matter, 46.13; N, 1.26; K₂O, 2.64; CaO, 6.44; P₂O₅ (a) soluble in boiling 24% HCl, 3.33; and (b) citrate soluble, 2.55%.

Application of the manure alone (1000 kilos. per hectare) to a poor, sandy soil increased the yield of peas, but was without effect on oats, owing to the deficiency of nitrogen in the soil. When applied in conjunction with other manures, humus-silicic acid gave similar results with peas, and very slightly increased the yield of oats.

N. H. J. M.

Analytical Chemistry.

Simplified Apparatus for Gas Analysis at a High Temperature. ANTOINE DE SAPORTA (*Chem. Zentr.*, 1908, ii, 1377—1378; from *Rev. gen. chim. pure appl.*, 1908, 11, 311—314).—The apparatus consists essentially of a distilling flask, a repeatedly bent delivery tube, a graduated cylinder, and a small trough filled with mercury placed in a larger vessel containing water. In the delivery tube just before it reaches the graduated cylinder and under the surface of the mercury is a small hole. If now, from whatever cause, the evolution of gas ceases, mercury ascends into the delivery tube, and equilibrium is restored, so that absorption can never take place. L. DE K.

Quantitative Folded Filter Papers. F. HART (*Chem. Zeit.*, 1908, 32, 1228).—The author advocates more general use of folded filter papers for quantitative work where rapid filtration is required; their use is recommended, especially when working with fine quartz-sand and colloidal precipitates. J. V. E.

Pressure-equalising Attachment for Desiccators. EDWIN DOWZARD (*Amer. J. Pharm.*, 1908, 80, 588).—The following arrangement has been devised in order to obviate the lifting of the lid of a desiccator caused by the expansion of the air when a hot crucible or basin is placed in it, and the subsequent reduction of the pressure on cooling. A calcium chloride U-tube is placed in the lower part of the desiccator, and carries an arm which passes through a perforated rubber stopper in the side of the desiccator. E. G.

Estimation of Halogens in Organic Compounds. C. W. BACON (*Chem. News*, 1909, 99, 6; *J. Amer. Chem. Soc.*, 1909, 31, 49—52).—The following details are given for successfully carrying out halogen determinations by Stepanoff's method (Abstr., 1905, i, 335). Let w represent the number of grams of halogen compound taken (about 0.2) in a dry Kjeldahl flask; it is warmed under a reflux condenser with $156w$ c.c. of, at least, 98% alcohol if the compound contains chlorine, $68w$ c.c. if it contains bromine, or $44w$ c.c. if it contains iodine. The addition of sodium must extend over 30 minutes, the weight of metal required being $19.5w$ grams, $8.5w$ grams, or $5.5w$ grams, according as the substance contains chlorine, bromine, or iodine. When all the sodium is added, the solution is gently boiled for an hour, allowed to cool to $50-60^{\circ}$, diluted freely with water, and acidified with nitric acid. A moderate excess of silver nitrate is added, and, when quite cool, the excess of silver nitrate is estimated volumetrically by Volhard's method. If the halogen involved is chlorine, the precipitate should be filtered off; with bromine or iodine this is not necessary; when copiously diluted with water, the presence of alcohol does not interfere with titration. J. V. E.

Detection and Estimation of Chlorates. JUAN FAGES VIRGILI (*Anal. Fis. Quim.*, 1908, 6, 459—476).—Two solutions are recommended as a means of detecting chlorates in the absence of certain oxidising agents (enumerated below): the first, *A*, a solution of 50 grams of aniline hydrochloride in 1000 c.c. of hydrochloric acid, D 1.12; the second, *B*, a solution of 50 grams of the same salt in 1000 c.c. of hydrochloric acid, D 1.14. *B* is used instead of *A* when the solution to be tested is dilute, so that more of the latter has to be used in the test. This is generally carried out by taking 1 drop to 1 c.c. of the solution (or a small fragment to 1 gram of solid) in a test tube, and adding 1 c.c. to 4 c.c. of solution *A*; a chlorate produces an intense blue coloration. This is primarily due to chlorine being liberated and acting on the aniline salt, so that a number of oxidising agents (chlorine, hypochlorites, hypobromites, bromates, iodates, peroxides, chromates, manganates, permanganates, vanadates, and ferricyanides) also produce it; but dilute nitric acid, solutions of nitrates, and nitrites do not give the blue colour, so that the test is very useful for detecting chlorates in many special cases, for example, in nitres, explosives, urine. By means of it, 0.00007 gram of potassium chlorate can readily be detected. In presence of bromides or iodides, the reagent does not give an indication with chlorates or other oxidising agents; in such a case, the haloids have to be first removed

by adding silver nitrate in excess, and then sodium chloride to precipitate the excess of silver; the filtered solution is used as just stated.

In the absence of oxidising agents, the solutions *A* and *B* can be used to estimate small quantities of chlorates colorimetrically. Solution *A* is used for quantities of 0.0001 to 0.0022 gram per 5 c.c., and *B* for quantities from 0.0005 to 0.0070. Twenty c.c. of the reagent are then added to 5 c.c. of the solution. For larger quantities of chlorate up to 0.01 gram, 40 c.c. of *B* are added to 10 c.c. of the solution. The colour obtained after twenty minutes is compared with that of a series of solutions containing known quantities of chlorate, and differing from one tube to another by 0.0005 gram for quantities between 0.005 and 0.01 gram, and by 0.00025 for quantities between 0.002 to 0.005 gram. Another method is to make the colour comparison by means of successive dilution until the shades correspond. The results obtained are very good. W. A. D.

Detection of Fluorine in Beer. JULES FLAMAND (*Bull. Soc. chim. Belg.*, 1908, 22, 451—453).—One litre of beer deprived of carbon dioxide by shaking is rendered alkaline by addition of ammonium carbonate and ammonia, a few c.c. of saturated sodium sulphate solution are added, and the liquid is heated to boiling. A 10% solution of barium chloride is added, and, after boiling for ten minutes, the precipitate is allowed to settle; the clear liquid is decanted, and the deposit is collected on a filter, which is then at once placed in a drying oven; the precipitate need not be washed.

When dry it is detached from the filter, transferred to a platinum crucible, and gently ignited. When cold, the crucible is placed in a cold water-bath. A little sulphuric acid is added, and the crucible covered with a paraffin-coated glass plate on which some lines have been engraved. The plate must be kept cool by any suitable arrangement, and the water-bath is then heated to boiling and kept so for an hour. If fluorine is present, the usual etching will be obtained.

L. DE K.

Estimation of "Neutral" Sulphur in Urine. LEO HESS (*Chem. Zentr.*, 1908, ii, 1290; from *Berlin klin. Woch.*, 1908, 45, 1452—1453).—Five hundred c.c. of urine are mixed with 25—50 c.c. of hydrochloric acid and excess of barium chloride, and heated to boiling in a flask fitted with a bulb apparatus containing alkaline pyrogallol; the heating is then continued for six hours on the water-bath. After twenty-four hours, the liquid is filtered, rendered alkaline with sodium hydroxide, and saturated with chlorine. After the lapse of a few hours, the liquid is acidified with hydrochloric acid and boiled. The barium sulphate thus formed represents the "neutral" sulphur.

L. DE K.

Estimation of Sulphuric Acid as Barium Sulphate. ERNST RUPPIN (*Chem. Zeit.*, 1908, 33, 17—18).—Barium chloride should be added to the boiling acid solution all at once, and in quantity about twice that actually required. The precipitate should then be boiled

four times in succession with acidified water. Better results are, however, obtained by precipitating the sulphate in presence of sodium hydrogen carbonate (about 0.5 gram to 1 gram of sulphate); the co-precipitated carbonate is then re-dissolved by addition of hydrochloric acid. The barium sulphate thus obtained is, after careful washing, perfectly pure.

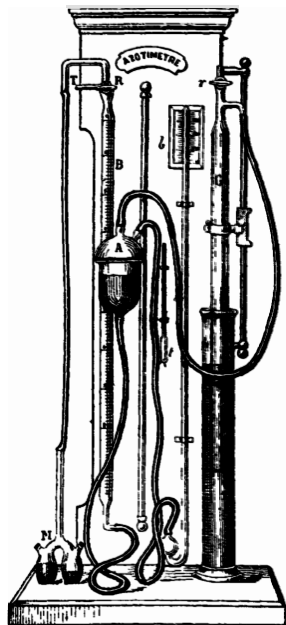
L. DE K.

Estimation of Sulphuric Acid in Leather. JOHANNES PAESSLER and ARNOLDI (*Chem. Zentr.*, 1908, ii, 1297; from *Collegium*, 1908, 358—362).—Five grams of the finely-divided sample are placed in a platinum boat and mixed with 5 c.c. of 10% sodium carbonate and 1.5—1.8 grams of cobaltic oxide. If only combined sulphate is to be estimated, no sodium carbonate is used. After drying, the mixture is heated in a slow current of oxygen; the boat is placed either in a wide combustion tube or else in Schopper's electric apparatus.

L. DE K.

Nitrometer [Volumeter] with Barometric Correction. HERMAN (*Bull. Soc. chim. Belg.*, 1908, 22, 440—444).—The nitrometer, which, however, is suitable for a more extended application, will be readily understood from the figure.

The reservoir *A* is filled with a sufficient quantity of water, and the stopcock *R* is turned in such a manner that the interior of the burette *B* is in communication both with the outer air and the mixer *M*. The air-tap *r* of the gasometer should be open. *M*, which contains the substance, and also the reagent needed to liberate the gas, is attached to the burette, and the water level is brought to zero by raising the reservoir. Stopcock *R* is then turned so as to shut off the air, but to still leave the connexion with the burette. At this moment the reaction is started by allowing the contents of *M* to mix; it is seized by the stem and well shaken. The gas evolved displaces the liquid in the burette, and when the water level shows no further alteration, the reservoir is lowered and the levels are restored. The barometric correction is made by reducing the pressure of the gas evolved to 760 mm. *R* is then turned so as to close the upper part of *B*. If the pressure indicated by the barometer exceeds 760°, the bell jar is raised after closing the air-tap *r*. The mercury level falls while the volume of gas in the burette is increasing. If the pressure is less than 760 mm., the reverse happens. In either case the pressure is brought to 760 mm., and this will be the same both in the barometer and the burette, as both are connected with the reservoir. The



thermometer employed has a scale attached to it for correction for temperature and tension of aqueous vapour, but this scale is not shown in the figure. A table is given for correcting the volume of the gas for the temperature of 17°, also for 0°, and in the dry state. To save calculation, the burette is also graduated so as to show the weight in milligrams of the gas.

L. DE K.

Estimation of Phosphoric Acid as Ammonium Phosphomolybdate. HENRI PELLET (*Ann. Chim. anal.*, 1908, 14, 7—11).—Chesneau's process (Abstr., 1908, ii, 427) is recommended for the estimation of phosphorus in iron and steel, and for the accurate estimation of very minute quantities of phosphoric acid in general.

L. DE K.

Estimation of Phosphoric Acid in Basic Slags by Weighing the "Yellow Precipitate." ZYGMUNT ROMAŃSKI (*Chem. Zeit.*, 1909, 33, 46—47).—Fifteen c.c. of the sulphuric acid solution prepared as usual (= 0.15 gram of the sample) are neutralised with 15% sodium hydroxide solution, using phenolphthalein as indicator. Five c.c. of acid mixture (34 c.c. of sulphuric and nitric acid, D 1.2, up to one litre) are added, and the whole heated to boiling. Fifty c.c. of molybdate solution are added, and, after remaining overnight, the precipitate is collected at the pump on a Neubauer crucible, washed with 1% nitric acid, then with alcohol, and finally with highly volatile light petroleum, D 0.7. After drying at 40°, it is weighed; multiplication by 0.03496 gives the amount of phosphoric anhydride.

When dealing with citrate-soluble acid, 20 c.c. of the solution (= 0.2 gram sample) are mixed with thirty c.c. of the above acid, heated to boiling, and precipitated with fifty c.c. of molybdate solution.

The molybdate solution should be prepared as follows: four litres of nitric acid and 1600 grams of ammonium nitrate are placed in a ten-litre flask, and the temperature is raised to 20°. Six hundred grams of ammonium molybdate are dissolved in 2800 c.c. of hot water, cooled to 30°, and then poured into the acid liquid with constant shaking. When clear, the reagent is filtered and ready for use.

L. DE K.

Estimation of Mineral Constituents in Vegetable Substances. L. VUAFLART (*Bull. Assoc. Chim. suc. dist.*, 1908, 26, 448—455).—Phosphoric acid is generally estimated by burning the substance in the presence of calcium oxide, but even this does not prevent a loss of the acid, particularly in the case of wheat. It is, therefore, advisable to destroy the organic matters by heating the substance in a Kjeldahl flask with sulphuric acid and a globule of mercury, adding afterwards some nitric acid to complete the oxidation; the phosphoric acid is then estimated by the molybdate process. Potassium may be estimated as usual, after destroying the organic matters with sulphuric and nitric acids, but equally accurate results are obtained by moistening the substance with sulphuric acid and subsequent ignition. Chlorine will be retained completely in the ash if the substance is mixed previously with calcium oxide (5 : 2). Sulphur

and sulphates may be estimated without loss by boiling the substance with nitric acid, expelling the excess of the latter, neutralising with sodium carbonate, and, finally, heating the dry mass. Manganese is estimated in the ash by the lead peroxide method. Nitrates are best estimated as nitric oxide in the Schloessing apparatus. The author removes interfering matters by adding to the hot aqueous extract treble the volume of alcohol. After a few days, the solution is filtered, and the filtrate concentrated to a few c.c. L. DE K.

Estimation of Silver. FRANZ MAWROW and G. MOLLOW (*Zeitsch. anorg. Chem.*, 1909, 61, 96—99).—On the addition of hypophosphorous acid to a boiling solution of silver nitrate, heating being continued until the liquid is clear, a black precipitate of silver separates, immediately becoming grey; this is collected, washed with 96% alcohol until free from acid (water causes it to pass through the paper), dried, and weighed as silver. The operation is complete in ten to fifteen minutes, and gives accurate results. The presence of organic acids is without influence.

Lead is precipitated by hypophosphorous acid as lead hypophosphite. C. H. D.

Estimation of the Hardness of Water. KLUT (*Chem. Zentr.*, 1908, ii, 1953; from *K. Prüf.-Anst. Wasserversorg. Abwasserbeseit.*, 1908, 10, 75—85).—From a comparison of methods for estimating the hardness of water, it is found that gravimetric methods alone are trustworthy, although for rapidly ascertaining the total hardness of a hard water containing much magnesium, Clark's soap method gives good results. The Wartha-Peeifer-Lunge gravimetric method is not so simple, or so accurate as the soap method. Carbonate hardness is best determined by Lunge's method of titration, using *N*/10 acid and methyl-orange as indicator. The adoption of the terms *carbonate hardness* instead of "temporary hardness," and *mineral acid hardness* for "permanent hardness," is advocated.

J. V. E.

Precipitation of Magnesium as Ammonium Magnesium Phosphate. ERCOLE RAFFA (*Gazzetta*, 1908, 38, ii, 556—566).—The author has made a number of experiments to determine the conditions influencing the precipitation of magnesium as ammonium magnesium phosphate.

The amount of precipitate obtained increases with the proportion of ammonia present, but never reaches the theoretical quantity if the precipitation is carried out in the cold (compare Neubauer, *Abstr.*, 1896, ii, 674). The presence of much ammonia or of ammonium chloride is useless to prevent precipitation of magnesium hydroxide. The only effect of excess of ammonia is to diminish the solubility of the ammonium magnesium phosphate, an advantage which is often counteracted or greatly diminished by the possible formation of more complex phosphates, such as $\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2$.

For the gravimetric estimation of magnesium, the following procedure is recommended. The precipitant consists of an *N*/2 solution

of ammonium disodium phosphate, obtained by mixing equivalent quantities of ammonia and of the phosphate; the magnesium solution should contain 0.3—0.5% of magnesium. To 20—25 c.c. of the reagent, 10 c.c. of the magnesium solution are rapidly added, the mixture being shaken. After depositing, the precipitate is filtered off on to a tared filter or Gooch crucible, washed with 2.5% ammonia solution until all the chlorine is removed, and converted into pyrophosphate in the ordinary way.

The volumetric estimation of magnesium requires: (1) a standard solution of uranyl acetate, 1 c.c. = 0.005 gram P_2O_5 = 0.0067 gram PO_4 ; (2) a $N/2$ ammonium disodium phosphate solution (*vide supra*), titrated at the time of using with the uranyl acetate solution. The magnesium solution should contain 0.3—0.5% of magnesium, and should be perfectly neutral. Into a cylinder having a ground-in stopper, and without constriction, are placed 40 c.c. of the ammonium disodium phosphate solution and 10 c.c. of the magnesium solution; the mixture is well shaken, allowed to settle, and filtered through a dry filter. An aliquot part of the filtrate is mixed with 1—2 c.c. of acetic acid, and the residual phosphate estimated by titration with the uranyl acetate solution.

T. H. P.

Estimation of Zinc with Ferrocyanide. ERWIN RUPP (*Chem. Zeit.*, 1909, 23, 3—4).—A solution is prepared containing 4—5% of potassium ferrocyanide. Ten c.c. of this are diluted to 50 c.c., 6 grams of potassium sodium tartrate are added, and then an excess of $N/10$ iodine. After one hour, the liquid is titrated as usual with $N/10$ sodium thiosulphate. One c.c. of $N/10$ iodine = 0.0212 gram of ferrocyanogen.

When titrating zinc, a suitable volume of the neutralised solution is added to a judicious excess of the ferrocyanide solution diluted to 50—100 c.c., and containing 5 grams of sodium potassium tartrate. After twenty to thirty minutes, the excess of ferrocyanogen is titrated as directed. The iodine is without action on the precipitate formed. It must be remembered, however, that this precipitate is not zinc ferrocyanide, for this, in contact with excess of potassium ferrocyanide, rapidly forms a double compound, $2K_2Zn_3(FeCy_6)_2$.

L. DE K.

The Use of the Rotating Anode in Electrolytic Separations. MARY E. HOLMES (*J. Amer. Chem. Soc.*, 1908, 30, 1865—1874).—The advantage of rotation over stationary electrodes even with low currents is demonstrated. On examining the tables given, the following points are noticed. Separation of cadmium from aluminium and magnesium is always possible. The best conditions for the separation of cadmium from chromium are the use of a high current with phosphoric acid as electrolyte; the separation also succeeds with a low current in presence of sulphuric acid. Separation of cadmium from iron is possible with a high current, but not with a low one. Separations of cadmium from cobalt and zinc are possible with a low, but not with a high, current. Separation of cadmium from nickel succeeds best with a high current. Separation of cadmium

from manganese succeeds best with a high current, but satisfactory results are also obtained with a low current, using formic acid as electrolyte.

L. DE K.

Assay of Lead Sulphides. FELIX JACOBSON (Chem. Zentr., 1908, ii, 1291; from *Gummi Zeit.*, 1908, 22, 1200).—Commercial lead sulphide often contains sulphate, and therefore it is necessary to estimate the true sulphide, which is readily done by heating with fuming hydrochloric acid and collecting the hydrogen sulphide evolved in an ammoniacal solution of silver nitrate. Any free sulphur may be extracted by boiling with a suitable solvent.

L. DE K.

Detection of Mercury in Organs by means of the Microscope. C. LOMBARDO (Chem. Zentr., 1908, ii, 1788; from *Arch. Farm. speriment.*, 1908, 7, 400).—The following methods, in which the mercury is reduced to the metallic state by means of stannous chloride, are stated to be capable of detecting the presence of one part of mercury in 4,000,000.

Five c.c. of the filtered liquid (urine, stomach contents, etc.) are mixed with 5 c.c. of stannous chloride solution (prepared by dissolving 12 grams of stannous chloride in a mixture of 25 c.c. of hydrochloric acid and 75 c.c. of water) and submitted to centrifugal action for a few minutes. The precipitate is then examined under the microscope. The presence of a small quantity of albumin aids the reaction, and practically every mercury salt, with the exception of the sulphide, may be detected by the test.

The second method described consists in placing parts of the organs in either 70% alcohol or 10% formaldehyde solution for about two days, then washing them with water, and immersing them in the stannous chloride solution; the pieces are next washed successively in water, alcohol, and xylene, and embedded in paraffin. Sections are cut, and, after the removal of the paraffin, are examined microscopically; the mercury is seen as small globules. The tests will not detect the presence of mercury in decomposed organs, probably owing to the mercury having been converted into the sulphide. W. P. S.

Volumetric Estimation of Mercuric Salts. H. MORAWITZ (*Zeitsch. anorg. Chem.*, 1908, 60, 456—458).—The author titrates mercuric chloride by means of "pure" *N*/10 potassium cyanide, which has been freed from any carbonate by addition of barium chloride. As indicator and catalyst, a saturated solution of *p*-nitrophenol in *N*/50 hydrochloric acid is employed, of which 10 drops are added. When checking this solution, 100 drops are used and the result divided by 10. The number of c.c. of cyanide used are then deducted from those used in the mercury titration. In these circumstances, mercuric chloride behaves like a dibasic acid.

Probably other mercuric salts may be converted into chloride by means of an alkali chloride.

L. DE K.

Estimation of Ceria and other Rare Earths in Rocks. MAX DITTRICH (*Ber.*, 1908, 41, 4373—4375. Compare Meyer, D.R.-P. 202523, and Hauser, Abstr., 1908, ii, 987).—The presence of iron

salts affects the precipitation of cerium as cerous oxalate. The best precipitating agent is ammonium oxalate, and when iron salts are present it is necessary to use a very large excess of the precipitating reagent. For example, with 0.2 gram of cerous sulphate and 15 c.c. of a concentrated solution of ferric salt, 200 c.c. of saturated ammonium oxalate are necessary. The precipitate is perfectly white and free from iron compounds, and should be washed with dilute ammonium oxalate solution.

J. J. S.

Colloidal Reaction for some Metallic Salts. EDMUND STIASNY (*Chem. Zentr.*, 1908, ii, 1296; from *Collegium*, 1908, 348).—A solution of an aluminium salt, even if containing but 0.01 mg. per c.c., gives a flocculent precipitate when 5 c.c. are boiled with 5 c.c. of tannin solution (1 : 1000) and 10 c.c. of *N*-sodium sulphate. Sodium acetate may also be used, and acts in the cold.

Similar precipitates are obtained with the salts of calcium, barium, strontium, magnesium, zinc, lead, chromium, and iron, but not so distinctly as in the case of aluminium; manganese, however, gives a good reaction when sodium acetate is used.

L. DE K.

Estimation of Manganese in Pig Iron by the Persulphate Method. H. KUNZE (*Stahl u. Eisen*, 1908, 28, 1715—1716).—Two grams of pig iron or one gram of spiegel are dissolved in a 500 c.c. graduated flask with 30 c.c. of nitric acid, D 1.2. The flask is filled up, the graphite allowed to settle, and 25 c.c. of the liquid taken. To this are added 10 c.c. of the same nitric acid, and 5 c.c. *N*/10 silver nitrate (for pig iron), or 15—20 c.c. for spiegel. The solution is oxidised with persulphate to convert the manganese into permanganate, and titrated in the usual way (compare Rubricius, *Abstr.*, 1905, ii, 766).

C. H. D.

Influence of Copper on the Titration of Iron by the Zimmermann-Reinhardt Method. K. SCHRÖDER (*Zeitsch. öffentl. Chem.*, 1908, 14, 477—492).—A series of experiments to study the influence of copper on the accuracy of the estimation of iron by Zimmermann-Reinhardt's volumetric process (reduction with stannous chloride, addition of mercuric chloride, and titration with permanganate).

The presence of copper either slightly increases or decreases the amount of iron found; sometimes there is a compromise. The final conclusion arrived at is as follows: quantities of copper not exceeding 0.01% may be neglected in ordinary analyses of iron ores if the operations are conducted with due speed. But with more copper present, and in reference analyses, the copper should be first removed. Iron wire should not be used as a means of standardising permanganate if it is not free from copper, and the stannous chloride should be tested for that metal.

L. DE K.

Molybdates of Nickel and Cobalt. HERMANN GROSSMANN (*Bull. Soc. chim.*, 1909, [iv], 5, 5).—A reply to Pozzi-Escot (*Abstr.*, 1908, ii, 1042), pointing out that the latter has confused W. Marckwald with E. Marckwald, and that it was to the second of these investigators

the author attributed correctly the process for the detection of nickel in presence of cobalt, referred to in his previous paper (Abstr., 1908, ii, 230).
T. A. H.

Volumetric Estimation of Chromium with Potassium Ferricyanide. HERMANN BOLLENBACH and E. LUCHMANN (*Zeitsch. anorg. Chem.*, 1908, 60, 446—455).—The chromic solution, which must be free from metals precipitable by hydrogen sulphide, also from cobalt, nickel, manganese and ferrous salts and other reducing inorganic or organic substances, is poured into a freshly prepared solution of 4 to 12 grams of pure potassium ferricyanide to which 50 c.c. of 2*N*-sodium hydroxide have been added. After thorough stirring, aqueous barium hydroxide is added until all the chromate formed has precipitated, and the precipitate is collected on a double filter and well washed. The filtrate is acidified with dilute hydrochloric acid, and titrated with permanganate solution which has been standardised, say, with pure potassium ferrocyanide. If the permanganate contains exactly 3.546 grams per litre, 1 c.c. will represent 0.001947 gram of chromium. Chromates must be reduced by means of sulphurous acid, the excess of which is then removed by boiling.
L. DE K.

Reaction of Uranium and Cadmium Salts. P. LEMAIRE (*Ann. Chim. anal.* 1909, 14, 6—7).—The reagent consists of a 5% solution of thiosinamine, to 100 c.c. of which are added when required 5 c.c. of sodium hydroxide. To 3—4 c.c. of the alkaline reagent are added 2—3 drops of the solution to be tested, and the mixture is heated to boiling. Cadmium and uranium are the only metals which yield a yellow precipitate.
L. DE K.

Estimation of Antimony and Tin. EDWARD CAHEN and GILBERT T. MORGAN (*Analyst*, 1909, 34, 3—9).—The results are given of a detailed examination of several methods which have been proposed for the estimation of these two metals. Vortmann and Metzl's process (Abstr., 1905, ii, 655) was found to be trustworthy for the separation of antimony from tin, and for the estimation of the former metal if certain precautions, such as the absence of nitric acid or other oxidising agent, etc., are observed. The method does not, however, admit of the estimation of tin by any simple process. It is recommended that the antimony trisulphide obtained should be heated to a temperature of 150—180° in an atmosphere of carbon dioxide before being weighed. The method described by Czerwek (Abstr., 1906, ii, 708) gave good results in the case of tin, but was quite untrustworthy for the estimation of antimony. The best method was found to be that of Henz (Abstr., 1904, ii, 150).
W. P. S.

Estimation of Tin in Tin-Plate. KARL MEYER (*Zeitsch. angew. Chem.*, 1909, 22, 68—69).—Twenty to fifty grams of the cleansed material are cut up into small pieces and placed in a spacious basin. Sufficient water is added to cover the metal, and this is then heated at 80°, when 1 to 2.5 grams of sodium peroxide are added. When the effervescence ceases a little, another gram of the peroxide is added,

and, when the evolution of gas ceases altogether, the flame is removed and the undissolved iron is examined for any tin. Should there still be some left, more peroxide is added, and the whole heated to boiling. Finally, the iron is washed with boiling water, then with alcohol, dried, and weighed.

Any lead present is also dissolved in the alkaline liquid. If desired, the true amount of tin may be estimated in the solution. L. DE K.

Organic Analysis with Sodium Peroxide. M. EMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1909, 14, 5—6).—A slight modification of Von Koneck's process. The nickel crucible is fitted with a lid which can be tightly closed by means of a bayonet joint, and is fitted with a tube 3 mm. in diameter and 7—8 cm. in height. 0.2 Gram of the substance is carefully mixed with 4—5 grams of sodium peroxide and introduced into the crucible. After fixing on the lid, a slight heat is applied with a small flame, when very soon the action sets in, causing the crucible to become white hot. After cooling for ten minutes, the lid is removed, and the crucible is placed in a vessel filled with water. The process gives satisfactory results for the estimation of the halogens; nitrogen is converted into nitrate, sulphur into sulphate, and phosphorus and arsenic are also retained as phosphate and arsenate. The author, however, cannot recommend the process for the estimation of the carbon. L. DE K.

A New Colour Reaction of Petroleum. CHARLES ARRAGON (*Chem. Zeit.*, 1908, 33, 20—21).—Equal volumes of petroleum and nitric acid, D 1.4, free from nitrous acid, are well shaken for half a minute. Pure American petroleum turns a fine violet, whilst the acid layer turns yellow. Austrian, Gallician, and Russian petroleum turns intensely yellow, the acid becoming brown. In the case of mixtures, the whole first turns a pale violet, and then suddenly changes to yellow. In this manner, 10% of Austrian oil may be detected in American petroleum. L. DE K.

Some Reactions and Properties of Essential Oils. LOUIS DUPARC and ALF. MONNIER (*Arch. sci. phys. nat.*, 1908, 26, 609—639).—This research was undertaken in order to discover a simple method of detecting absinthe and similar liqueurs containing thujone. A modified form of Legal's reagent is suggested for this purpose.

Preliminary experiments on the determination (a) of the quantities of water necessary to just produce turbidity in alcoholic solutions of various essential oils, (b) of the quantities required to just ensure "complete precipitation" of oils from such solutions, and (c) observations on the opacities of such "completely precipitated" preparations, showed that these methods could not be employed satisfactorily for distinguishing between liqueurs containing thujone and those free from this constituent, but containing other oils. Similarly, the iodometric method devised by Sanglé-Ferrière and Cuniasse (*Abstr.*, 1903, ii, 247, 336, 337) for the estimation of essential oils in absinthe was found to give different results even with the same distillate under the same conditions, and is therefore untrustworthy.

Cuniasse's observation (Abstr., 1907, ii, 413) that Legal's reagent gives a deep red coloration with oils containing thujone, such as those of wormwood and tansy, was confirmed. Of the other essential oils and their constituents tried, citral is the only one likely to occur in liqueurs which gives a red colour likely to be mistaken for that given by thujone, although somewhat similar colours are also given by oils of vervain, caraway, and rue. Red colorations are also given by rum, brandy, and other spirits, due to the aldehydes they contain. The application of the test has therefore been modified. To 100 c.c. of the liqueur, 1 c.c. of aniline and 1 c.c. of syrupy phosphoric acid are added, and the mixture heated during one hour in a reflux apparatus. The mixture is then distilled, and 90 c.c. collected. To 10 c.c. of this distillate, 2 c.c. of zinc sulphate solution (10%), 0.5 c.c. of sodium nitroprusside solution (10%), and, after cooling, 4 c.c. of sodium hydroxide solution (5%) are added. The cooled liquid is acidified with 2—3 c.c. of acetic acid, when, if thujone is present, a gooseberry-red precipitate is formed. Citral gives an orange-red precipitate under similar conditions, but this constituent, if originally present, would be eliminated by the preliminary treatment of the liqueur. The precipitate formed is much more stable than the red colour given by Legal's reagent. If very small quantities of thujone are present, a preliminary concentration of the oils in the liqueur is effected by precipitating them with water and extracting with light petroleum, which is then removed by careful distillation, the residue being dissolved in 60° alcohol.

T. A. H.

Relation between the Cryoscopic Points of Wines and their Alcoholic Strength. W. MESTREZAT (*Ann. Chim. anal.*, 1909, 14, 11—14).—The author has found that the alcoholic degree of wines may be determined with sufficient accuracy by dividing the cryoscopic points by 0.44.

The apparatus resembles a Winkler cryoscope (for milk testing). It is composed of a Violette-tube, in which moves, by way of a stirrer, a platinum wire having a spiral at its lower end; a thermometer, divided to $1/50^{\circ}$, occupies the axis of the tube. Twenty-five c.c. of the wine are placed in the apparatus, which is then cooled in a mixture of ice and salt to -6° or -7° . The thermometer gradually lowers, but then suddenly rises up to a fixed point, which is the cryoscopic point.

L. DE K.

Estimation of the Total Acidity of Wines. OTTORINO CARLETTI (*Boll. chim. farm.*, 1908, 47, 787—788).—When the acidity of a red wine is estimated by titration with sodium hydroxide solution in presence of phenolphthalein, the change of colour of the liquid can be easily seen if only the light traversing the solution, and not the reflected light as well, be observed. For this purpose the author uses a box blackened inside and having a circular hole in the top just large enough to admit the beaker used in the titration, and another slightly smaller hole in the bottom; the height of the box should be rather less than that of the beaker. A white porcelain plate, rotatable about a horizontal axis, is so arranged that the maximum of

light is reflected into the beaker. For the titration with $N/10$ sodium hydroxide solution, 10 c.c. of wine diluted with a few c.c. of water are taken, together with five drops of a 1% alcoholic solution of phenolphthalein. T. H. P.

Some of the Fatty Acids occurring in Butter Fat. R. K. DONS (*Zeitsch. Nahr. Genussm.*, 1908, 16, 705—725).—In a previous paper (Abstr., 1908, ii, 238), the author has given a method for the estimation of caprylic [octoic] acid in butter fat, and, as this method depends on the different solubility of the lower fatty acids in hot water, he now gives the results of an investigation on the solubility and volatility of these acids. Capric acid [decoic acid], although by itself slightly soluble in cold water, is not extracted by hot water from mixtures containing higher fatty acids; octoic acid dissolves to a slight extent, and, when a mixture of fatty acids is shaken with several successive quantities of hot water, small amounts of this acid are found in each of the extracts. Hexoic acid is completely extracted from mixtures with higher fatty acids on repeated treatment with hot water, and butyric acid is obtained in solution by shaking the fatty acid mixture once with water. The total quantity of octoic acid in a mixture of butter fatty acids may be estimated by the method described previously if about 1250 c.c. of distillate are collected and allowance made for the small quantity of the acid extracted from the fatty acids by the hot water. A method for the estimation of decoic, lauric, and myristic acids is also suggested; it is based on the different rates at which these acids distil in a current of steam. W. P. S.

Colour Reaction of Oleic Acid. Quick Method of Identifying Vegetable Fibre. A. MANEA (*Chem. Zentr.*, 1908, ii, 1702; from *Bul. Soc. Stiente Bucuresti*, 1908, 17, 256—257).—Cellulose, as, indeed, all vegetable fibres, when mixed with strong sulphuric acid and oleic acid or its esters, gives a red coloration when water is added to the solution so as to cause it to become warm. Stearic, palmitic, margaric, butyric, and isobutyric acids do not behave in this manner, neither do animal fibres when in presence of concentrated sulphuric acid and oleic acid give this coloration. It is thus possible to use this reaction for discriminating between animal and vegetable fibres, and also for identifying oleic acid. Various fractions of crude petroleum, more especially that boiling at 250° , give a similar colour reaction when care is taken that the addition of water to the strong sulphuric acid does not greatly increase the temperature. J. V. E.

Nature of the Chromophore Group in the Resorcinol Test for Tartaric Acid. GEORGES DENIGES (*Bull. Soc. chim.*, 1909, [iv], 5, 19—24).—Results of the application of the resorcinol test (Abstr., 1896, ii, 80) to a large number of substances show that the characteristic red to reddish-violet colour is only given by those containing the complex $\text{HO}\cdot\overset{\overset{|}{\text{C}}}{\underset{\underset{|}{\text{C}}}{\text{C}}}\cdot\text{OH}$. This group may be present as such, as in ethylene glycol, or it may be partly, or wholly, esterified, as in β -chlorolactic acid or dibenzoyltartaric acid. In order that the group

should behave as a chromophore, the spare affinities of the carbon atoms, as shown above, must be united to (1) hydrogen atoms (ethylene glycol and its derivatives), or (2) carbon, itself united to hydrogen (homologues of ethylene glycol), or (3) a carbinol grouping. The colour produced is most intense when the chromophore is in the near neighbourhood of a carboxyl group, as in tartaric, tartronic, and trihydroxyglutaric acids. These rules are also applicable when resorcinol is replaced by other polyhydric phenols, such as phloroglucinol.

Applied in the following manner, the test may be used to distinguish glyceric, tartaric, and tartronic acids. Two c.c. of a mixture of 10 c.c. each of sulphuric acid (D 1.84) and acetic acid, with 1 c.c. of a 2% solution of resorcinol, are heated to boiling and 0.1 c.c. of a solution of the acid (0.005% in water) added. With glyceric acid, the liquid acquires immediately a pink tint, passing rapidly into gooseberry-red. Tartaric acid gives a pomegranate-red, appearing more slowly, and with a solution one-tenth the above strength the colour is wine-red. With tartronic acid a dead-leaf colour appears slowly. On boiling each of these liquids, the red colours of the first two become intensified, whilst the colour of the third changes to wine-red.

Substances such as ethylidenelactic acid contain the chromophore, but do not give the colour reaction, owing to their decomposition by the sulphuric acid used.

T. A. H.

Separation of Benzoic and Cinnamic Acids. K. SCHERINGA (*Pharm. Weekblad.*, 1908, 45, 1535—1536).—A reply to de Jong (*Abstr.*, 1908, ii, 993). The author admits that benzoic acid is formed if the excess of permanganate added is not removed quickly.

A solution of benzoic acid in ether may be evaporated and the residue dried at 40° on a water-bath without any appreciable loss of acid.

L. DE K.

Microscopic Analyses of Soluble, Crystallisable Substances. [Salicylic Acid. Caffeine.] ANNIBALE FERRARO (*Boll. chim. farm.*, 1908, 47, 789—790).—In order to decide whether a sample of salicylic acid is pure, the author evaporates a drop of its ethereal solution on a microscope slide, and examines the crystalline residue under the microscope, similar examination being made of ethereal solutions of salicylic acid mixed with similar powders, such as benzoic acid. By such means, the approximate proportions of the components in a mixture can be estimated.

The purple-red colour obtained by treating caffeine with nitric acid or chlorine, and subsequently with ammonia, is sometimes not clearly shown by caffeine extracted from coffee by means of chloroform or ether, but the caffeine can be rendered evident by evaporating a drop or two of the chloroform or ethereal extract and examining the residue under the microscope; it is, however, found that the appearance of the prismatic crystals of caffeine varies with the solvent used and with the concentration of the solution from which they are deposited.

T. H. P.

Objections to the Use of Potassium Dichromate as a Preservative of Milk 'Destined for Analysis. A. MONVOISIN (*Compt. rend.*, 1908, 147, 1403—1404).—In addition to the disadvantages already mentioned by Grélot (*Abstr.*, 1907, ii, 513), there is the further objection that milk containing potassium dichromate always produces a blue coloration with *p*-phenylenediamine; hence it is impossible to decide whether the milk has been boiled or whether hydrogen peroxide has been added. G. B.

Detection and Estimation of Formaldehyde in Milk. HERBERT S. SHREWSBURY and ARTHUR W. KNAPP (*Analyst*, 1909, 34, 12—13).—To 5 c.c. of milk contained in a test-tube are added 10 c.c. of concentrated hydrochloric acid containing 0.1% of nitric acid; the mixture is shaken vigorously, and kept for ten minutes in a water-bath at a temperature of 50°. The tube and its contents are then cooled rapidly to about 15°. A violet coloration denotes the presence of formaldehyde, and its intensity indicates the amount, which may be estimated by comparison with standard mixtures of milk and formaldehyde treated in the same manner. The acid reagent should be freshly prepared. W. P. S.

Estimation of Aldehydes in Oil of Lemon. ALEXANDER H. BENNETT (*Analyst*, 1909, 34, 14—17).—The method proposed is a modification of that described originally by Walther (*Abstr.*, 1900, ii, 173); the use of sodium hydrogen carbonate is discontinued, owing to the objection that the carbon dioxide evolved carries off hydroxylamine. The details of the modified process are as follows. Twenty c.c. of the oil of lemon are mixed with 20 c.c. of *N*/2-alcoholic hydroxylamine hydrochloride solution, and to the mixture are added about 8 c.c. of *N*/1-alcoholic potassium hydroxide solution and 20 c.c. of alcohol. The mixture is boiled gently under a reflux apparatus for thirty minutes, and then cooled. The condenser is washed, and the contents of the flask are diluted by the addition of about 250 c.c. of water, the solution being then rendered neutral to phenolphthalein and titrated with *N*/2-sulphuric acid, using methyl-orange as indicator. The number of c.c. of acid required is subtracted from the number used in a blank experiment in which no oil of lemon is present, and the difference multiplied by 0.076 to obtain the weight of citral. W. P. S.

Estimation of Small Quantities of Impurities in *o*-Toluidine and *o*-Nitrotoluene. ARNOLD F. HOLLEMAN (*Rec. trav. chim.*, 1908, 27, 458—462).—In addition to an account of work published previously (*Abstr.*, 1905, i, 272), this paper contains details of the analysis of two samples of commercially "pure" *o*-toluidine, which were found to contain 0.9% and 4.1% respectively of impurities. The method already described (*loc. cit.*) can be applied to the analysis of *o*-nitrotoluene after reduction with iron and hydrochloric acid. W. O. W.

Estimation of Alkaloids. Bitter Principles and Glucosides with the Zeiss Immersion Refractometer. FRANZ UTZ (*Chem. Zeit.*, 1909, 33, 47—49).—A preliminary paper. Successful attempts have been made to determine the quantity of some alkaloids from their refraction in the Zeiss instrument. The following have as yet been tried. *Caffeine* in aqueous solution, *morphine* in methyl alcohol, also the hydrochloride in acid and aqueous solutions, *quinine*, also the hydrochloride, in methyl alcohol, and *brucine* in methyl alcohol solution.

L. DE K.

An Error in the Estimation of Caffeine by Juckenack and Hilger's Method. K. LENDRICH and RUDOLF MURDFIELD (*Zeitsch. Nahr. Genussm.*, 1908, 16, 647—658).—Experimental evidence is given that caffeine cannot be extracted completely from a perfectly dry residue, such as is obtained in the method described by Juckenack and Hilger (*Abstr.*, 1897, ii, 611), by means of carbon tetrachloride. The extraction of the alkaloid is, however, complete if the residue is moist. It is therefore recommended that the aqueous extract of the coffee should be treated, as described by Juckenack and Hilger, with aluminium hydroxide and sodium hydrogen carbonate and filtered. The portion of the filtrate taken for the estimation is evaporated, mixed with powdered aluminium hydroxide and sand, and, while still in a moist condition, extracted in a Soxhlet apparatus for about ten hours with carbon tetrachloride.

W. P. S.

The Caffeine-content of Raw Coffee and a Modification of Juckenack and Hilger's Method for Estimating Caffeine. RUDOLF HEFELMANN (*Zeitsch. offentl. Chem.*, 1908, 14, 448—450).—From 0.864 to 1.669% of caffeine was found in specimens of commercial unroasted coffee beans; these results lie very close to the figures (1.00 to 1.75%) given by the German Food Regulations as the limits for the caffeine-content of unroasted coffee. It is also pointed out that coffee free from caffeine is now on the market. Juckenack and Hilger's method for the estimation of caffeine (*Abstr.*, 1897, ii, 611) tends to give too low results unless the residue, after extraction with carbon tetrachloride, is moistened, mixed with magnesium oxide, re-dried, and subjected to a further extraction with this solvent.

W. P. S.

The Theobromine-content of Cocoa and a New Method for the Estimation of Theobromine. ADOLF KREUTZ (*Zeitsch. Nahr. Genussm.*, 1908, 16, 579—584).—A portion of the theobromine occurring in cocoa is extracted together with the fat in the process described by the author (*Abstr.*, 1908, ii, 641) for the estimation of the latter; cocoa also contains a quantity of theobromine in the form of a glucoside, and this portion can be separated only after treating the cocoa with an acid. The method now proposed for the estimation of the total theobromine is as follows. From 1.5 to 2 grams of the cocoa are treated with chloral alcoholate as described (*loc. cit.*), and the residue of fat obtained is, after being weighed, dissolved in cold carbon tetrachloride; the theobromine present in the fat remains

insoluble, and is separated by filtration. The solution of the fat in carbon tetrachloride is evaporated, and the residue of fat weighed. The difference between the two weighings gives the amount of theobromine. The residue of cocoa obtained in this part of the process is then dried and boiled with 50 c.c. of 4% sulphuric acid for forty-five minutes in a reflux apparatus. The hot solution is next neutralised by the addition of moist barium carbonate, and evaporated to dryness; the residue is mixed with sand, extracted with chloroform for five hours in a Soxhlet apparatus, and the residue of theobromine obtained on evaporating the solvent is weighed. From the results of estimations given, it is seen that the two kinds of theobromine cannot be separated from each other quantitatively; the total amount of theobromine found in various cocoas varied from 1.99 to 3.85%.

W. P. S.

Detection of Morphine. C. REICHARD (*Pharm. Zentr.-h.*, 1908, 49, 951—954).—Morphine may be identified by means of the reactions given previously by the author (*Abstr.*, 1905, ii, 68; 1906, ii, 637), and also by the blue coloration which is obtained when a neutral morphine solution is mixed with ferric chloride or ferric acetate solution. Titanic acid dissolved in concentrated sulphuric acid gives with morphine a reaction similar to that obtained with iodic acid. In every case, better reactions are obtained if the morphine is tested in the solid state and not in solution. It is also pointed out that morphine is partly converted into dehydromorphine in the animal body, and that this should be remembered when testing for morphine in cases of suspected poisoning. Dehydromorphine may be detected, or distinguished, from morphine by the shape of its crystals, its very slight solubility in dilute acids, and by giving a blood-red coloration with the formaldehyde reagent mentioned previously.

W. P. S.

Estimation of Proteins in Milk treated with Formaldehyde.
Direct Estimation of Formaldehyde in Milk. ANGELO AGRESTINI (*Chem. Zentr.*, 1908, ii, 1640—1641; from *Staz. sperim. agrar. ital.*, 41, 520—529).—A criticism of Denigès' mercury process for the estimation of proteins in milk. In the case of samples containing formaldehyde, the addition of a little 10% hydroxylamine hydrochloride solution is recommended before adding the mercury reagent. The presence of formaldehyde may thus be proved by titrating before and after addition of hydroxylamine hydrochloride.

L. DE K.

Estimation of Albumin in Urine. ADOLF JOLLES (*Ber. Deut. pharm. Ges.*, 1908, 18, 598—599).—One hundred c.c. of the urine are placed in a beaker and, if necessary, neutralised with acetic acid, 5 c.c. of formalin reagent are added, and the liquid is heated on the boiling water-bath for thirty minutes. The albumin is then at once collected on a weighed filter, dried at 110°, washed first with boiling water, then with alcohol and ether, again dried at 110°, and weighed. Any co-precipitated mineral matter is allowed for, as usual.

The reagent is prepared by mixing 50 c.c. of 1% acetic acid, 50 c.c. of commercial formaldehyde, and 15 grams of sodium chloride.

L. DE K.

A New Albuminometer. L. E. WALBUM (*Chem. Zentr.*, 1908, ii, 1632; from *Deutsch. med. Woch.*, 1908, 34, 1728—1729).—The principle of the method consists in the fact that trichloroacetic acid gives a turbidity with weak solutions of albumin. The degree of turbidity is then determined in the author's apparatus, which is based on comparison with a standard milky glass. The results are, however, only approximate.
L. DE K.

Separation of Caseinogen from Human Milk. RODOLPHE ENGEL (*Biochem. Zeitsch.*, 1908, 14, 234—237).—The milk is diluted five-fold and acidified with acetic acid; the mixture is cooled for two to three hours with occasional shaking, then warmed to 40° for a few minutes, and finally filtered.
W. D. H.

Phenolphthalein as a Reagent for Blood. M. EMMANUEL POZZI-ESCOR (*Bull. Soc. chim. Belg.*, 1908, 22, 415—416).—It has been stated by Delarde and Benoit (*Compt. rend. Soc. Biol.*, 1908, 64, 990) that an alkaline solution of phenolphthalein forms a more delicate test for blood than tincture of guaiacum. The author finds that the reagent obtained by dissolving one gram of phenolphthalein in 50 c.c. of sodium hydroxide solution, and decolorising by reduction with excess of zinc dust, is re-coloured in the presence of hydrogen peroxide, not only by fresh blood, but also by extract of malt, saliva, the ash of blood, pus, most organic secretions and vegetable extracts, certain urines free from blood, and by a very large number of metallic salts, such as those of cobalt, manganese, iron, and lead. The conclusion is drawn that, as a test for blood, the reagent is absolutely valueless.
E. H.

Clinical Methods for the Detection of the Colouring Matters of Blood and Some Related Colouring Matters. OTTO SCHUMM (*Arch. Pharm.*, 1909, 247, 12—27).—A critical résumé of the methods available for the detection of blood in urine, fæces, stomach contents, etc., in the course of which the delicacy and best conditions for the application of the absorption spectrum test, the guaiacum (compare *Abstr.*, 1907, ii, 320), aloin, benzidine (*Abstr.*, 1907, ii, 827), and potassium cyanide tests are discussed, as also the hæmochromogen and hæmatoporphyrin tests. Lastly, the detection of urobilin in urine and fæces by a modification of the zinc chloride test is dealt with.
T. A. H.

Reaction of Bile Acids with Rhamnose and δ -Methylfuraldehyde. CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 14, 349—350).—The reaction mentioned by Jolles (*Abstr.*, 1908, ii, 998) has been described previously by Neuberg and Rauchwerger (*Abstr.*, 1905, ii, 122). The same reaction is given, not merely by bile acids, but also by cholesterol and camphor and terpene derivatives.
J. J. S.

Detection of Urobilin in Urine. EDUARD STRAUSS (*Münch. med. Woch.*, 1908, No. 49, reprint).—The urine is acidified with a few c.c. of acetic acid, and precipitated with about a fourth the volume of lead acetate; the filtrate is extracted with amyl alcohol, which, after this

treatment, readily dissolves out the urobilin. The extract gives the characteristic fluorescence with ammonium zinc chloride. S. B. S.

Simplification of the Jakoby-Solm's Ricin Method for the Estimation of Pepsin. MAX EINHORN (*Chem. Zentr.*, 1908, ii, 1295; from *Berlin klin. Woch.*, 1908, 45, 1567—1568).—The modified apparatus consists of a vacuum glass vessel with a stand for twelve calibrated pepsin tubes; it is filled with water at 50—60°, and well corked. Each tube is marked 2, 3, 3·5 c.c., and at its lower end it is graduated in millimetres. Each tube is filled with the 1% ricin solution up to 2 c.c., the diluted pepsin solutions (gastric juice) are then added up to 3 c.c., and finally *N*/10 hydrochloric acid up to 3·5 c.c. The corked tubes are shaken and placed in the vacuum vessel. After thirty minutes, those tubes are noted in which the precipitate has quite disappeared, and at the same time the height of the precipitate in the others is noted. Normal gastric juice when diluted 10 to 20 times gives a precipitate disappearing in thirty minutes; if there is still a precipitate with a ten-fold dilution, the pepsin content is insufficient, and if it disappears with a forty-fold dilution the amount of pepsin is excessive. L. DE K.

Soil Analysis. C. BLOCH and M. HOFFMANN (*Bied. Zentr.*, 1908, 37, 721—722; from *Mitt. landw. Inst. Univ. Breslau*, 1907, 4, Heft 1—2).—In Thiele's method of soil sampling (*ibid.*, 3, Heft 2), ten samples are taken with a spade ten times at equal distances for an area of $\frac{1}{4}$ hectare. The number of samples is then reduced to ten, or 40 per hectare, by mixing. The samples were found to yield unsatisfactory results, the percentages of nitrogen varying from 0·1450 to 0·1556.

To obtain samples for mineral analysis, a spadeful of soil was taken five times at equal distances (on a surface of 25 square metres) after removing about 5 cm. of surface soil. This was repeated five times, and in this manner, five average samples obtained. The samples were obtained from four plots which had received each year (1) potassium, (2) nitrate, (3) no manure, and (4) complete manure; the total nitrogen and mineral constituents were determined in each. The potassium results in (4) varied from 0·0169 to 0·0672, and the other results were more or less divergent.

The results show that, whilst it would be incorrect to select concordant results and ignore the others, approximately correct results can generally be obtained by this method by calculating the total means and the probable errors. Even then, however, it was not always found possible to obtain indications of continuous manuring.

N. H. J. M.

General and Physical Chemistry.

Change in Refractive Index with Temperature. I. K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1909, 31, 86—107).—Measurements of the refractive index of certain liquids for the C, D, F, and G lines were made with a Pulfrich refractometer at short intervals of temperature from about 20° to 70°. For the six typical liquids examined, the refractive index alters in a linear manner with the temperature. The results for the D line are given by the following equations, t representing the temperature: Diisoamyl, $n_D/1.41750 + t/3173.24 = 1$; dimethylaniline, $n_D/1.56845 + t/3143.19 = 1$; n -heptyl alcohol, $n_D/1.43141 + t/3867.43 = 1$; benzyl alcohol, $n_D/1.54875 + t/3644.12 = 1$; n -butyric acid, $n_D/1.40580 + t/3558.99 = 1$; acetylacetone, $n_D/1.45987 + t/2703.32 = 1$. The respective densities at different temperatures, and the dispersions at 10° and 80°, are also given, and the results are compared with those obtained by previous observers.

The values of the three usual expressions for the refraction: $(n^2 - 1)/d$, $(n - 1)/d$, and $(n^2 - 1)/(n_s^2 + 2)d$, have been calculated at intervals of temperature between 10° and 80°. In all cases the refraction increases or decreases continuously with rising temperature. The observed values of the molecular refractivity for the six compounds in question are in fair agreement with those calculated from the atomic refractions according to Brühl.

The refractive index of freshly distilled ethyl acetate is slightly different from that obtained after it has been kept for some time: a result ascribed to isomeric change. G. S.

Absorption Spectra of Neodymium and Praseodymium Chlorides in Water, Methyl Alcohol, Ethyl Alcohol, and Mixtures of these Solvents. HARRY C. JONES and JOHN A. ANDERSON (*Proc. Amer. Phil. Soc.*, 1908, 47, 276—297).—The absorption spectra were obtained by passing the light from a spark between carbon terminals saturated with uranium and molybdenum salts through the solution, and photographing the spectra produced by a grating. The red end of the spectrum was obtained from a Nernst filament.

The absorption spectrum of an alcoholic solution of neodymium or praseodymium chloride differs considerably from that of the aqueous solution. The bands of the alcoholic solution lie nearer to the red than those of the aqueous solution, and in the case of praseodymium chloride an additional strong band appears. The solutions in methyl and in ethyl alcohol are closely similar. In mixtures of alcohol and water, the two spectra are superposed. All the solutions show considerable deviations from Beer's law. The theory of Ostwald, that the absorption is due mainly to the ions, is insufficient to account for the facts, and it is considered that the formation of solvates (combina-

tions of the solvent with parts of the dissolved substance) must be assumed. Both the molecules and the ions formed from them are considered to be in combination with the solvent. C. H. D.

Test of Beer's Law of Absorption. F. STUMPF (*Physikal. Zeitsch.*, 1909, 10, 29—32).—The light absorbed by a layer of solution of 1 mm. thickness has been compared with that absorbed by 1500 mm. of a second solution, the concentrations being in the ratio 1500:1. For solutions of aminoazobenzene in benzene, Beer's law is satisfied within the limits of the estimated experimental error. For this and other coloured substances in ethyl-alcoholic solution, deviations were found, but the author considers that the two differently concentrated solutions are not strictly comparable, because of dissociation changes. H. M. D.

Polymerism as the Cause of the Difference of Colour of Halides and Sulphites. ARTHUR HANTZSCH (*Ber.*, 1909, 42, 68—85).—The colour of many haloid salts, inorganic and organic, increases in intensity with the atomic weight of the halogen. Explanations of the phenomenon have hitherto been evaded or attempted by the theory of the ionisation of chromophores (Decker, *Abstr.*, 1904, ii, 702). This explanation is untenable, for, amongst other objections, the author points out that true ionisation is immeasurably rapid, whereas Decker has in some cases been able to follow his colour changes colorimetrically; moreover, the author has shown previously that, in the absence of constitutive change, undissociated salts and their ions are optically identical.

The colour change in question is to be referred to polymerisation, although at present definite evidence has been obtained only in the case of organic halides. For example, of the 5-phenyl-10-methyl-acridonium halides, the yellow solution of the chloride and the blackish-brown solution of the iodide are shown to be unimolecular and termolecular respectively by the ebullioscopic method. Since the anhydrous solids have similar colours, they may be assumed to be unimolecular and termolecular respectively. In dissociating solvents the termolecular iodide passes more or less into the unimolecular form; the greater the concentration of the solution, and (more important) the smaller the dissociating action of the solvent, the greater is the amount of the dark-coloured termolecular modification; for example, in alcohol the iodide is yellowish-brown, and in water, yellowish-green.

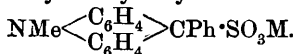
The chloride in aqueous or alcoholic solution is, optically, almost identical with the phenylmethylacridonium salts of oxy-acids, which conform to Beer's law.

Evidence for the equilibrium of the termolecular and the unimolecular modifications in the solid state is found in the bromide, which in the anhydrous condition is distinctly darker than the chloride, and therefore may be regarded as a solid solution of the brownish-black termolecular bromide in the yellow unimolecular modification; the hydrate of the bromide is yellowish-green, so that by

the addition of the water of crystallisation the termolecular form has been changed almost completely into the unimolecular.

Very interesting is the behaviour of 5-phenyl-10-methylacridonium sulphite. In contradistinction to the sulphate and the selenite, which possess the typical yellowish-green colour of the unimolecular salts, the sulphite can only be obtained in a dark green or a brown modification. The dark green sulphite, which separates from aqueous or alcoholic solution, is changed to the brown form in chloroform, whilst the converse change of the brown to the green is slowly accomplished by alcohol or ether. Unfortunately, the molecular complexity of these forms cannot be determined, but it is only rational to suppose that the brown sulphite, like the brown iodide, is termolecular; the dark green sulphite is regarded as bimolecular.

The double salts with alkali sulphites, $(C_{20}H_{16}N)_2SO_3 \cdot M_2SO_3$, which are colourless and stable only in alkaline solution, are probably ψ -sulphites, namely, phenylmethyl-dihydroacridinesulphonates,



They are decomposed by water into the alkali sulphite and the dark green acridonium sulphite, and behave generally like the leuco-sulphonates of the triphenylmethane dyes examined by Hantzsch and Osswald.

Results similar to the preceding have also been obtained with 5-phenylacridonium, acridonium, and methylacridonium salts; the majority of the salts are yellowish-green, but the iodides are brown and the sulphites olive-green and brown; their examination is rendered difficult by their instability and slight solubility. Quinolinium and isoquinolinium salts are usually colourless, but abnormal yellow iodides and sulphites have been obtained which dissolve in chloroform without change of colour. 1-Methylpyridinium halides are colourless; the fused iodide is deep yellow, but becomes colourless again at the ordinary temperature.

o-Diazophenylene sulphide methiodide, $C_6H_4 \left\langle \begin{array}{c} N:N \\ \end{array} \right\rangle S_2MeI$, is usually obtained in golden-yellow needles (Jacobson, Abstr., 1894, i, 123), but by the addition of ether to a chloroform solution, which has been kept for some hours, or heated for a few seconds, or inoculated with a trace of bromine or iodine, an amorphous, gelatinous, dark green modification is precipitated, which changes quantitatively into the yellow form at 80° or in contact with alcohol or chloroform. The green form is probably a polymeride.

Since all the preceding colour changes are time phenomena, they must be referred, not to a mere change in the degree of dissociation, but to chemical changes, that is, to polymerisation. Moreover, since the salts retain in the solid form the same colour as they have in solution, the colour of the solid salts must also be referred to different degrees of polymerisation, and not to different states of aggregation.

The experimental part of the paper deals with the preparation of the preceding salts, their colour in different solvents, the measurement of the extinction coefficients of their solutions, and wherever

possible, the determination of their molecular weights by the ebullioscopic method. C. S.

Measurement of Rotatory Dispersive Power in the Visible and Ultra-violet Regions of the Spectrum. T. MARTIN LOWRY (*Proc. Roy. Soc.*, 1908, A, 81, 472—474).—An account is given of improvements which have been made in the method of determining rotatory dispersive power. As a result of these, the intense line spectra yielded by metallic arcs can be used for polarimetric measurements. For this purpose, a parallel beam from the arc is thrown on to the slit of a constant deviation spectroscope. An achromatic lens, which is substituted for the observing tube, is used to throw a magnified image of the slit on to the polarising prisms which give a triple field. By suitably adjusting the constant deviation prism, the whole field can be illuminated with monochromatic light of any desired wave-length.

For observations with ultra-violet light, an arc passed between a carbon and a magnetite electrode is used. A beam from this is thrown by a quartz condenser on to the field of the polarising Foucault prisms, and by means of a quartz-calcite lens, substituted for the analyser-telescope, a diminished image of the field is thrown on to the slit of an ultra-violet spectroscope. The spectrum is photographed, and the line, for which the intensity in the three parts of the field is the same, is identified on the negative.

The rotations produced by 100 mm. of methyl camphorcarboxylate at 20° are recorded for wave-lengths ranging from $\lambda=6708$ to $\lambda=4359$. H. M. D.

Certain Optical and Magneto-optical Properties of Crystals at Low Temperature. JEAN BECQUEREL (*Compt. rend.*, 1909, 148, 158—161. Compare Becquerel and Onnes, *Abstr.*, 1908, ii, 338).—The author controverts a few of the conclusions arrived at by Du Bois and Elias (*Ann. Physik*, 1908, 27, 233).

In an absorption spectrum the width of the bands is proportional to the square of the absolute temperature, provided that width be defined as the difference in wave-lengths of the two vibrations with maximum difference in refractivity. This law holds good down to -190°, but beyond that the bands often enlarge again.

The changes of frequency produced by a magnetic field are independent of temperature. R. J. C.

Electro-chemistry of Light. IV. WILDER D. BANCROFT (*J. Physical Chem.*, 1909, 13, 1—90. Compare *Abstr.*, 1908, ii, 788).—A compilation of extracts from papers in which the phenomenon of solarisation has been investigated or discussed. H. M. D.

The Radioactive Elements. I. DANIEL STRÖMHOLM and THE SVEDBERG (*Zeitsch. anorg. Chem.*, 1909, 61, 338—346).—The radioactive elements are usually found in such small quantities as to render a study of their chemical reactions impossible. Light may be thrown on their chemical relations by observations of their isomorphism.

Ammonia is added to a solution of thorium nitrate, precipitating all elements of the thorium series except thorium-*X*. The solution is concentrated, and various salts are then dissolved in different portions of it, crystallising on cooling. In this way, thorium-*X* is found to be carried down by barium and lead nitrates and by barium chloride, but not by potassium, bismuth, or lanthanum-ammonium nitrates. This indicates that thorium-*X* is isomorphous with barium and lead. It is not precipitated by hydrogen sulphide, and the conclusion is drawn that thorium-*X* belongs to the group of alkaline earth metals. The same result was obtained on crystallising the salts from an old solution of thorium nitrate.

Of the other elements of the series, thorium-3 appears to be isomorphous with thorium, and thorium-2 possibly with lanthanum, although it may be complex.

C. H. D.

A Few Chemical Changes Induced by Radium. New Method for the Detection of Amygdalin. H. JERMAIN M. CREIGHTON (*Trans. Nova Scotia Inst. Sci.*, 1908, 12, 34—48).—In these experiments radium bromide of activity 1,000,000 was employed, enclosed in a glass tube so that only α - and β -rays were used.

Two squares of white tin, $25 \times 25 \times 1$ mm., were placed in two compartments of a lead box, separated by a lead partition. The end of the radium tube was placed about 1 mm. above one square, and the apparatus kept at 0° for four months. Both squares were then found to be coated with grey tin, the one that had suffered bombardment more so than the other. The interior, and particularly the top, of the compartment containing the radium was coated with lead carbonate. Probably the rays had ionised the lead and rendered it more active to the moist carbon dioxide in the air. (The ends of the box were left open.)

A solution of hydrogen peroxide, 4.832 grams per litre, was submitted to the action of the radium in the dark, and the amount of the decomposition was measured by the increased pressure. The peroxide solution alone, or in the presence of lead nitrate, did not decompose, but when influenced by the radium rays decomposition ensued, and more rapidly when lead nitrate was present; the pressure of the oxygen at first increased and then showed a decrease, due to the formation of ozone.

The effect of radium on chloroform is to increase its ionisation, so that an opalescence is more rapidly produced with silver nitrate.

A saturated aqueous solution of amygdalin, submitted to the action of radium for four to ten days, did not contain dextrose or hydrogen cyanide. When a saturated solution of amygdalin is boiled with a few drops of Fehling's solution, the blue colour almost disappears, and a bluish-white, gelatinous precipitate (copper amygdalate ?) is formed; the change is more complete with amygdalin that has been submitted to the action of radium. Two identical solutions containing amygdalin and hydrochloric acid, one of which had been submitted to the action of radium, were examined for dextrose. In the one solution the amount of dextrose increased with time and remained constant; in the other, which had suffered bombardment, the dextrose reached a

maximum and then decreased, showing that the radium caused it to change into some new compound.

The glass tube containing the radium bromide had been kept for a year in a hollow brass tube. On the surface of the brass a grey deposit was formed, which contained copper, but not zinc or lead, and was probably copper oxide.

Amygdalin may be detected by boiling its solution with a few drops of Fehling's solution, whereby ammonia is evolved. C. S.

Radioactive Products Present in the Atmosphere. W. WILSON (*Phil. Mag.*, 1909, [vi], 17, 321—325).—The radioactive deposit collected by an exposed wire charged to a high negative potential was found by Blanc in Rome to consist of 60—70% of thorium deposit and the remainder radium deposit. A wire exposed in Manchester gathered an active deposit containing on the average 62% of thorium product. It is calculated from the known radioactive constants of the two deposits that air contains 3700 times as much radium as thorium emanation. The ratio given by Dadourian (*Abstr.*, 1908, ii, 453), which is greatly in excess of this figure, is shown to be wrongly calculated. It appears, however, that American air contains relatively less thorium emanation than European air. The author computes that the earth's crust contains 1.42 times as many disintegrating atoms of thorium as of radium, and assuming that uranium is the parent substance of radium, there is about seven times as much thorium as uranium, that is, 10^{-6} gram thorium per c.c. of the earth's crust. R. J. C.

Radioactive Behaviour of the Water of Gratz and its Environs. ALBERT WELLIK (*Monatsh.*, 1909, 30, 89—124).—All the eighty-one samples of spring and well waters from the neighbourhood of Gratz examined by the author contained radioactive emanation. The activity often changes considerably in passing from one spring to another quite close, and seems to increase with the geological age of the rocks. To what extent the activities of the wells remain constant is unknown; variations may be produced by meteorological influences, such as change of barometric pressure, rainfall, etc. The emanation of all the wells dies away according to an exponential law, the period being identical with that corresponding with radium emanation; the law and the period are the same in water as in air. The curves of the induced activity agree well both with the corresponding curves obtained by Curie for radium and with Rutherford's theoretical formula for radium induction; in the case of two of the wells, these curves seem to indicate the presence of thorium.

Many of the waters exhibit a not inconsiderable residual activity, pointing to the presence of dissolved radium salt in very small amount. T. H. P.

Some Properties of the Radium Emanation. ERNEST RUTHERFORD (*Mem. Manchester Phil. Soc.*, 1908—09, 53, No. II, 1—2).—A comparatively small amount of radium emanation is absorbed by cocoanut charcoal at ordinary temperatures. One gram of charcoal

absorbs 0.03 cubic mm. emanation at $+10^{\circ}$ and 0.06 cubic mm. at -40° .
R. J. C.

Metallic Radiation. ERIK BUCH ANDERSEN (*Physikal. Zeitsch.*, 1909, 10, 54—57. Compare Russell, Abstr., 1898, ii, 287; 1899, ii, 720; Saeland, Abstr., 1908, ii, 789).—A summary is given of observations relating to the photographic activity of metals. The activity is supposed to be connected with the oxidation of the metals, which in the process emit a radiation of very small penetrating power. The active rays are capable of converting oxygen into ozone, which accounts for the observed liberation of iodine from potassium iodide.

H. M. D.

Nature of the α -Particle. ERNEST RUTHERFORD and T. ROYDS (*Phil. Mag.*, 1909, [vi], 17, 281—286; *Mem. Manchester Phil. Soc.*, 1908, 53, No. 1, 1—3. Compare Rutherford and Geiger, Abstr., 1908, ii, 794; Dewar, Abstr., 1908, ii, 921).—In order to prove that an α -particle consists of an atom of helium plus a positive charge, the purified emanation from 0.12 gram of radium was compressed into a capillary tube with walls 0.01 mm. thick. This capillary tube was known to be impermeable to helium, but the α -particle and also radium-A and radium-C could pass through it into a stout outer tube, where the spectrum could be examined. Although after twenty-four hours no trace of helium was detected, the spectrum gradually developed until, after six days, all the lines of helium could be seen. This helium must have been produced from α -particles which, after traversing the glass, had slowly lost their charge.

It was supposed that the α -particles were projected into the glass of the outer tube and only slowly liberated as helium. This hypothesis was confirmed by placing a cylinder of lead foil, free from helium, round the capillary tube containing the emanation. Whether the lead was enclosed in a vacuous tube or surrounded by air during its bombardment by the α -particles, the spectrum of helium could be detected in the gas which came out of it in a few hours.
R. J. C.

The Range of the α -Rays. WILLIAM DUANE (*Ann. Physik*, 1909, [iv], 28, 443—444. Compare Abstr., 1908, ii, 553).—The author showed previously that the charge of the α -particles and their ionising effect are stopped by practically the same thickness of air. This conclusion was criticised by Aschkinass (Abstr., 1908, ii, 920) on the ground that the two series of measurements were not carried out under the same conditions. Reasons are now given to show that the experimental method used yields correct results.
H. M. D.

α -Rays of Radium-B and Atmospheric Radioactivity. FREDERIC A. HARVEY (*Physikal. Zeitsch.*, 1909, 10, 46—48).—The active deposit collected on a negatively charged wire suspended in the atmosphere emits at first some very easily absorbed rays. These have been found to be due to radium-B. The range of these α -rays in air under normal conditions is 2.6—3.0 mm.

Further observations on wires which had been connected with a negative potential of 5000 volts, and exposed for periods of three

to twenty-four hours, indicate that the half-decay period of the active deposit is by no means constant. In twenty-six experiments made under different atmospheric conditions, this period was found to vary from thirty-four minutes to five and two-thirds hours. The variation is attributed to differences in the proportion of induced thorium activity in the collected deposit. The potential of the charged wire influences this proportion. In two experiments under the same atmospheric conditions, the exposed wire was charged to 2000 and 4000 volts; the proportions of induced thorium activity were respectively 11.6 and 7.2%. The relative amount of thorium activity also depends on barometric fluctuations. In two perfectly similar experiments on the same day, during one of which the barometer was rising, and during the other slowly falling, the proportions of induced thorium activity were found to be respectively 17.8 and 26.5%. H. M. D.

The Number and the Absorption by Matter of the β -Particles emitted by Radium. WALTER MAKOWER (*Phil. Mag.*, 1909, [vi], 17, 171—180).—The number of β -particles expelled by one gram of radium per second has been re-determined, the experimental arrangement adopted being designed to obviate errors arising from secondary radiation efforts. Radium emanation was used instead of radium, the emanation being contained in a very thin-walled capillary glass tube. This tube, covered with aluminium leaf to render it conducting, was suspended in the axis of a glass cylinder, silvered on the inside, and connected with a pump, by means of which it could be exhausted as perfectly as possible. An insulated brass cylinder surrounding the emanation tube was connected with a quadrant electrometer, whilst the emanation tube itself could be connected with a battery of accumulators. The β -rays which reach the brass cylinder under the conditions of the experiment consist chiefly of the rays from radium-*C*, together with a small proportion of the rays from radium-*B*. A correction is introduced for the absorption of the former by the glass of the emanation tube, and the result is then obtained that the number of β -particles emitted per second by the radium-*C* in equilibrium with one gram of radium is 5.0×10^{10} . When the β -rays are absorbed by glass, the electric charge carried by these remains in the glass, indicating that the rays are actually stopped and not merely scattered. H. M. D.

Absorption of the Different Types of β -Rays, together with a Study of the Secondary Rays excited by them. V. E. POUND (*Phil. Mag.*, 1909, [iv], 17, 126—153).—The author has investigated the secondary radiation emitted from the front and back of metal plates when these are subjected to the action of γ -rays and of different types of β -rays. By means of a magnetic field a pencil of the required type of radiation could be deflected into an ionisation chamber.

The observations show that the β -rays from radium and its disintegration products are unable to produce ionisation effects on the far side of plates of aluminium, tin, and lead of thickness 7, 2.5, and 0.9 mm. respectively.

The maximum secondary radiations from the front side of plates of

these metals are obtained when the thicknesses of the plates are respectively 0.4, 0.24, and 0.16 mm. The penetrability of this secondary radiation excited by the β -rays increases with the density of the metal acting as reflector.

Observations with γ -rays show that the transmitted secondary rays from lead and tin are more penetrating than those from aluminium. It is also found that the ionisation due to transmitted secondary radiation, when β -rays are allowed to pass through very thin sheets of aluminium, is greater than the ionisation which would have been caused by the absorbed primary rays.

H. M. D.

Absorption of β -Rays by Liquids. NORMAN CAMPBELL (*Phil. Mag.*, 1909, [vi], 17, 180—190).—The absorption of the β -rays of uranium by water and certain aqueous solutions has been examined. Experiments with layers of water of different thicknesses, and with varying quantities of water poured on to filter-paper contained in the absorption tray, show that in neither case is the absorption strictly exponential. The values of the coefficient also differ in the two cases, and the author doubts whether liquids possess a true absorption-coefficient defined as a quantity occurring in an exponential equation.

The relationship between the values of λ/ρ (λ being the absorption coefficient and ρ the density) for solutions of sodium iodide, potassium nitrate, and potassium carbonate and the corresponding values for the solvent and the respective solutes is not a linear one. The deviations from the linear relationship are quite different in the various solutions examined.

H. M. D.

Effect of Pressure on the Natural Ionisation in a Closed Vessel, and the Ionisation produced by the γ -Rays. W. WILSON (*Phil. Mag.*, 1909, [vi], 17, 216—225).—The closed vessel containing the electroscope consisted of a cylindrical iron vessel having walls 1.5 inches thick and an iron water-jacket about 0.5 inch in thickness. The observations were made with pressures reaching up to 45 atmospheres.

Under the influence of γ -rays the ionisation increases with the pressure of the contained air, although not so rapidly. This is due to the fact the secondary rays from the sides of the vessel contribute considerably to the ionisation. From the equation which represents the ionisation-pressure curve, it is calculated that the ratio of the ionisation due to the secondary and primary rays at atmospheric pressure is 6.6.

The curve connecting the natural ionisation with the pressure of the air in the vessel is a straight line, which curves over towards the pressure axis at low pressures. The form of the curve suggests that the ionisation is the sum of two effects. One of these is independent of the pressure, and is due to radiations from the sides of the vessel. The second effect is proportional to the pressure, and is due chiefly to an emanation mixed with the air, and to a smaller extent to a very penetrating form of radiation. The emanation, if it is one of those already known, must be that of radium.

H. M. D.

Grating Spectrum of Radium Emanation. T. ROYDS (*Phil. Mag.*, 1909, [vi], 17, 202—204. Compare Rutherford and Royds, *Abstr.*, 1908, ii, 787).—Three photographs of the spectrum have been obtained using a concave grating 3.5 inches wide, ruled with 15,000 lines to the inch, the radius of curvature being 1 metre. About thirty-five of the more intense lines previously obtained in the prism spectrum are found on the photographs, together with four new lines which lie further in the ultra-violet region. The wave-lengths of the lines are recorded, and are in good agreement with the prism spectrum measurements.
H. M. D.

New Phenomenon in the Activation with Actinium. OTTO HAHN (*Physikal. Zeitsch.*, 1909, 10, 81—88).—The active deposit which is deposited on a negatively-charged electrode exposed to the action of actinium preparations consists of three rapidly-decaying products, actinium-*A*, -*B*, and -*C*, and of a small quantity of a much more slowly decaying product. The amount of the slow-decay product varies considerably with the conditions of the activation, but the activity due to it may amount to as much as 0.25% of the total original activity.

Examination of the slow-decay product has shown that it consists of actinium-*X*. The deposition of this on the negative electrode is not due to its volatility or to the formation of a short-lived emanation between radio-actinium and actinium-*X*, but is a consequence of the explosive nature of the decomposition of the radio-actinium atoms. Some of the resulting actinium-*X* atoms are forced out from the molecular aggregate in the explosion process, and under the influence of the electric field are carried to the negative electrode. In accordance with this, it is found that the residual activity of the active deposit diminishes when the distance between the negative electrode and the actinium preparation is increased. When the electrode is uncharged or is charged positively, the active deposit shows practically no residual activity.

In agreement with the explanation given, it has been found that pure actinium-*X* has no residual activity, whilst the residual activity of radio-actinium is independent of the proportion of actinium-*X* which is mixed with it.
H. M. D.

Radiation of Uranium-*X*. HEINRICH W. SCHMIDT (*Physikal. Zeitsch.*, 1909, 10, 6—16).—A method of separating uranium-*X* is described by means of which a product is obtained the specific activity of which is much greater than those yielded by previous methods. The active substance is first separated from acetone solution by the addition of freshly-precipitated ferric hydroxide according to Moore and Schlundt's method; the active hydroxide is then dissolved in hydrochloric acid, a little barium chloride added, and the barium precipitated by the addition of dilute sulphuric acid. Although all the uranium-*X* is not precipitated with the barium sulphate, the activity of this is about 5000 times that of the original uranium nitrate.

With the active preparation, measurements of the absorption and of

the deviation in a magnetic field have been made for both the hard and soft β -rays.

From the magnetic experiments with the hard β -rays, the velocity of these is found to be 2.76×10^{10} cms. per sec., and the ratio of the charge to the mass 0.67×10^7 . The observations with the soft rays indicate definitely that these also are negatively charged.

The absorption curves for the hard rays are found to depend very largely on the experimental arrangement. The observations can only be partly explained by the assumption that the rays are unevenly distributed in the absorbing medium or that the velocity of the particles diminishes somewhat as the length of path traversed increases. The proportion of β -rays reflected from a thick plate is greater for the hard than for the soft rays; a minimum value for the reflected radiation can be calculated.

The soft β -rays are absorbed by aluminium according to an exponential law.
H. M. D.

Formation of Helium from Uranium. FREDERICK SODDY (*Physikal. Zeitsch.*, 1909, 10, 41—42).—The experiments have in part been described previously (Abstr., 1908, ii, 921). Further observations with a larger quantity of uranium nitrate containing 1850 grams of uranium confirm the previous estimate that the rate of production of helium is approximately $2 \times 10^{-12}(\text{year})^{-1}$. Experiments have been commenced with sylvine, which, according to Strutt, contains relatively large quantities of helium. If helium is produced at all, its rate of formation is less than $2.5 \times 10^{-12}(\text{year})^{-1}$.
H. M. D.

Electrically Charged Centres of Small Mobility in Gases. MAURICE DE BROGLIE (*Ann. Chim. Phys.*, 1909, [viii], 16, 1—69).—A detailed account of work already published (compare Abstr., 1907, ii, 664; 1908, ii, 344).
M. A. W.

[Calculation of the Ratio of the Electric Charge to the Mass of the Molecule of Mercury Vapour.] ROBERT POHL (*Physikal. Zeitsch.*, 1909, 10, 90).—The author points out that Fürstenau's calculation of e/m for mercury vapour (compare this vol., ii, 12) does not represent a new method for obtaining this ratio. Analysis of the method of calculation shows that what is proved is the validity of the equation $C_v = 3.0$ for monatomic gases, C_v being the molecular heat at constant volume.
H. M. D.

The Hardness and Electrical Resistance of Solid Solutions of Metals. CARL BENEDICKS (*Zeitsch. anorg. Chem.*, 1909, 61, 181—186. Compare Kurnakoff and Schemtschuschny, Abstr., 1908, ii, 932).—The author claims priority for certain conclusions as to the hardness and electrical resistance of solid solutions. For solid metallic solutions of the type AB^{0-n} , the resistance is a linear function of the concentration of B up to considerable values of n . The conductivity does not show this proportionality. For aggregates of two kinds of crystals, however, the conductivity shows a greater regularity than the resistance, the relation being generally a linear one.
C. H. D.

Electrical Conductivity of Pure Hexane. GEORGE JAFFÉ (*Ann. Physik*, 1909, [iv], 28, 326—370).—Experiments have been made to ascertain whether a liquid insulator has a specific electrical conducting power. Hexane was chosen for examination because of the relative ease with which electrically conducting impurities can be removed from it. The apparatus was similar to that used in the investigation of the conducting power of gases. Synthetic hexane and hexane from light petroleum were examined, the method of purification consisting in repeated distillation and prolonged subjection to the influence of the current.

It has been found that hexane, purified in this way, has a definite minimum conducting power which is constant for different samples of hexane. For sufficiently high potential differences (above 200 volts per cm.), the current is independent of the potential, indicating that the conductivity is not due to electrolytic dissociation of the hexane. Under the particular conditions of the experiment, the conductivity was found to be 12.6 times as large as that of air, corresponding with the production of 216 ions per c.c. per second. These facts show that hexane behaves like a very dense gas.

The conductivity is independent of the temperature, but varies with the nature of the material of the vessel in which the hexane is contained. In a brass cylinder, two-thirds of the conductivity is due to the influence of external radiation, the remainder to the action of rays emitted by the cylinder. When the external rays are cut off by surrounding the cylinder with a thick block of lead, the conductivity of the hexane experiences a corresponding diminution. The absorption coefficient of the external radiation is 0.458 cm.^{-1} , which value agrees with that for hard γ -rays. The conductivity is unipolar in character, and this is attributed to the emission of β -rays by the material of the containing cylinder.

The dependence of the conductivity on the material of the containing vessel was investigated by observations in vessels of aluminium, silver, copper, and platinum. The conductivity due to the rays emitted by these metals diminishes in the order in which they are written.

Experiments with heptane and light petroleum show that these have a limiting minimum conductivity nearly equal to that of hexane.

H. M. D.

Dissociation Equilibrium of Binary Electrolytes. ALBERT REYCHLER (*J. Chim. Phys.*, 1909, 7, 58—67).—General considerations on electrolytic dissociation on the basis of the author's views on "mobile ions" (*Abstr.*, 1904, ii, 534).

G. S.

Production of Permanent Magnets from Specimens of nearly Pure Copper. J. G. GRAY and A. D. ROSS (*Physikal. Zeitsch.*, 1909, 10, 59—61).—Samples of nearly pure copper were subjected to various kinds of treatment and then placed between the poles of an electro-magnet giving a field of about 3000 C.G.S.-units. The samples were afterwards examined for permanent magnetism by means of a sensitive magnetometer.

No residual magnetism could be detected when a sample of copper of high conductivity was subjected to the action of the magnetic field at the ordinary temperature or at -190° . The same result was obtained when the sample was hammered whilst under the influence of the field. After having been heated to a bright red heat and slowly cooled, the result was the same, but after rapid cooling by immersion in water considerable residual magnetism was found.

Electrolytic copper containing less than 0.04% iron gave similar results. Moreover, when the rapidly cooled electrolytic copper was magnetised at -190° , the residual magnetism was about twice as large as that found when the same sample was magnetised at the ordinary temperature. When such a copper magnet was heated to 100° and 400° and then slowly cooled, the residual magnetism fell respectively to 60 and 30% of the original amount, and after heating to 600° it had completely disappeared.

A sample of very pure electrolytic copper, which was specially prepared for these experiments, showed no trace of permanent magnetism after heating to a red heat and rapid cooling. The last experiment indicates that the magnetic proportions of ordinary electrolytic copper are due to the small traces of iron present. The observed effects are, however, much greater than correspond with the amount of iron present, and, as an explanation of the facts, the authors suggest that a magnetic compound of iron and copper is formed. H. M. D.

Thermal Effect of the Magnetic Transformation of Nickel and Cobalt. IWAN I. SHUKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1748—1752).—The author has carried out experiments to ascertain whether the loss of magnetic properties by nickel at 340° and by cobalt at about 1000° is accompanied by any heat effect.

First of all, the *E.M.F.* of platinum-nickel and platinum-cobalt thermocouples were measured against those of a platinum-platinum-rhodium couple at different temperatures, all the ends of the thermocouples being soldered by means of gold. The curves obtained, based on a large number of observations, change their character at about the temperatures at which the two metals lose their magnetic properties.

The electrical conductivity of cobalt has not been investigated at temperatures as high as its magnetic transformation point; but from the data for nickel, it may be assumed that the conductivity curve for cobalt should exhibit a break in the temperature-interval $900-1000^{\circ}$. There is hence a close connexion between magnetic properties, electrical conductivity, and thermo-electric properties. In order to ascertain whether these various properties can undergo sudden change unaccompanied by a heat effect, the cooling curves of nickel and cobalt were investigated by Roberts-Austen's differential method, the difference of temperature being measured between a piece of platinum and a piece of nickel or cobalt cooling under identical conditions. In the case of cobalt, a slight but distinct heat effect was observed at 985° , but for nickel there was no indication of any such effect between 600° and 180° . With nickel, then, as the magnetic properties, electrical conductivity, and thermo-electric properties may change

suddenly without any accompanying heat effect, these properties must depend on the internal structure of the atom and not on a molecular transformation, such as a change from one allotropic modification to another.

T. H. P.

Two New Forms of Laboratory Electric Furnace. K. FRIEDRICH (*Metallurgie*, 1908, 5, 703—705).—A small furnace giving rapid heating has an iridium tube, open at both ends, 120 mm. long, 19.7 mm. diam., and 0.4 mm. thick. A fire-clay cylinder with a mica window for observation protects against loss of heat. Such a furnace can be raised to 1600° in half a minute, using 900—1000 amperes at 3 volts.

For maintaining a uniform and constant temperature, a cylinder of fire-resisting material is used in which a platinum spiral is embedded. Such a furnace can be raised to 1200 — 1300° in thirty minutes with a current of 2—2.5 amperes at 220 volts.

C. H. D.

A Method of Calculating the Number of Degrees of Freedom of a Molecule among which the Partition of Energy is Governed by the Principal Temperature. H. BATEMAN (*Mem. Manchester Phil. Soc.*, 1908—1909, 53, No. III, 1—9).—Boltzmann has formulated a law expressing the ratio of the specific heats of a gas in terms of the number of degrees of freedom of the molecule the energy of which is governed by the principal temperature. The author assumes that valency is a degree of freedom fulfilling the condition mentioned, and hence that each atom possesses a number of degrees of freedom represented by three + its valency under the circumstances. A molecule has all the degrees of freedom of its constituent atoms minus the number of conditions which must be satisfied in order that the geometrical configuration may remain permanent.

This theorem leads to a set of simple rules, by the aid of which the ratios of specific heats of eighteen elements and compounds are calculated with surprising approximation to the experimental values.

R. J. C.

Explanation of the Negative Coefficient of Expansion of Silver Iodide. GRINNELL JONES (*J. Amer. Chem. Soc.*, 1909, 31, 191—200. Compare this vol., ii, 214).—Fizeau (*Ann. Phys. Chem.*, 1867, 132, 292) determined the coefficient of expansion of three different varieties of silver iodide, and found it to be negative in each case. This fact has now been studied in the light of Richards' hypothesis of compressible atoms. It is shown that changes in the volume of substances with increasing temperature are due to three causes: (1) an increase in the space between the molecules on account of the increased violence of the molecular vibrations; (2) an increase in the volume of the molecules due to a decrease in cohesion; and (3) a change in the volume of the molecules due to a change in the chemical attraction of the atoms for each other. A study has been made of the free energy of formation of silver iodide and also of silver

chloride and bromide. The results show that in the case of silver iodide the affinity of the silver and iodine increases with rising temperature, which should tend to produce a diminution in volume, and this is in agreement with the fact that silver iodide actually contracts when heated.

It is pointed out that, in general, substances with a low coefficient of expansion are stable at high temperatures, whilst substances with a high coefficient of expansion are unstable. E. G.

Supercooling and Chemical Constitution. KARL DRUCKER (*Verh. deut. Naturforsch. Aerzte.*, 1907, ii, 92—94).—Small amounts (1—2 c.c.) of a number of typical substances were allowed to cool very gradually, and the temperatures at which solidification took place noted. Among the substances examined, urethane and bromoform showed very little tendency to supercooling; for benzene, ethylene dibromide, and *p*-xylene the tendency was greater, and acetophenone, nitrobenzene, acetic acid, and anethole showed considerable supercooling. The tendency to supercooling seems to be greatest for those substances showing considerable change of complexity with alteration of temperature. Only in the case of formamide did the supercooling appear to be influenced by the degree of purity of the substance.

G. S.

Volatility of Arsenic and Thallium in Vacuum and a Method of Calculating the Boiling Points of Metals. FRIEDRICH KRAFFT and A. KNOCKE (*Ber.*, 1909, 42, 202—206).—The relationship existing between the temperature at which a metal commences to volatilise and its boiling point in a complete vacuum and its boiling point under a pressure of 760 mm. (compare Krafft, *Abstr.*, 1905, ii, 144) also exists between the temperatures at which substances sublime. It is shown that arsenic in a vacuum commences to volatilise at 96°, and sublimates rapidly at the constant temperature of 325°; under 760 mm. pressure it sublimates constantly at 554°. The difference between the first and second values and the second and third values is 229°. Consequently, if two of these values are known, it is possible to calculate the third; thus, thallium in a complete vacuum commences to volatilise at 174° and boils constantly at 818°; the difference is 644°; consequently, the boiling point of thallium under a pressure of 760 mm. must be about 1462°.

W. H. G.

Volatilisation of Difficultly Volatile Metals, particularly Platinum and Iron, in Evacuated Glass Vessels. A. KNOCKE (*Ber.*, 1909, 42, 206—210. Compare preceding abstract).—An investigation on the volatility of various metals in a complete vacuum. The values given are the lowest temperatures at which volatilisation of the metal could be detected: calcium, 398°; strontium, 375°; barium, 355°; magnesium, 415°; platinum, 540°; iridium, 660°; palladium, 735°; iron, 755°; cobalt, 640° and nickel, about 750°.

W. H. G.

Volatilisation and Sublimation at Minimum Temperatures in a Vacuum, particularly of High Molecular Carbon Compounds. CHR. J. HANSEN (*Ber.*, 1909, 42, 210—214).—An investigation on the volatility of certain organic compounds in a vacuum in which the cathode light disappears. The following are the lowest temperatures at which volatilisation of the substance can be detected: lauric acid, 22°; myristic acid, 27°; palmitic acid, 32°; stearic acid, 38°; laurone, 40°; myristone, 46°; palmitone, 52·7°; stearone, 58°, and dotriacontane, 63°. In a complete vacuum, phenanthrene loses 12% of its weight at about 20° in twelve hours; anthracene loses 1% at 35° in six hours; phenanthraquinone loses 0·15% at 36° in ten hours; anthraquinone loses 0·08% at 36° in ten hours; retene loses 2·2% at 36° in fourteen hours; chrysene is volatile at 60°, and alizarin volatilises at 38—39°, but not at 36°. Maleic acid and phthalic acid sublime undecomposed in a complete vacuum at about 80° and 115—117° respectively.

W. H. G.

Molecular Weights of Inorganic Salts in Methyl Acetate. JOHANNES SCHROEDER and HANS STEINER (*J. pr. Chem.*, 1909, [ii], 79, 49—65).—An investigation on the state of inorganic salts dissolved in methyl acetate.

The molecular elevation of the boiling point of methyl acetate, using naphthalene, diphenylamine, benzil, and camphor as normal substances, was found to be 20·61, from which is calculated the latent heat of vaporisation, $w = 105·3$ (compare Gernhardt and Beckmann, *Abstr.*, 1896, ii, 236).

The following salts were investigated: the thiocyanates of potassium and sodium; the chloride, bromide, iodide, and thiocyanate of lithium, calcium nitrate, barium iodide, cobaltous bromide, zinc nitrate, cadmium iodide, cuprous chloride and bromide, mercuric chloride, bromide, iodide and nitrate, stannous chloride, and bismuth chloride; their solubilities in the boiling solvent were estimated, and, without exception, the molecular weights derived from the elevation of the boiling point of the solution were much smaller than the theoretical values; the conclusion is drawn, therefore, that these salts, particularly in dilute solutions, are largely dissociated into their respective ions.

The laws which are found to apply to the dissociation phenomena of salts in aqueous solutions are only in part applicable to solutions in methyl acetate. The alteration in the degree of dissociation of the solute which accompanies the change of concentration in this solvent follows a different course to that of aqueous solutions. It is not improbable that some of these irregularities are due to the difficulty of obtaining certain salts in an anhydrous state.

W. H. G.

Thermochemistry of Phosphorus. JOHN C. THOMLINSON (*Chem. News*, 1909, 99, 40).—In a previous communication (*Abstr.*, 1907, ii, 153) the conclusion was drawn that phosphorus behaving as a quadrivalent element would have a heat of combination = 32·025 cals., and oxygen as a univalent element = 71·228 cals., or when bivalent, 52·545 cals. Employing these values, formulæ have been arrived at which give a theoretical heat of combustion in agreement with that

found, and are intended to express the whole reaction of combustion of a particular variety of phosphorus with oxygen. J. V. E.

Thermochemical Investigations of Organic Compounds: Aromatic Series. W. SVENTOSLAVSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1692—1715. Compare this vol., ii, 23).—In continuation of his previous work on aliphatic compounds, the author analyses the thermochemical data for aromatic hydrocarbons and for members of all classes of oxygen-containing aromatic compounds. The general results confirm those arrived at from a study of the aliphatic compounds, and lead to the following additional conclusions.

In benzene, as in all mono- and polycyclic derivatives of it, there exists complete saturation of the atomic linkings, since, quite independently of any increase of the benzene structure, the heat required for the complete rupture of the nucleus is equal to $9y + 6x$, where x and y represent the linkings C-H and C-C, and have the same magnitudes as in methane and ethane. The degrees of saturation of the linking C-O in acids, alcohols, ethers, aldehydes, ketones, and quinones have been determined. The heat of formation of the linking C-O in the ether, $\text{CH}_3\cdot\text{O}\cdot\text{CH}_3$, is 6 Cals. greater than the heat of formation of the same linking in the alcohol, $\text{CH}_3\cdot\text{OH}$.

The heats of formation of unsaturated linkings increased in any class of compounds with the molecular weight, and also increase in passing from a normal to an iso-structure. In the different classes of compounds investigated, the heats of formation of an unsaturated linking depends only on the atoms and groups surrounding it. Thus the replacement of the hydrogen in the hydroxyl group of an alcohol or an acid causes a considerable increase in the heats of formation of adjacent unsaturated linkings. T. H. P.

Alteration of the Transition Temperature of Glauber's Salt by a Third Substance. EUGEN VON BIRON and S. P. MALSCHEVSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1619—1635).—The authors have determined the changes produced in the transition temperature of decahydrated sodium sulphate and in the solubility of the salt by the presence in various concentrations of the electrolytes, sodium chloride, bromide, iodide, and chromate, and of the non-electrolytes, dextrose and alcohol.

The temperature of transition of the pure decahydrate was found to be 32.45° (compare Richards and Wells, *Abstr.*, 1903, ii, 411), solubility determinations at this temperature giving results varying from 49.37 to 49.76 grams of anhydrous sodium sulphate per 100 grams of water, the mean being 49.59.

The molecular depressions of the transition temperature produced by the electrolytes are very nearly the same as those caused by dextrose. The depressions due to ethyl alcohol are considerably less than the others, as would be expected from the fact that the alcohol is associated in the liquid state. The depressions caused by the electrolytes employed increase with the concentration, but in the case of dextrose such increase is almost negligible. This difference is readily explainable as due to the electrolytic dissociation of the electrolytes. The molecular

depressions produced by equimolecular solutions of sodium chloride, bromide, and iodide diminish markedly in the order NaCl, NaBr, NaI. The solubility of sodium sulphate in equimolecular solutions of these three salts also diminishes in the same series, but this fact is independent of the electrolytic dissociation of the salts. The theory of these various phenomena is discussed. T. H. P.

Thermodynamics of Binary Mixed Liquids. EMIL BOSE (*Zeitsch. physikal. Chem.*, 1909, 65, 458—485).—Part of the results described in this paper have already been published (Abstr., 1907, ii, 435; 1908, ii, 84).

A complicated formula is deduced connecting the heat of admixture of two liquids with the composition of the mixture. The formula is applied to the experimented data obtained for the systems formed by mixing water with methyl, ethyl, and propyl alcohols respectively (*loc. cit.*), and it is shown that in all three cases there are regular and periodic differences between the observed and calculated values for the heat given out. The deviations are ascribed to the fact that in all three systems both components are associated. G. S.

Compressibilities of the Chlorides, Bromides, and Iodides of Sodium, Potassium, Silver, and Thallium. THEODORE W. RICHARDS and GRINNELL JONES (*J. Amer. Chem. Soc.*, 1909, 31, 158—191).—Richards (Abstr., 1902, ii, 305; 1903, ii, 132; 1904, ii, 704) in a study of the significance of changing atomic volume has pointed out that the volumes of both solids and liquids probably depend on both the chemical and cohesive forces existing within them. In order to ascertain the connexion between the internal pressures and the external volumes of substances, it is necessary to know the compressibilities of both elements and compounds through a wide range of pressure. The compressibilities of a number of substances have already been determined (Abstr., 1904, ii, 384; 1907, ii, 858).

In the present paper, the compressibilities of the chlorides, bromides, and iodides of sodium, potassium, silver, and thallium have been determined by a slight modification of the method used in the earlier work. The results obtained between 100 and 500 megabars (the megabar being the pressure of a megadyne per sq. cm.) are as follows: sodium chloride, 4.1×10^{-6} ; sodium bromide, 5.1×10^{-6} ; sodium iodide, 6.9×10^{-6} ; potassium chloride, 5.0×10^{-6} ; potassium bromide, 6.2×10^{-6} ; potassium iodide, 8.6×10^{-6} ; silver chloride, 2.2×10^{-6} ; silver bromide, 2.6×10^{-6} ; silver iodide, 3.9×10^{-6} ; thallous chloride, 4.7×10^{-6} ; thallous bromide, 5.1×10^{-6} ; thallous iodide, 6.7×10^{-6} .

The relative values of these compressibilities have been correlated with the volatility, surface tension, internal stress, and heat of formation of the salts, and also with the compressibility of the elements and the contraction which occurs during the formation of the salts from their elements.

The results of this work support the hypothesis which has been put forward with regard to the volumes of liquids and solids, and afford further evidence of the significance of changing atomic volume. E. G.

Relation between the Compositions of the Vapour and Solution with Binary Mixtures exhibiting a Maximum or Minimum [Pressure]. A. E. MAKOVETZKI (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1715—1735).—Starting from the principle of dynamic equilibrium, the author deduces that, for binary mixtures of liquids exhibiting a maximum or minimum, the relation between the concentrations of the two components in the liquid (x_2 and $1 - x_2$) and gaseous (x_1 and $1 - x_1$) states is expressed by the formula $x_2/(1 - x_2) = Kx_1/(1 - x_1)$, that is, the coefficients of distribution of the components in the two states bear to one another a constant relation. The above expression confirms and is a simplified form of van der Waals' equation: $x_2/(1 - x_2) = e^{d\mu_1/dx_1}x_1/(1 - x_1)$. The results obtained on examining mixtures of the ether of ethylene glycol and water, carbon disulphide and acetone, carbon disulphide and methylal, ethyl iodide and ethyl acetate, and acetone and chloroform, are in good agreement with those calculated on the basis of the above formula.

The work of van der Waals, Margules, Gibbs, von Zawidzki (Abstr., 1901, ii, 6), Konowaloff (Abstr., 1907, ii, 602), and Dolezalek (this vol., ii, 22) is discussed. T. H. P.

Measurement of the Surface-tension and other Physical Constants of Acetic Acid-Water Mixtures. LEO GRUNMACH (*Ann. Physik*, 1909, [iv], 28, 217—257).—The surface-tension, refractive index, and electrical conductivity of mixtures of acetic acid and water have been measured. The values of the surface-tension, obtained by determining the wave-lengths of capillary waves generated on the surface of the liquid mixtures, decrease continuously as the percentage of acetic acid in the mixture increases. There is therefore no apparent connexion between the surface-tension and the viscosity, for the viscosity increases with the acetic acid concentration to a maximum which corresponds approximately with the mixture of maximum contraction and then decreases.

The refractive index increases with the proportion of acetic acid in the mixture, attains a maximum for a mixture containing 87% of this, and then decreases. The composition of this mixture of maximum refractive index differs from that of the mixture corresponding with maximum contraction and maximum density.

The electrical conductivity measurements relate to mixtures containing from 43.9 to 99.6% of acetic acid. The specific conductivity diminishes continuously with increasing proportion of acetic acid, and there is no evidence of any abnormal change at the concentration which corresponds with the maximum contraction.

H. M. D.

Anomalies in the Viscosity of Anisotropic Liquids in a Condition of Hydraulic Flow. EMIL BOSE (*Physikal. Zeitsch.*, 1909, 10, 32—36).—Measurements have been made of the times of flow of anisaldazine through a capillary tube at temperatures in the neighbourhood of the clearing temperature and under different hydrostatic pressures. When, as a result of an increase in the hydrostatic driving pressure, the Poiseuille condition of flow is replaced

by the hydraulic condition, the anomalies exhibited by the viscosity of the anisotropic liquid are found to diminish. The observations support the author's view that anisotropic liquids represent molecular aggregates in which the molecules tend to move by preference in the direction of the long axes of the molecules. H. M. D.

Laws of the Molecular- and Viscosity-Diffusion of Gases through Tubes. MARTIN KNUDSEN (*Ann. Physik*, 1909, [iv], 28, 75—130).—The author has determined the rate at which hydrogen, oxygen, and carbon dioxide pass through capillary tubes under different conditions. By alteration of the gas pressure the ratio between the mean free path of the molecules and the radius of the capillary tube was made to vary between very wide limits. McLeod gauges, connected with two gas reservoirs on opposite sides of the capillary tube, were used to determine the absolute pressure values as well as the pressure fall.

When the radius of the tube is very small in comparison with the mean free path of the molecules, molecular diffusion takes place at a rate which is proportional to the driving pressure and inversely proportional to the square root of the density of the gas.

When the radius of the tube is not very small or very large in comparison with the mean molecular free path, the rate of passage through the tube is determined partly by molecular diffusion, and partly by a movement regulated by Poiseuille's law. In these circumstances, the quantity of gas which passes through the tube in unit time under the influence of unit fall of pressure decreases at first as the pressure increases, a minimum value being attained when the pressure is still very small, and beyond this the quantity increases uniformly with the pressure. A considerable part of the paper deals with the theory of the phenomenon. H. M. D.

Osmotic Pressure of Sucrose Solutions at 25°. HARMON N. MORSE and WILLIAM W. HOLLAND (*Amer. Chem. J.*, 1909, 41, 1—19. Compare Abstr., 1908, ii, 671, 1019).—With the object of ascertaining the temperature-coefficient of the osmotic pressure, it was decided to measure the pressure of sucrose solutions in concentrations from 0.1 to 1.0 weight-normal at intervals of five degrees from 0° to 30°. Of these, measurements at 10° and 15° have already been recorded (*loc. cit.*), and the authors now publish in customary form the pressure measurements of the usual ten concentrations of solution at 25°. Tables giving a summary of the progress made up to the present time are also appended, from which it is seen that the osmotic pressure is throughout higher than the corresponding gas pressure, the mean ratio being 1.06 : 1 in all cases from 5° to 25°. J. V. E.

Cohesion Pressure (Haftdruck). The Theory of Solutions. ISIDOR TRAUBE (*Ber.*, 1909, 42, 86—94).—The paper is a summary of the author's work appearing elsewhere (*Verh. Deut. Phys. Ges.*, 1908, 10, 480; and in its physiological relationships (Abstr., 1908, ii, 565).

All forms of energy can be expressed as the product of an intensity and a capacity factor. Against the modern theories of osmotic

pressure and electrolytic dissociation, the author levels the reproach that only the capacity factor has been considered. The intensity factor, which he calls the cohesion pressure and which represents the force with which a solute is retained in a solution, has been altogether neglected, although its examination in solutions is as necessary as that of potential in electrochemistry.

Gibbs has proved thermodynamically that a solute which diminishes the surface-tension of a solvent tends to accumulate in the surface layer, and vice versa. This principle is enunciated by the author in the form: the more a solute diminishes or increases the surface-tension of a solvent, so much the smaller or the greater is its cohesion pressure. Accordingly, the difference of the surface-tensions of a solvent and a solution is a measure of the cohesion pressure.

In osmosis, the driving force is the difference of the surface-tension, not the osmotic pressure. If equimolecular aqueous solutions of amyl alcohol and of sugar are separated by a membrane, equilibrium is not established (as it should be by the ordinary theory, since the number of particles on both sides of the membrane is equal), because amyl alcohol, which diminishes greatly the surface-tension of water, has a smaller cohesion pressure than sugar, which increases the surface-tension.

By measuring the surface-tension of salt solutions, the author has been able to arrange ions in the order of their cohesion pressures. There is scarcely a property of solutions for which this order is not wholly or approximately retained. Such properties have been examined as the capacity of hydration, diminution of solubility, compressibility, diminution of vapour pressure, depression of the freezing point, internal friction, mobility and electrical conductivity, diminution of the specific heat, heat of solution, heat of neutralisation, optical activity, specific volume, velocity of reaction, refraction and absorption of light, and valency. Since the internal pressure of most organic liquids is approximately the same, the author states that those organic liquids have the greatest solubility which have the greatest cohesion pressure. This deduction is confirmed without exception.

The relations between surface-tension and partition-coefficients and between surface-tension and adsorption (compare Freundlich, *Abstr.*, 1907, ii, 155) are very briefly referred to. With regard to the vapour pressure of aqueous solutions of volatile, organic substances, the author finds, in conformity with his theory, that the vapour pressure of substances of the same boiling point in aqueous solution is so much the greater the greater their cohesion pressure, and that substances of the same cohesion pressure have vapour pressures so much the greater the lower the boiling point.

Reference must be made to the original paper (*loc. cit.*) for evidence of the following statements.

The approximately equal heats of neutralisation of strong acids and strong bases is a consequence of the fact that the difference between the cohesion pressure of any strong acid and its salt with a given strong base is approximately the same; with regard to weak acids, however, it is found that, in consequence of the small cohesion

pressure of, for example, acetic acid, the work necessary to separate acetic acid from its solvent is just so much less than the work in the separation of a strong acid as corresponds with the difference of the work of ionisation.

The greater the cohesion pressure of a substance or its ions the greater is the degree of ionisation.

For organic substances of small cohesion pressure, the square root of the cohesion pressure is proportional to the molecular volume, and therefore to the molecular refraction and to the sum of the valencies (Abstr., 1907, ii, 205); the contraction of the co-volume is, in aqueous solution, proportional to the cohesion pressure.

The whole behaviour of colloids, such as albumin, etc., is explained by the fact that their cohesion pressure in water is practically nil.

The cohesion pressure is an ionising force, and the omission of its consideration in the theory of electrolytic dissociation has led to disastrous results. The theory of Arrhenius, which the author regards as fundamentally erroneous, is concerned only with changes in the capacity factor, that is, with the number of particles in the solution, and does not take into account the fact that changes of the cohesion pressure must play an important rôle. The abnormal behaviour of concentrated solutions is connected with the cohesion pressure. C. S.

Guldberg and Waage's Law from the Point of View of the Theory of Probabilities. S. VOINITSCH-SJANOSCHENTZKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1676—1684).—A mathematical paper, in which the author shows that the law of Guldberg and Waage can be deduced by applying the theory of probabilities to the atomic-molecular hypothesis, no further assumptions being required.

T. H. P.

Three-phase Equilibrium, showing a Pressure Minimum, in the Case of a Dissociating Compound of Two Components. I. GERARD H. LEOPOLD (*Zeitsch. physikal. Chem.*, 1909, 65, 428—441).—A theoretical paper. The different forms of curve for a three-phase system in which a minimum value for the pressure occurs are discussed and figured. The theoretical conclusions have been tested by experiments with chloral alcoholate and with aniline hydrochloride; the results are to be communicated in a later paper.

G. S.

Behaviour of Sulphuric Acid in Ester Formation. ANTON KAILAN (*Monatsh.*, 1909, 30, 1—27).—Measurements of the velocity of formation of ethyl hydrogen sulphate at 25° in dilute and in concentrated aqueous alcohol and with various concentrations of sulphuric acid show that the reaction is unimolecular. The esterification constants, calculated from the equation for unimolecular reactions, are expressed as a function of the water-content (w) and of the concentration of the sulphuric acid (c) by the following equation, the time being in hours: $1/k = 99.80 + 7.578/c - 1.101/c^2 + (123.7 - 85.00/c + 14.43/c^2)w + (106.5 + 251.8/c - 25.47/c^2)w^2$. This equation

holds for $w = 0.05 - 1.4$ and for $c = 0.12 - 0.6$; also for $w = 0.1 - 0.2$, it is correct up to $c = 1.4$.

The addition of water causes less retardation in the formation of ethyl hydrogen sulphate than in the formation of ethyl chloride. The addition of alcoholic hydrogen chloride causes an increase in the velocity of formation of ethyl hydrogen sulphate varying from about 30% to 60% according to the concentrations of the hydrochloric and sulphuric acids; this increase is considerably less than would be expected if the catalysis were produced by the hydrogen ions.

The constant of esterification of β -phenylpropionic acid by alcoholic sulphuric acid at 25° varies with the concentrations of water ($w = 0.06 - 1.3$) and sulphuric acid ($c = 0.16 - 0.69$) according to the expression: $1/k = 0.0824 + 0.2515/c + 0.01752/c^2 + (-1.319 + 2.246/c - 1.336/c^2)w + (-0.0480 - 0.2062/c + 0.1091/c^2)w^2$.

In alcohol containing little water, the increase of the esterification velocity effected by sulphuric acid is only about one-third of that produced by hydrochloric acid. In general, the influence of added water is less with sulphuric than with hydrochloric acid, as regards both decrease of the reaction velocity and also the deviation of the value of k from proportionality to the concentration of the catalyst.

T. H. P.

Steric Hindrance. I. Theory of Esterification of Organic Carboxylic Acids. ARTHUR MICHAEL (*Ber.*, 1909, 42, 310—317. Compare Rosanoff and Prager, this vol., ii, 32; Prager, ii, 33).—Victor Meyer found that, in the esterification of aromatic acids by means of alcohol and hydrogen chloride, the greater the mass of the substituent, especially in the ortho-position, the lower the esterification (*Abstr.*, 1894, i, 463; 1895, i, 93; 1896, i, 547). A similar rule was found by Sudborough and Lloyd to hold for substituted acetic acids (*Trans.*, 1898, 73, 81; 1899, 75, 467; compare also Gyr, this vol., ii, 33). Menshutkin (*Abstr.*, 1882, 595), without the use of a catalyst, found that the replacement of hydrogen in acetic acid lowered the velocity of esterification, but Lichty (*Abstr.*, 1895, ii, 157; 1896, ii, 557) found that the substitution of chlorine increased the velocity, a result in direct opposition to that obtained with a catalytic agent. Goldschmidt's view (*Abstr.*, 1906, ii, 219) that the true agent in catalytic esterification is a complex ion composed of the hydrogen ion and alcohol is rejected, and the opinion is expressed that a Kekulé "double molecule" is first of all formed, composed of hydrogen chloride and carbinol, for which there is experimental evidence (Archibald and McIntosh, *Trans.*, 1904, 85, 919), rather than combination between organic acid and catalyst. Such a "double molecule," it is thought, would be richer in chemical energy, and would resemble the acid more than the alcohol in properties. This would unite with the carboxylic acid, which would then decompose directly into ester, water, and halogen acid. In the case of alcohol and organic acid, the ortho-acid first formed would decompose into ester and water. Menshutkin's results are explained by the positive methyl group diminishing the free chemical energy of the carbonyl radicle, where chlorine, being nega-

tive, would increase it. This increase in the negative character of the acid itself, although increasing the esterification of the acid by the direct method, would diminish the attraction of acid for the halogen acid-carbinol molecule, and therefore a decrease in the esterification would result. The following table is given for the two methods:

	Direct.	Catalytic.		Direct.	Catalytic.
Formic acid	100.0	1124.0	<i>n</i> -Butyric acid.....	53.9	50.0
Acetic „	71.9	104.0	<i>iso</i> Butyric acid.....	11.8	2.6
Chloroacetic acid.....	102.8	78.8	<i>n</i> -Valeric acid	—	53.5
Dichloroacetic acid.....	253.1	2.1	<i>n</i> -Hexoic „	53.6	54.6
Propionic acid	66.7	91.9	<i>n</i> -Octoic „	50.0	54.7

The numbers are relative, and those in the first column are not comparable with those in the second. The paper concludes with a discussion of the influence of substitution in the various positions, the relative great decrease from propionic to butyric acids being emphasised; also, the analogous results obtained with aromatic acids and the influence of fluorine are explained on the author's hypothesis (compare also Goldschmidt, this vol., ii, 129).

W. R.

Steric Hindrance. II. Influence of Substituents in Aromatic Carboxylic Acids on their Esterification. ARTHUR MICHAEL and K. J. OECHSLIN (*Ber.*, 1909, 42, 317—330. Compare preceding abstract).—The influence of substituents like chlorine, bromine and iodine, nitroxyl, methyl and hydroxyl on the esterification of benzoic acids by the direct method was carried out by heating solutions of these acids, strength 1/100 mol. in 7.5 c.c. methyl alcohol, at temperatures like 135° or 165° in a closed tube, and, after a suitable period, the tube was opened and the contents titrated with *N*/10 barium hydroxide solution. The following table indicates the character of the results obtained after seventeen hours' heating at 135°:

	%.	Affinity constant.
Benzoic acid	20.0	0.006
<i>o</i> -Nitrobenzoic acid	21.2	0.616
<i>m</i> -Nitrobenzoic „	57.4	0.034
<i>p</i> -Nitrobenzoic „	40.0	0.040
<i>o</i> -Toluic acid.....	12.2	0.012
<i>m</i> -Toluic „	20.0	0.005
<i>p</i> -Toluic „	21.0	0.005
<i>o</i> -Chlorobenzoic acid	25.6	0.132
<i>p</i> -Chlorobenzoic „	37.3	0.0093

The small effect of chlorine and nitroxyl in the ortho-position is very marked, especially as compared with the effect of the methyl group; the influence exerted by a *m*-nitro-group is extraordinary: 74% can be obtained as ester at 165° after twenty hours. These results are directly opposed to those obtained by the indirect method; thus, for instance, with a catalyst, *o*-nitrobenzoic acid is only slightly esterified, and with the meta- and para-acids the esterification velocity is only two-thirds of the value for benzoic acid. Without a catalyst, the ratio is acid : *o* : *m* : *p* = 1 : 1 : 3 : 2. Similar experiments were carried

out with butyric, the two crotonic, and the four chlorocrotonic acids, and with ortho-disubstituted benzoic acids. From the results of these experiments, the following conclusions are drawn : (1) In the presence of a catalyst, the velocity of esterification is conditioned chiefly by the affinity between acid and catalyst, and the results only show the influence of the substituent on this attraction. (2) The influence of substituents on the velocity of esterification of the carboxyl group can only be ascertained by the direct method. These furnish no experimental results which support the idea that the space occupied or the mass of the substituent influence the phenomena. (3) It is the chemical nature of the substituents which is the determining factor. (4) Although the indirect method shows a similarity to exist between acetic, crotonic, and benzoic acids, with the direct method it is only in the case of the meta- and para-aromatic acids that this analogy holds ; with the ortho-compounds it is only partial.

W. R.

Present Status of the Solvate Theory. HARRY C. JONES (*Amer. Chem. J.*, 1909, 41, 19—57).—This communication is a summary of the work carried out and published during the past ten years by Jones and his co-workers (compare Abstr., 1899, ii, 587, 628 ; 1900, ii, 262, 526 ; 1902, ii, 489 ; 1903, ii, 55, 131, 634, 637 ; 1904, ii, 235, 386, 710, 711 ; 1905, ii, 445, 509, 687, 794 ; 1906, ii, 66, 327, 329, 737, 827 ; 1907, ii, 147, 211, 212, 438 ; 1908, ii, 19, 259, 260, 474, 1011).

J. V. E.

Forms of Matter. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 27—38. Compare this vol., ii, 132).—In this continuation of the previous paper it is shown that the formation of the hydrosol form of barium sulphate is induced by increasing the number of centres of crystallisation ; this can be effected by increasing the viscosity of the liquid medium or by increasing the degree of association of the reacting components of the solution. In the author's experiments the viscosity was increased by the use of nearly saturated solutions of zinc chloride or manganous thiocyanate, the reacting components in the first case being cadmium sulphate and barium chloride, and in the second, barium thiocyanate and manganous sulphate. The degree of association is increased by replacing the solvent water by solvents of smaller dissociating power. The conditions which thus favour the formation of the hydrosol form of barium sulphate are applicable to all substances.

From the observed facts relating to precipitation phenomena, the author shows how the conditions necessary for the production of typical colloids in the form of fully developed crystals can be deduced. So-called typical colloids can be obtained in the crystalline form by allowing extremely dilute solutions of the reacting components to interact slowly ; in the case of very slightly soluble substances, increase of the solubility by suitable means also favours the formation of crystalline particles. The actual methods which have been used in the numerous cases recorded in the literature depend on one or other of these artifices. The influence of the concentration of the reacting solutions on the structure of precipitated aluminium hydr-

oxide has been examined. Solutions of ammonia and aluminium chloride more concentrated than $N/500$ give rise to "amorphous" forms. Solutions less concentrated than $N/2500$ yield microscopic, crystalline forms. The phenomena thus observed with aluminium hydroxide (a "colloid") and barium sulphate (a "crystalloid") are exactly parallel; the quantitative differences are simply due to the fact that aluminium hydroxide is very much less soluble in water than barium sulphate.

H. M. D.

Hydrogels in the Mineral Kingdom. FELIX CORNU (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 15—18).—The author gives a list of minerals which belong to the group of hydrogels. These gels are products of all normal weathering processes, whether these take place in silicate rocks or in the oxidation zones of ore deposits.

For every mineral hydrogel it is possible to find a corresponding crystalloid form; such corresponding forms are grouped in a table by the author. The mineral gels are characterised by certain general properties in respect of form, cleavage, optical behaviour, etc.

H. M. D.

Theory of Tanning. ANDREA RICEVUTO (*Gazzetta*, 1909, 39, i, 28—34).—When a current is passed through a colloidal gelatin solution, the gelatin particles move towards either the anode or the cathode according as the reaction of the liquid is alkaline or acid, whilst no transport takes place if the reaction is neutral.

The author has carried out similar experiments on tannin, sumach, and a number of other tanning materials, which, as would be expected, in presence of an acid or a base assume a charge opposite in sign to that of the gelatin, whilst in neutral solution no precipitation occurs on mixing solutions of gelatin and the tanning material. It is noteworthy that dialysis removes the acidity from some of the original tanning materials, but not from others.

The author regards the determining cause of the phenomenon of tanning as the diversity of the electric charges carried by the colloidal particles, the action of the acid present being of the highest importance.

T. H. P.

Atomic Weight Formula Based on the Law of Mass Action and Avogadro's Rule. AUGUST L. BERNOULLI (*Zeitsch. physikal. Chem.*, 1909, 65, 391—427).—A more detailed account of work already published (Abstr., 1908, ii, 1001). The agreement between the international values of the atomic weights and the "kinetic" values calculated according to the author's theory is in some cases only moderate, but the agreement is better when, instead of the international values, "reduced" values calculated from the experimental data on the basis of some fundamental kinetic values are used.

G. S.

Molecular Diameters. WILLIAM SUTHERLAND (*Phil. Mag.*, 1909, [vi], 17, 320—321).—The author points out that Jeans in his estimate of the diameters of various molecules (Abstr., 1905, ii, 14) neglected the effect of cohesive forces on viscosity, conductivity, diffusivity, and deviation from Boyle's law. A correction, $\sqrt{T/(T+C)}$, is there-

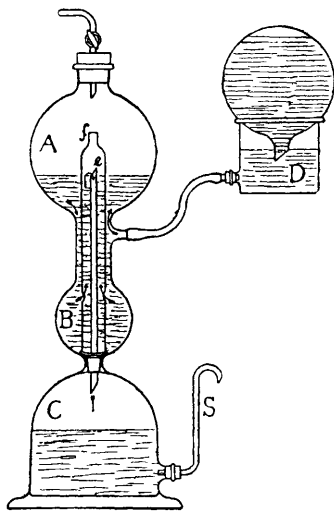
fore applied, where T is the absolute temperature and C is a parameter proportional to the mutual potential energy of two molecules in contact. A revised table of diameters of twelve gaseous molecules is given.

R. J. C.

Molecular Dimensions on the Basis of the Kinetic Theory of Gases. MAX REINGANUM (*Ann. Physik*, 1909, [iv], 28, 142—152).—A criticism of the values obtained by Sirk (*ibid.*, 1908, [iv], 25, 894) for the dimensions of molecules. These numbers are deduced on the false assumption that the molecules are elastic spheres having no action on one another. When the attractive forces are taken into account, a different series of equations is obtained. In some cases the calculated results are in error, because of the fact that the coefficients of viscosity used in the calculations are about 50% too large.

H. M. D.

Continuous Apparatus for Preparation of Gases Evolved in the Cold. MAXIME GASNIER (*Bull. Soc. chim.*, 1909, [iv], 5, 56—58).—The apparatus shown possesses the advantage over Kipp's and others of the same class that the supply pressure remains constant whatever the amount of gas taken. Acid runs from constant level D into bulb A containing the solid reagent. The saline solution produced sinks by gravity into B , whence it eventually finds its way through tube e into the reservoir C , and is run off by syphon S . Insoluble sediment settles in B . If the rate of evolution of gas is not too fast, the liquid in C contains no free acid. The apparatus is more suitable to deliver a steady stream of gas during a long period than for an intermittent duty. It can be flushed out with water without opening. R. J. C.



Apparatus for Simultaneously Extracting a Solid and Filtering the Solution so Obtained. FREDERICK RECORD (*Chem. News*, 1909, 99, 53. Compare Abstr., 1908, ii, 575).—The apparatus previously described, being made entirely of glass, required considerable skill for its construction. A slightly modified form, of simpler construction, has now been devised. The inner vessel, containing the filtering disk, is made separate from the outer vessel, being supported therein and held in position by a cork fitting into the mouth of the outer vessel.

J. V. E.

Inorganic Chemistry.

Hypohalogenous Acids and Hypohalogenites. II. Kinetics of the Hypobromites in Weak Alkaline Solution. ANTON SKRABAL (*Monatsh.*, 1909, 30, 51—76. Compare Abstr., 1907, ii, 448).—The author has investigated the kinetics of the decomposition of a hypobromite into bromide and bromate in a solution containing hydroxyl ions in small, but constant, concentration. This constancy of concentration was effected by the use of sodium carbonate and sodium hydrogen carbonate in proportions sufficiently large compared with that of the hypobromite. With reference to the concentration of hypobromite, the decomposition of the latter is of the second order, the velocity of formation of bromate being proportional to the concentration of hydrogen ions. Diminution of the concentration of the hydroxyl ions is accompanied by increase of the velocity of the change, which is also accelerated by the presence of electrolytes, this accelerating action being especially marked in the case of the bromides. The following kinetic equation represents the decomposition: $-d[\text{HBrO}]/dt = [\text{H}']\{[\text{Br}'] + e[E]\}K[\text{HBrO}]^2$, $[E]$ being the concentration of the electrolyte and e and K constant factors. The action of an electrolyte is very approximately proportional to the number of ionic charges, but is independent of the nature of the electrolyte.

From the fact that, with small concentration of the electrolyte, the reaction proceeds according to the equation: $-d[\text{HBrO}]/dt = [\text{H}'][\text{Br}']K[\text{HBrO}]^2$, the conclusion is drawn that the mechanism of the reaction is similar to that of the hypiodite reaction (*loc cit.*). Accordingly, in the hypobromite solution, an equilibrium, $\text{HBrO} + \text{Br}' + \text{H}' \rightleftharpoons \text{Br}_2 + \text{H}_2\text{O}$ or $2\text{HBrO} + \text{Br}' + \text{H}' \rightleftharpoons \text{HBr}_3\text{O} + \text{H}_2\text{O}$, must be rapidly set up, the reaction determining the velocity being the decomposition of Br_2 or HBr_3O into bromide and bromate.

T. H. P.

The System Hydrogen Bromide and Bromine. ERNST H. BÜCHNER and B. J. KARSTEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 11, 504—508).—Sealed tubes containing weighed quantities of bromine and hydrogen bromide, dried by passing over phosphoric oxide, were placed in a mixture of alcohol and solid carbon dioxide or of calcium chloride and ice, and the temperature allowed to rise very slowly. The tubes were continually shaken, and the temperatures at which the last trace of solid disappeared were recorded. The end melting points, when plotted, indicate that there is an eutectic at about -95° , the composition corresponding with about 5 mols. % bromine. According to the curves no compound is formed. Although certain facts point to the formation of compounds between hydrogen bromide and bromine in solution, the authors point out that this is only true of ionising solvents, and that the union is probably determined by the bromine ion. In non-ionising solvents it is improbable that such union takes place.

H. M. D.

Revision of the Atomic Weights of Iodine and Silver. GREGORY P. BAXTER and GEORGE S. TILLEY (*J. Amer. Chem. Soc.*, 1909, 31, 201—221; *Zeitsch. anorg. Chem.*, 1909, 61, 293—319).—With the object of obtaining a trustworthy value for the ratio of the atomic weight of silver to that of oxygen, careful analyses have been made of iodine pentoxide, the ratio of the atomic weights of silver and iodine being already known with great exactitude. A method is described for preparing pure iodic acid, and confirmation has been obtained of the existence of the compound $\text{I}_2\text{O}_5 \cdot \text{HIO}_3$ (compare Groschuff, *Abstr.*, 1906, ii, 16). Iodic acid is almost completely converted into the pentoxide when heated at 240° , but a small quantity of water remains. The analysis of the iodine pentoxide was effected by dissolving the substance in water, reducing it to hydriodic acid with a suitable reducing agent, and titrating the hydriodic acid against a weighed amount of silver. It was found that hydrazine was the most satisfactory reducing agent, and that sulphur dioxide could not be used, as silver iodide occludes silver sulphate.

Iodine pentoxide has D_4^{25} 4.80. Experiments have been carried out which prove that this substance does not absorb appreciable quantities of air.

Two series of analyses have been made in which three different samples of iodine pentoxide and four samples of pure silver were employed. The ratio $2\text{Ag} : \text{I}_2\text{O}_5$ has been found to be 0.646230, whence the atomic weight of silver is 107.850, and that of iodine, 126.891 ($O = 16$). E. G.

Colour of Iodine Solutions. JOEL H. HILDEBRAND and BEN LEON GLASCOCK (*J. Amer. Chem. Soc.*, 1909, 31, 26—31).—Since Beckmann (*Abstr.*, 1907, ii, 340) showed that the molecular weight of iodine in all solvents corresponds with the formula I_2 , it has usually been accepted that the brown colour of certain solutions of iodine is connected with combination between the latter and the solvent. To test this view, the freezing-point depression produced by iodine and certain liquids, separately and then together, has been determined with bromoform and ethylene dibromide as solvents. Only for liquids which form brown solutions is the total depression less than the sum of the separate depressions, showing that combination has taken place.

The equilibrium between iodine and certain "active" solvents (those which can combine with iodine) has been investigated in such inactive solvents as carbon disulphide and carbon tetrachloride by a colorimetric method, and it is shown that for ethyl alcohol, acetic acid, ethyl acetate, and nitrobenzene the respective compounds contain 1 molecule each of the solvent and iodine. From the displacement of the equilibrium with temperature, it is calculated that the heat of combination of iodine and ethyl acetate is 3,600 cal. per mol. G. S.

Behaviour of Solutions of Hydriodic Acid in Light in the Presence of Oxygen. H. JERMAIN M. CREIGHTON (*Trans. Nova Scotia Inst. Sci.*, 1908, 12, 49—60).—The object of the investigation is to account for the fact that the amount of iodine liberated from

a solution of hydriodic acid or of acidified potassium iodide by oxygen and light reaches a maximum and then falls to zero.

The solution used contained one volume of aqueous potassium iodide (1 gram per litre) to eight volumes of dilute sulphuric acid (1 vol. of acid, D 1.84, to 5 vols. of water). The liberated iodine was titrated by *N*/1250 sodium thiosulphate.

A preliminary experiment showed that evaporation of the iodine is not wholly responsible for its disappearance, and also that the change of the iodine is accelerated by sunlight.

The acidified potassium iodide solution, 500 c.c., absorbed about 25 litres of oxygen in ten weeks, but neither iodine nor iodate could be detected in the solution, and strong reducing agents failed to liberate any iodine. The nature of the product is still a mystery.

C. S.

Polyiodides. F. OLIVARI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 717—722).—The freezing-point curves have been determined for mixtures of metallic iodides with iodine, using an ordinary cryoscopic apparatus.

Mercuric iodide does not form a polyiodide; the curve has a eutectic point at 101.4° and 12.5 molecular % HgI_2 . The curve for mixtures of calcium iodide and iodine has no distinct maximum, but an almost horizontal branch, having a eutectic point on the iodine side. The polyiodide, if formed, must be greatly dissociated at the melting point.

Tetramethylammonium iodide and iodine give a freezing-point curve presenting several maxima; some of the results are uncertain, owing to the hygroscopic nature of the substances. The polyiodide $\text{NMe}_4 \cdot \text{NI}_3$ crystallises well in silky needles.

Phenyltrimethylammonium iodide forms four polyiodides, RI_4 , RI_5 , RI_7 , and RI_9 ($\text{R} = \text{NPhMe}_3$), freezing at 112°, 83°, 63°, and 25° respectively. The results confirm the conclusion of Abegg and Hamburger (*Abstr.*, 1906, ii, 747) that the stability of the polyiodides increases with the electro-positive character of the cation.

C. H. D.

Fluoro-salts. FRITZ EPHRAIM and PAUL BARTECZKO (*Zeitsch. anorg. Chem.*, 1909, 61, 258—264).—A tabular review of the known double fluorides is given. The Werner co-ordination number 6 is exceeded in a large number of cases. The number of hydrofluoro-metallic acids is also larger than with other halogen acids. The type $\text{M}'_5\text{M}''\text{F}_7$ is remarkable, a copper, cobalt, and nickel salt being known.

C. H. D.

Measurements of the Efficiency of Ozone Tubes. VII. EMIL WARBURG and G. LEITHÄUSER (*Ann. Physik*, 1909, [iv], 28, 1—16. Compare *Abstr.*, 1906, ii, 740, 741).—The action of an ozone tube, regarded as a system of condensers in series with one another, is subjected to mathematical treatment. Some experiments are communicated which show the influence of the current strength and the frequency on the efficiency. With increasing current strength

the efficiency falls, but rises with increase in the frequency until a certain limiting value is reached. Ozonisers with an inner metal tube are more efficient than those with an inner tube of glass. At a given discharge potential, small ozonisers combined with a high frequency of discharge yield as much ozone as larger ozonisers with a smaller frequency.

H. M. D.

Production of Ozone from Oxygen and Atmospheric Air by means of Ozonisers. VIII. EMIL WARBURG and G. LEITHÄUSER (*Ann. Physik*, 1909, [iv], 28, 17—36. Compare preceding abstract).—The dependence of the yield of ozone on the amount of ozone already present in the gas operated on has been examined. Equations are deduced for the case in which the ozoniser contains a motionless and homogeneous mixture, and also for that in which a steady flow of gas is maintained through the ozoniser. In the latter case, the percentage of ozone in the gas acted on by the discharge increases gradually from one end of the tube to the other. The yields of ozone determined experimentally are, in most cases, in agreement with the theoretical formulæ, but when oxygen is passed through the ozoniser the observed limiting ozone concentration is greater than that expected theoretically.

In the second part of the paper, the authors have investigated the variation of the yield of ozone with the current density and with the form of the induced current as modified by placing an induction-free resistance in parallel current; further, with the temperature and the nature and form of the ozoniser. Per kilowatt hour, the best yields are obtained when the diameter of the discharge chamber is large, but, on the other hand, if a high concentration is required, the two tubes of the ozoniser should be comparatively close together.

H. M. D.

Formation of Ozone at Stationary Linear Electrodes. FRANZ FISCHER and KURD BENDIXSOHN (*Zeitsch. anorg. Chem.*, 1909, 61, 153—180. Compare this vol., ii, 136).—A device is described by which the length of the anode, consisting of a strip of platinum foil, 0.01 mm. wide and sealed into glass, could be varied. Such electrodes are stable, but not those of only 0.005 mm. width.

A critical current density is observed, at which the potential difference shows a sudden increase, the current at the same time falling slightly. The current density at which this occurs is independent of the anode area, and falls with increasing concentration of acid. When it is exceeded, the yield of ozone diminishes greatly. On reducing the current after this point has been passed, the original potential is not observed, one several volts higher being always found. This behaviour of the anode is found to be due to incrustation of the anode, at a high current density, with platinum sulphate. Experiment shows that platinum sulphate, $\text{Pt}(\text{SO}_4)_2$, is insoluble in concentrated, but soluble in dilute, sulphuric acid.

A reduction in the width of a stationary anode increases the yield of ozone, as does a reduction of temperature, the yield increasing to 27% when the electrolyte is cooled to -3.5° . Since, however, the

critical current density falls with decreasing temperature, a limit is set to the advantage to be derived from cooling. The critical point is also observed with rotating electrodes. C. H. D.

Dynamic Allotropy of Sulphur. II. [Binary] Systems containing Sulphur. HUGO R. KRUYT (*Zeitsch. physikal. Chem.*, 1909, 65, 486—510. Compare Abstr., 1908, ii, 1028).—In liquid sulphur there is equilibrium between the forms S_λ and S_μ . The theoretical part of the present paper contains a general discussion of the possible types of partial miscibility in liquid systems where a pseudo-binary substance, such as sulphur, forms one of the components, and no appreciable chemical reaction takes place.

A number of substances which react with sulphur between 100° and 200° are mentioned. Benzene, toluene, *m*-xylene, and triphenylmethane proved suitable for the investigation, as very little chemical reaction took place.

Benzene and sulphur are completely miscible above 160° and below 226°; the forms of the miscibility curves below and above these temperatures have been determined. Sulphur and toluene, and sulphur and triphenylmethane, show curves of similar type to the sulphur-benzene system; in the former system the limits of complete miscibility are 180° and 220°; in the latter case, 145° and 200°. The system sulphur—*m*-xylene gives a curve of entirely different type, as the components are not completely miscible in all proportions at any temperature within the limits employed. The types of curve observed are in accord with the theoretical deductions.

In several cases, notably in the system *m*-xylene-sulphur, retardation in the attainment of miscibility was observed, a result ascribed to the peculiarities in the behaviour of sulphur. G. S.

Statics of Liquid Sulphur in the Dark and under the Influence of Light. ALBERT WIGAND (*Zeitsch. physikal. Chem.*, 1909, 65, 442—457. Compare Abstr., 1908, ii, 676).—The melting point of pure monoclinic sulphur is 118·95°.

The equilibrium $S_{3 \text{ sol.}} \rightleftharpoons S_{3 \text{ insol.}}$ has already been determined by Schaum between 121° and 140°, and the author has now extended the observations from 117·1° to 119·6° by Schaum's method. The results fit in well with those of Schaum. From the results it is calculated that the heat of transition from the soluble to the insoluble form is -7180 cal. per gram-molecule, S_3 , at 118·34°, as compared with -6000 cal. at 126·3°, -5390 cal. at 131·0°, and -4700 cal. at 135·9, calculated from Schaum's observations.

Some preliminary experiments indicate that the equilibrium is slightly displaced by light in favour of the insoluble form. As a source of light, arc lamps were used.

The possible constitution of the S_3 molecule is discussed. G. S.

An Automatic Hydrogen Sulphide Generator. HOWARD WATERS DOUGHTY (*J. Amer. Chem. Soc.*, 1909, 31, 60—62).—A modification of the apparatus devised by Bradley (Abstr., 1899, ii, 413).

The essential difference consists in an arrangement for drawing off the spent acid as fast as it settles to the bottom of the sulphide compartment.
L. DE K.

Action of Sulphur Chloride, S_2Cl_2 , on Metallic Oxides. FRANÇOIS BOURION (*Compt. rend.*, 1909, 148, 170—171. Compare Abstr., 1907, ii, 690).—The joint action of chlorine and sulphur perchloride on some oxides is so violent that the oxide becomes incandescent, and a certain amount of oxychloride is formed instead of chloride. Ordinary sulphur chloride is now found to convert metallic oxides into chlorides even in those cases where the older method gave poor results.

The vapour of sulphur chloride is passed over the oxide contained in a tube heated just sufficiently to start the action, during which sulphur is liberated: $2MO + 2S_2Cl_2 = SO_2 + 2MCl_2 + 3S$. Most oxides are attacked slightly below or at the boiling point of sulphur, and the products are quite free from oxychloride. Samarium chloride prepared by this method contained 41.40% of chlorine, instead of the calculated 41.47%.
R. J. C.

Hyposulphites. VI. ARTHUR BINZ (*Ber.*, 1909, 42, 381—384. Compare Abstr., 1908, i, 940).—Purely theoretical. Reviewing recent work, the author decides that $O:SNa \cdot O \cdot SO_2Na$ best represents the constitution of sodium hypsulphite.
C. S.

Electrochemical Reactions Induced by Sulphur Ions. MARIO G. LEVI and E. MIGLIORINI (*Gazzetta*, 1909, 39, i, 110—120. Compare Levi and Voghera, Abstr., 1906, ii, 81, 348, 436).—As sodium thiosulphate may be formed electrolytically by the action of sulphur ions migrating and discharging themselves on sodium sulphite, the authors have made experiments to see whether other thio-salts and thio-organic acids are formed in this way.

With sodium arsenate, appreciable quantities of the thio-arsenate are formed, but with sodium antimonate and molybdate, no thio-salt is obtained; in all cases, most of the S'' -ions undergo oxidation to SO_4'' .

With formic and acetic acids, no thio-acid is formed, but hydrogen sulphide is always formed in the anode chamber containing the organic acid; the same phenomenon is observed when dilute sulphuric acid is used as anodic liquid. This hydrogen sulphide is formed electrochemically, and is not due to the direct action of the acid on the sulphide, since experiment shows that such action will not take place through the Puckall diaphragms employed in the time occupied by the electrolysis. The amount of hydrogen sulphide formed is proportional to the quantity of electricity passing if the current is low, but diminishes relatively when higher currents are used.

T. H. P.

Preparation of Hydrogen Selenide. HENRI WUYTS and AL. STEWART (*Bull. Soc. chim. Belg.*, 1909, 23, 9—11).—Moissan and Étard obtained hydrogen selenide by heating selenium with colophene,

an expensive hydrocarbon obtained by polymerisation of terebenthene. The authors find it advantageous to replace colophene with paraffin wax, which commences to boil at 380° . Paraffin wax is attacked by sulphur at 245° , but selenium requires a temperature of 335 — 340° .

A regular evolution of hydrogen selenide is obtained by heating selenium with four times its weight of paraffin in an air-bath. Organic selenium compounds which accompany the gas are mostly condensed at 60° . The hydrogen selenide may then be further purified by condensation by a mixture of solid carbon dioxide and acetone, and fractional distillation. The yield is 75 to 80% of the theoretical.
R. J. C.

Electrolysis of Solutions of Selenious Acid. I. CAMILLO MANUELLI and GUIDO LAZZARINI (*Gazzetta*, 1909, 39, i, 50—69).—When solutions of selenious acid are electrolysed, the acid undergoes simultaneous reduction to selenium and oxidation to selenic acid: $\text{H}_2\text{SeO}_3 + 2\text{H}_2 = 3\text{H}_2\text{O} + \text{Se}$ and $2\text{H}_2\text{SeO}_3 + 2\text{O} = 2\text{H}_2\text{SeO}_4$. Selenic acid may be conveniently prepared in this way, since the electrolysis gives rise neither to intermediate reduction products nor to complex acids, as is the case when sulphurous acid is electrolysed. The authors have studied the influence of the conditions of electrolysis on the yields of selenium and selenic acid; theoretically, 0.7388 gram of selenium should be separated at the cathode per ampere-hour, whilst at the anode a quantity of selenious acid corresponding with 1.4776 gram of selenium should be oxidised.

The results show that diminution of the concentration of selenious acid and increase of the concentration of selenic acid are accompanied by a fall in the current yield both of selenium and selenic acid. When a large anode and consequently a small anodic current density is employed, the yield of the oxidation product is large, whilst with a large cathode a high yield of selenium is obtained. The diminished yield of selenic acid obtained when the quantity of this acid increases is not due to the establishment of an equilibrium between the oxidation of the selenious acid and the reduction of the selenic acid, since in the electrolysis of the latter, only a small amount of reduction occurs. The yields at 54 — 58° are not markedly different from those at 25° .

T. H. P.

Atomic Weight of Tellurium. VICTOR LENHER (*J. Amer. Chem. Soc.*, 1909, 31, 20—24).—The method depends on the fact that when potassium telluribromide, K_2TeBr_6 , is heated strongly in a current of chlorine, and finally in hydrogen chloride, only potassium chloride remains behind; the latter is then weighed.

Tellurium ores from three different sources were employed. The oxide obtained from the ores was converted into the double bromide by the action of hydrobromic acid and potassium bromide; the double bromide was crystallised repeatedly from water containing a little dilute hydrobromic acid, and was finally kept over soda-lime in a vacuum for eight months.

As a mean of sixteen concordant experiments, the value $\text{Te} = 127.55$ was obtained ($\text{Cl} = 35.46$, $\text{Br} = 79.92$, $\text{K} = 39.095$), in exact agreement

with the International value. The products from different sources gave identical results. G. S.

Non-existence of Tellurium Oxychloride. VICTOR LENHER (*J. Amer. Chem. Soc.*, 1909, 31, 243—244).—Tellurium dioxide (1 mol.) unites at about 0° with hydrogen chloride (3 mols.), and, on raising the temperature, 1 mol. of hydrogen chloride is eliminated with formation of the compound $\text{TeO}_2 \cdot 2\text{HCl}$. When this substance is heated at 280—300°, it is not converted into the oxychloride, TeOCl_2 , as stated by Ditte (*Abstr.*, 1877, i, 45), but into a mixture of the tetrachloride and dioxide without the intermediate formation of an oxychloride. If the tetrachloride and dioxide are heated together, combination does not take place, but, on cooling, the original compounds are recovered unchanged. E. G.

Reaction between Fused Potassium Nitrate and Tellurium Dioxide. VICTOR LENHER and P. D. POTTER (*J. Amer. Chem. Soc.*, 1909, 31, 24—26).—When tellurium dioxide is fused with potassium nitrate, yellowish-brown substances are noticed swimming in the fused mass; on continued heating, the mass becomes clear, the conversion to potassium tellurate being then complete. The brown products have been isolated by extracting with water until nothing further dissolves, and on analysis prove to be compounds of potassium tellurate with tellurium dioxide in proportions depending on the time of heating and other conditions. The same brown compounds have been prepared by fusing together potassium tellurate and tellurium dioxide; they are insoluble in dilute acids and alkalis, but are slowly decomposed by hot strong hydrochloric acid with evolution of chlorine. Analogous compounds are obtained by fusing tellurium dioxide with sodium nitrate. G. S.

Atomic Weights of Nitrogen and Silver. THEODORE W. RICHARDS, PAUL KÖTHNER, and ERICH TIEDE (*J. Amer. Chem. Soc.*, 1909, 31, 6—20; *Zeitsch. anorg. Chem.*, 1909, 61, 320—337).—The method employed was the analysis of ammonium chloride by decomposing with silver nitrate and weighing the resulting silver chloride. The results of Scott (*Trans.*, 1901, 70, 147) are regarded as untrustworthy, because the solubility of silver chloride was not sufficiently allowed for; the earlier investigations of Stas are unsatisfactory for the same reason, and also because the ammonium salt was not free from organic impurities.

One specimen of the salt was prepared as follows: Organic impurities were removed by heating the ammonium sulphate with concentrated sulphuric acid and a little potassium permanganate until the solution became perfectly colourless (Kjeldahl). To a solution of the acid ammonium sulphate, pure calcium oxide was added, and the mixture placed in a desiccator, which also contained a platinum dish filled with hydrochloric acid. On exhausting, the ammonia was absorbed by the acid. Another sample was prepared by the electrolytic reduction of nitric acid, as described by Hinrichsen (*Abstr.*, 1908, ii, 494).

The samples were recrystallised from dilute ammonia, and perfect

neutrality and complete dryness were secured by subliming first in an atmosphere of ammonia and then in a Sprengel vacuum (to remove excess of ammonia), quartz vessels being used throughout. The methods employed are fully described.

The ratio $\text{NH}_4\text{Cl} : \text{AgCl}$ was determined by methods analogous to those fully described in previous papers, and nine very concordant results are quoted. From these and previous results of Richards and his co-workers, the following values are obtained: $\text{Ag} = 107.881$; $\text{Cl} = 35.4574$; $\text{N} = 14.0085$, based on $\text{O} = 16.000$ and $\text{H} = 1.0076$ (Morley). The results furnish striking evidence in favour of the low values for nitrogen and silver recently advocated from different quarters. G. S.

Products of the Arc and Spark Electric Discharge in Liquid Argon or Nitrogen. III. Tin Nitride and Pyrophoric Tin. FRANZ FISCHER and GEORGE ILIOVICI (*Ber.*, 1909, 42, 527—537. Compare Abstr., 1908, ii, 1034; this vol., ii, 139).—By using tin as electrode in argon, 86—114 mg. per hour of a substance was prepared which behaves abnormally, as compared with the other substances obtained (*loc. cit.*), towards cold concentrated nitric acid. It is slightly altered by exposure to air, and a special apparatus was constructed so that, not only the substance could be prepared, but it could also be heated in the absence of air. When heated to redness in a quartz tube, nitrogen was evolved (proved by spectrum and sparking with oxygen); the maximum amount obtained was 3.18%, but analysis of various specimens gave generally less nitrogen, and the substance is a mixture of metal, nitride, and some oxide.

Calcium as an electrode when placed in a gasometer removes the oxygen and nitrogen from argon. The calcium arc discharge acts best when the calcium sublimes on the walls of the vessel; by this means the argon is rendered very pure, the "substance" from the tin electrode discharge containing no oxygen and only 0.8% of nitrogen. In this case the tin was rendered pyrophoric, due to the fine state of division. W. R.

Chloroamine. FRITZ RASCHIG (*Verh. Ges. deut. Naturforsch. Aertze.*, 1907, II, i, 120—123).—The well-known hypochlorite colour reaction of aniline is or is not obtained according as ammonia is added after or before the hypochlorite and the aniline solutions are mixed. Moreover, whilst concentrated solutions of ammonium hydroxide and sodium hypochlorite immediately evolve nitrogen when mixed, gas is evolved from dilute solutions only after some time. These facts led the author to deduce the existence of a compound intermediate between ammonia and nitrogen. Solutions containing equal molecular quantities of ammonia and sodium hydroxide react quantitatively, thus: $\text{NaOCl} + \text{NH}_3 = \text{NH}_2\text{Cl} + \text{NaOH}$; by distilling the solution in a vacuum at a low temperature, *chloroamine*, NH_2Cl , can be obtained as an unstable, faintly yellow oil floating in the distillate water. The solution of chloroamine, obtained as above, yields with potassium iodide at first a brown solution and then a black precipitate of nitrogen iodide, and with potassium cyanide, cyanogen chloride, and

ammonia, oxidises sulphurous acid, and reacts with alkali hydroxides, the more rapidly the greater the concentration of the alkali, to form ammonia, nitrogen, and potassium chloride: $3\text{NH}_2\text{Cl} + 3\text{KOH} = \text{NH}_3 + \text{N}_2 + 3\text{KCl} + 3\text{H}_2\text{O}$. The reaction with ammonia is similar: (I) $3\text{NH}_2\text{Cl} + 2\text{NH}_3 = \text{N}_2 + 3\text{NH}_4\text{Cl}$, but in addition a small quantity of hydrazine is formed, (II) $\text{NH}_2\text{Cl} + \text{NH}_3 = \text{N}_2\text{H}_4, \text{HCl}$. After many trials the author has succeeded in hindering reaction I and accelerating reaction II to such an extent that by treating normal sodium hypochlorite solution with fifty times the calculated quantity of ammonium hydroxide in the presence of a little glue, 75–80% of the calculated quantity of the ammonia is converted into hydrazine. C. S.

Oxidation of Hydrazine. III. ARTHUR W. BROWNE and F. F. SHETTERLY (*J. Amer. Chem. Soc.*, 1909, 31, 221–237).—In earlier papers (Abstr., 1907, ii, 863; 1908, ii, 373) an account has been given of the oxidation of hydrazine sulphate by ammonium metavanadate, and potassium chlorate, bromate, and iodate. Experiments are now described on the behaviour of aqueous solutions of hydrazine sulphate towards potassium persulphate, permanganate, and perchlorate, hydrogen peroxide, sodium periodate, red lead, and lead and manganese dioxides, with the object of determining the amounts of azoimide and ammonia produced in each case under certain conditions.

When hydrazine sulphate was heated with potassium persulphate in presence of sulphuric acid, the maximum yield of azoimide was 40·3%, whilst that of ammonia was 1·5 mols. from 2 mols. of hydrazine. In alkaline solution, only small amounts of azoimide were produced and about 20% of ammonia. The methods described by Pannain (Abstr., 1904, ii, 638) and Rimini (Abstr., 1906, ii, 898) for estimating persulphates by means of hydrazine sulphate are inaccurate, on account of the formation of azoimide and ammonia.

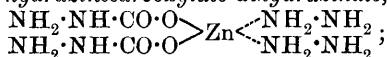
When hydrazine sulphate was treated in acid solution with potassium permanganate, maximum yields of 3·19% of azoimide and 1·65 mols. of ammonia from 2 mols. of hydrazine were obtained, whilst in alkaline solution only small quantities of azoimide were formed. Petersen (Abstr., 1893, ii, 605) has expressed the reaction between hydrazine sulphate and potassium permanganate in presence of sulphuric acid by the equation: $17\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4 + 13\text{O} = 13\text{H}_2\text{O} + 7(\text{NH}_4)_2\text{SO}_4 + 10\text{N}_2 + 10\text{H}_2\text{SO}_4$. It is now proved that the greater part of the hydrazine is converted into nitrogen and ammonia, as Petersen has stated, but that, under certain conditions, appreciable quantities of azoimide are formed.

With hydrogen peroxide in acid solution, maximum yields of 38·5% of azoimide and 1·10 mols. of ammonia from 2 mols. of hydrazine were produced, whilst in alkaline solution only small amounts of azoimide, and fairly large amounts of ammonia, were formed.

The maximum yields produced by potassium perchlorate in acid solution were 22·4% of azoimide and 44% of ammonia. When hydrazine sulphate was treated with sodium periodate in acid solution in presence of silver sulphate to prevent the liberation of iodine, considerable quantities of azoimide were formed. With lead dioxide in acid solution, maximum yields of 4·1% of azoimide and 13·2%

of ammonia were obtained. Red lead and manganese dioxide also oxidise hydrazine sulphate to azoimide and ammonia, the maximum yields in the latter case being 2.32% of azoimide and 1.53 mols. of ammonia from 2 mols. of hydrazine. E. G.

Action of Zinc on Hydrazine Hydrate. ERICH EBELER and E. SCHOTT (*J. pr. Chem.*, 1909, [ii], 79, 72—74. Compare Abstr., 1908, ii, 1029).—When zinc is partly immersed in hydrazine hydrate and exposed to the action of the air, a white, crystalline substance is formed with the evolution of hydrogen. Analyses show that this compound is *zinc hydrazinecarboxylate dihydrazinate*,



it does not give a precipitate with a solution of a chloride of an alkaline earth, but when the solution is boiled, the substance is hydrolysed and the carbonate of the alkaline earth precipitated.

W. H. G.

Action of Air and Oxidising Agents on Coals. OCTAVE BOUDOUARD (*Compt. rend.*, 1909, 148, 284—286).—In contact with air at 100°, coal readily undergoes oxidation, the increase in weight through absorption of oxygen may amount to 10%. After oxidation in this way, coal is found to contain humic acid, and to have lost its property of coking. Concentrated nitric acid causes more complete oxidation and increases the yield of humic acid.

Analyses are given of anthracite, coal, and lignite before and after oxidation. W. O. W.

Weight of Carbon Dioxide with a Table of Calculated Results. SAMUEL W. PARR (*J. Amer. Chem. Soc.*, 1909, 31, 237—243).—In view of the discrepancies between the various tables of the weights of 1 litre of carbon dioxide at different temperatures and pressures, a new series of values has been calculated. Dietrich (*Zeitsch. anal. Chem.*, 1864, 4, 142) published a table in which he employed the value 1.9678 for the observed weight of 1 litre of carbon dioxide at 0° and 760 mm., which agrees fairly well with those usually employed at the present time (compare Guye, Abstr., 1907, ii, 605). On correcting this value for the latitude 41° and an elevation of 100 metres, it becomes 1.9760. The coefficient of expansion of carbon dioxide at constant volume has been given by Chappuis as 0.0037135. Employing these values, a new table has been compiled, the calculations being made by means of the formula

$$W = 1.976(P - w - b)/760(1 + 0.0037135 \times t),$$

where W is the weight of 1 litre observed volume reduced to 0° and 760 mm.; P , the observed pressure; w , the correction for tension of aqueous vapour; and b , correction for barometer, glass scale.

E. G.

Properties of Hydrogels when Dehydrated. JAKOB M. VAN BEMMELN (*Chem. Weekblad*, 1909, 6, 63—82; *Zeitsch. anorg. Chem.*, 1909, 62, 1—23).—A continuation of the author's criticism (Abstr. 1908, ii, 838) of Tschermak's silicic acid formulæ (Abstr., 1905, ii, 816).

A. J. W

Phenomenon Observed in the Action of Hydrochloric Acid on very Dilute Alkali Amalgams. G. MCPHAIL SMITH (*J. Amer. Chem. Soc.*, 1909, 31, 31—35).—In the decomposition of the alkali amalgams by means of hydrochloric acid, a point is reached at which there is a sudden increase in the surface-tension of the amalgams, which is accompanied by the sudden evolution of a cloud of very small bubbles of hydrogen, and by a sudden fall in the potential between the amalgam and the solution. G. S.

Theory of Bell-chamber Process for Electrolysis of Alkali Chlorides. M. F. CHANCEL (*Bull. Soc. chim.*, 1909, [iv], 5, 58—61).—The author controverts some of Brochet's conclusions (Abstr., 1908, ii, 1034). The concentration of the alkali obtained in this process should be proportional to the conductivity of the salt solution, but independent of the mobility of hydroxyl ions. In order to obtain a theoretical yield of sodium hydroxide on the current used, the velocity of the liquid away from the cathode must exceed a certain minimum. With a slower flow a more concentrated solution is obtained, but the yield on the current is less, owing to the alkali hydroxide taking part in the electrolysis. In practice convection currents interfere, and the theoretical conditions are never realised. R. J. C.

Colloidal Potassium Chloride. CARL PAAL and KURT ZAHN (*Ber.*, 1909, 42, 277—290. Compare Abstr., 1906, ii, 351, 749; 1908, ii, 179).—Organosols of potassium chloride, similar to those of sodium chloride, are obtained by the action of ethyl chloroacetate, chloroacetophenone, chloroacetone, and acetyl chloride on ethyl potassiomalonate and its ethyl, benzyl, and *i*-amyl derivatives. The liquid and suspended organosols are more stable than those of sodium chloride, and contain, as a rule, a higher percentage of the salt; thus solid potassium chloride organosols containing 93.6 and 96.4% KCl have been obtained. On drying, however, the organosols pass quickly into solid irreversible gels. The intermediate colloidal solution, which is seemingly a homogeneous liquid, gives, on filtration through paper, the liquid gel, the solvent being separated. This liquid gel is converted by light petroleum into a solid reversible gel, this being re-converted into the liquid form by benzene, which gradually passes on keeping into the irreversible form. Increase in the molecular weight of the malonate does not give any increase in stability of the colloidal potassium chloride. There are, therefore, five forms of these adsorption compounds of colloidal potassium chloride: a solid and liquid organosol, a liquid gel, and two solid gels, one of which is reversible. The importance of solvents free from water in this work is emphasised. W. R.

Colloidal Potassium Bromide and Iodide. CARL PAAL and KURT ZAHN (*Ber.*, 1909, 42, 291—300. Compare preceding abstract).—Adsorption compounds of colloidal potassium bromide are obtained by the action of ethyl bromoacetate, bromoacetophenone, bromoacetone, and acetyl bromide on ethyl potassiomalonate and its ethyl and benzyl derivatives in benzene, xylene, or ether solutions. The potassium

bromide organosol cannot be obtained from the condensation of ethyl bromoacetate and ethyl potassiummalonate, the gel being formed, but it may be obtained from the potassium derivatives of ethyl ethyl- or benzyl-malonates. Liquid organosols and gels are given with benzene, whereas with ether the more stable solid organosol is obtained, which often may be preserved under ether for some days. On drying the organosols pass into irreversible gels. The liquid gels by transmitted light appear as cloudy liquids (compare sodium bromide, Abstr., 1908, ii, 179), due to separation of small quantities of irreversible gels, probably occasioned by traces of water. These substances are therefore less stable than the colloidal potassium chloride compounds.

By the action of ethyl β -iodopropionate on ethyl potassiumbenzyl-malonate in benzene or ether solution, there result a labile organosol as well as the irreversible gel of potassium iodide. W. R.

Double Salts of Ammonium Sulphate and Ammonium Nitrate. FRANS A. H. SCHREINEMAKERS and P. H. J. HOENEN (*Chem. Weekblad*, 1909, 6, 51—56).—From aqueous solutions of ammonium sulphate and ammonium nitrate at 30°, the two double salts, $(\text{NH}_4)_2\text{SO}_4 \cdot (\text{NH}_4\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4 \cdot (\text{NH}_4\text{NO}_3)_3$, have been isolated. They are decomposed by water, but are stable in presence of excess of ammonium nitrate. A. J. W.

Effect of Water on the Freezing Point of Molten $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. J. LIVINGSTON R. MORGAN (*J. Amer. Chem. Soc.*, 1909, 31, 251—252; *Zeitsch. anorg. Chem.*, 1909, 61, 347—348).—An acknowledgment of the error in calculation pointed out by Cock (this vol., ii, 18) in Morgan and Benson's paper on molten hydrated salts as solvents for the freezing-point method (Abstr., 1907, ii, 747). E. G.

Rapid Preparation of Calcium Phosphide for the Evolution of Hydrogen Phosphide. CAMILLE MATIGNON and R. TRANNOY (*Compt. rend.*, 1909, 148, 167—170).—Hydrogen phosphide, usually prepared by the action of dilute acid on aluminium phosphide, may also be prepared from calcium phosphide. Calcium phosphate, the source of all phosphorus compounds, is intimately mixed with the correct amount of aluminium powder and ignited. A mixture of calcium phosphide, aluminium oxide, and a trace of calcium results, which readily yields hydrogen phosphide with acidified water. The gas is not spontaneously inflammable, and its only impurity is a small proportion of hydrogen.

A small acetylene generator may be employed, or the powdered phosphide may be placed in a flask with water, and dilute hydrochloric acid run in from a dropping funnel. R. J. C.

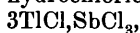
Double Fluorides and Chlorides of Univalent Thallium. FRITZ EPHRAIM and PAUL BARTECZKO (*Zeitsch. anorg. Chem.*, 1909, 61, 238—257).—Thallous fluoride is best prepared by dissolving thallium in dilute sulphuric acid, removing lead as sulphide, precipitating thallous sulphide from alkaline solution, and dissolving in hydrofluoric acid.

Ferric thallous fluoride, $3\text{TlF}, 2\text{FeF}_3$, prepared by evaporating a solution of ferric and thallous fluorides, the former being in excess, separates in bright pink crystals.

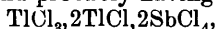
Chromic thallous fluoride, $3\text{TlF}, 2\text{CrF}_3$, prepared in similar manner, forms a green, crystalline powder. The *aluminium* compound, $3\text{TlF}, 2\text{AlF}_3$, forms white crystals. All these salts are decomposed only slowly by sodium carbonate, especially the aluminium compound, indicating the presence of complex ions.

An aqueous solution of thallous and lead chlorides deposits only the original mixture of salts on evaporation. In hydrochloric acid solution, *thallous lead chloride*, $\text{TlCl}, \text{PbCl}_2$, is formed, and crystallises in six-sided, elongated leaflets.

Thallous chloride dissolves in molten antimony trichloride, and on the addition of concentrated hydrochloric acid, the *double salt*,



is precipitated in light yellow, lustrous scales. When antimony pentachloride is used in the same way, it rapidly loses chlorine, and a *double salt* of thallous chloride and antimony tetrachloride is obtained as a dark violet solid, $\text{TlCl}, \text{SbCl}_4$, the yellow *compound* first formed, which is probably $\text{TlCl}, \text{SbCl}_5$, being unstable, and blackening in the air. By passing chlorine into a solution of thallous chloride in antimony trichloride, a black, felted mass is obtained, containing quadrivalent antimony, and probably having the formula



part of the thallium being oxidised to the thallic state.

Thallous bismuth chloride, $3\text{TlCl}, \text{BiCl}_3$, prepared in hydrochloric acid solution, forms large, very thin, colourless plates, rapidly breaking up into opaque, white scales. When a less excess of bismuth chloride is employed, a second *compound*, $6\text{TlCl}, \text{BiCl}_3$, is obtained, resembling the first in appearance.

Thallium is best estimated as iodide, a slight excess of potassium iodide being added at $50-60^\circ$. After twelve hours, the precipitate is collected on a Gooch filter, using only very gentle suction, and washed with pure water.

C. H. D.

Burning of Admixtures on Refining Copper in a Reverberatory Furnace. V. VANJUKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1649—1675).—After discussing the literature of the purification of copper by the so-called Swansea or dry refining process, the author gives the results of his own investigations in this direction.

Before the copper is melted in the reverberatory furnace, its temperature apparently falls, whilst during boiling the temperature rises, the exothermic reaction: $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} = 6\text{Cu} + \text{SO}_2 + 39 \text{ Cal.}$ then taking place. The end attained by the second refining is the removal of arsenic and antimony; the fact that only a slight amount of arsenic is burnt away during the first refining is explained by the layer of slag and sulphur compounds covering the copper, this layer preventing oxidation. Up to the end of the oxidation period, sulphur exists in the copper in the forms of cuprous sulphide and sulphur dioxide. The course of the refining was followed by analysing the gases evolved.

T. H. P.

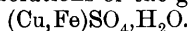
Ancient Copper Objects from Transcaucasia. WLADIMIR A. SKINDER (*Bull. Acad. Sci. St. Petersburg*, 1909, 1, 75—78).—The specimens investigated were covered with a greenish-red layer, which in one case reached a depth of 2 mm. Three specimens were analysed, with the following results: (1) Copper = 94.75%, iron = 0.37%, sulphur = 0.39%. (2) Copper = 96.80%, sulphur = 0.13%. (3) Copper = 97.01%, antimony = 0.05%, iron = 0.45%. The remainder in each case consisting of silicon, carbon dioxide, and oxygen in the adhering slag.

The superficial layer of the first specimen consists of malachite mixed with a small quantity of silica. Z. K.

Solid Solutions in the Dissociation of Cupric Oxide. LOTHAR WÖHLER and W. FREY (*Zeitsch. Elektrochem.*, 1909, 15, 34—38. Compare Abstr., 1907, ii, 33).—Metallic copper is not formed in the dissociation of cupric oxide; cuprous oxide has, therefore, a lower dissociation pressure than cupric oxide. The first small quantities of cuprous oxide formed by the dissociation of cupric oxide diminished the pressure at which oxygen is in equilibrium with the mixture of oxides in a very marked way. If the oxide is not heated for very long, the same equilibrium pressure is attained, at a given temperature and for a given composition, whether oxygen has been removed from a higher oxide or caused to combine with a lower one. Very prolonged heating, however, somewhat diminishes the pressure. This is probably due, in part at least, to false equilibrium, resulting from the very slow rate of solution of cuprous and cupric oxide in each other.

T. E.

Phase Equilibrium of the Red Cupri-ferrous Sulphates. ARTHUR J. ALLMAND (*Zeitsch. anorg. Chem.*, 1909, 61, 202—237).—The red or yellow salts obtained by Étard (Abstr., 1879, 104) and by Scott (Trans., 1897, 71, 564) by the action of sulphuric acid on a concentrated mixed solution of cupric and ferrous sulphates correspond in composition with solid solutions of the general formula



This does not account for the colour, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ being white, and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, pale blue. The possibility that cuprous-ferric salts may also be present is not to be tested analytically, on account of the reactions taking place when the salts are dissolved in water.

In the study of the phase equilibrium, 60 c.c. of a 0.8 molar solution of cupric and ferrous sulphates were taken, and 75 c.c. of concentrated sulphuric acid added, in an atmosphere of carbon dioxide. The mixture was then shaken for three weeks in a thermostat at 25°, and the liquid and solid phases analysed separately, the solid being previously washed, first with sulphuric acid of the same concentration as the mother liquor, and then with alcohol.

The brown colour of the mixed salts increases in depth from both ends of the series, reaching a maximum in the crystals containing 18% Fe and 16% Cu. All the crystals are microscopically homogeneous. When heated gently in a test-tube, their reddish-brown colour becomes chocolate-brown, and finally mauve, the original colour being restored on exposure to air.

Only a very small quantity of ferric iron is present, and is to be regarded partly as an impurity, being formed by the reaction $\text{Cu}^{++} + \text{Fe}^{++} \rightarrow \text{Cu}^{+} + \text{Fe}^{+++}$. The quantity of SO_4 is always somewhat deficient, the salts being slightly basic in spite of the acidity of the solution. This basicity is probably due to hydrolysis of the ferric salt.

The curves expressing the relation of the liquid and solid phases present certain peculiarities, the origin of which is not fully explained. It appears that cupric sulphate dissolves in solid ferrous sulphate in the form of normal molecules up to about 75%. Beyond this limit, polymerisation occurs.

The red colour is not due to ferric salts or to cuprous oxide. A suggestion is made that the cause of the colour may be an oscillation of electrons, due to the presence of metals in different stages of oxidation, as in Baly's explanation of the colour of organic compounds, since ferric ferrocyanide and ferrous ferricyanide, in which similar conditions occur, are also coloured.

C. H. D.

Preparation of Metallic Aluminium from Aluminium Silicate. MAX MOLDENHAUER (*Metallurgie*, 1909, 6, 14—19).—Aluminium silicate may be freed from silicon by reducing with carbon in the presence of ferric oxide, when iron silicide is formed. In practice, the dry clay, having the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, is fused in an electric furnace with ferro-silicon (10% Si), the products being alumina, containing 13.4% SiO_2 , and an iron silicide, containing 49% Si. The alumina is then fused in a separate furnace with hæmatite and carbon, the products being practically pure alumina and 10% ferro-silicon. The alumina is freed from mechanically admixed ferro-silicon by grinding and extracting with a magnet, and is electrolysed in solution in cryolite.

The freezing-point curve of mixtures of cryolite and alumina shows a rapid fall from the freezing point of cryolite (975°) to a eutectic point at 880° and 20% Al_2O_3 .

C. H. D.

The Apparent Retardation of Fusion of Aluminium. CAMILLE MATIGNON (*Bull. Soc. chim.*, 1909, [iv], 5, 91—92).—With reference to von Bolton's observation that aluminium wire may be heated above its melting point without losing its shape (*Zeitsch. Elektrochem.*, 1908, 14, 766), the author points out that he has recorded this fact already (*Mon. Sci.*, 1900, [iv], 14, 357), and explained it as due to the formation of a protective layer of alumina.

T. A. H.

Sodium Alum. WARREN R. SMITH (*J. Amer. Chem. Soc.*, 1909, 31, 245—247).—The existence of sodium alum (Augé, Abstr., 1890, 1059; Wadmore, Proc., 1905, 21, 150) has been confirmed, and experiments are described which prove that it is a definite chemical compound. It is a true alum, since it forms mixed and layer crystals with other alums. The following solubility data are recorded, which express the number of grams of the anhydrous salt, $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$, contained in 100 grams of a saturated solution.

At 10°, 26.9; at 15°, 27.9; at 20°, 29.0; at 25°, 30.1, and at 30°, 31.4. The quantities of the crystalline salt contained in 100 grams of the saturated solution are: at 10°, 50.8; at 15°, 52.7; at 20°, 54.8; at 25°, 56.9, and at 30°, 59.4. E. G.

The Constitution of Blast-Furnace Slags. M. THEUSNER (*Metallurgie*, 1908, 5, 657—667).—Finely-powdered slags containing 25—31% SiO₂, 14—18% Al₂O₃, and 43—51% CaO, were extracted with various solvents, the composition of the solution and of the residue being determined in each case by analysis. Citric acid, ammonium citrate, and ammonium chloride were used as solvents. The basicity of the slags depends on the ratio of lime to silica, and is practically independent of the proportion of alumina.

From the more basic slags, solvents at first extract lime, the ratio of alumina to silica in the residue remaining constant, whilst less basic slags are less attacked, and the residue contains more lime than the residue from the originally more basic specimens.

Acid slags are found, microscopically, to contain much melilite, which is absent from the basic slags. An artificial melilite behaves towards solvents in exactly the same manner as an acid slag. Artificial mixtures in different proportions show that the attack by solvents is greatest when the ratio of silica to alumina is highest.

Water attacks the slags much less readily than salt solutions. The lime is chiefly dissolved, small quantities of silica and alumina being also taken up in a colloidal form. C. H. D.

Magnetisable Manganese Alloys. X. Manganese-Aluminium-Copper. FRIEDRICH HEUSLER and FRANZ RICHARZ (*Zeitsch. anorg. Chem.*, 1909, 61, 265—279).—Forged alloys containing 20% or less manganese, and 6% or more aluminium, the remainder being copper, are entirely non-magnetic when quenched from a red heat in water or mercury, but after heating for several hours in boiling xylene, a maximum degree of magnetisability is reached, and the alloy is found to be free from hysteresis. The same alloys, slowly cooled, show hysteresis, which is the greater the slower the cooling through the critical range. The magnetic susceptibility decreases rapidly with increase in the proportion of aluminium.

The variation of magnetic properties with composition is expressed on a diagram with triangular co-ordinates. The conclusion is drawn that the maximum susceptibility is obtained when the alloys have the composition AlM₃, in which M represents manganese and copper, which replace one another isomorphously in the compound. In this isomorphous series, the magnetic susceptibility increases with increasing manganese, and a maximum should be reached by the compound AlMn₃, which is to be examined for its magnetic properties.

C. H. D.

The Production of Malleable Cast-Iron. FEDERICO GIOLITTI, F. CARNEVALI, and G. GHERARDI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 748—754. Compare Wüst, *Abstr.*, 1908, ii, 287).—The pearlitic zone observed by Wüst is also observed in mild steel (0.05%C) exposed

to pure methane at 1100° , under which conditions carbon is freely deposited. The carbon varies in the first place regularly with the depth, increasing from the outside inwards, but, in cooling, segregation takes place, the ferrite crystals at the surface, and the cementite crystals lower down, growing at the expense of the intermediate zone. It is shown microscopically that the process of decarburisation depends much more on the action of gases than on the diffusion of solid carbon.

C. H. D.

The Structure of Hardened Steel. W. J. KURBATOFF [and, in part, M. M. MATWEIEFF] (*Metallurgie*, 1908, 5, 721—728).—Austenite is best prepared by quenching steel containing 1.8—2.2% of carbon from 1250° in mercury at 130° . No change is produced by heating such steel containing austenite at 65 — 85° for several months. At 118° recrystallisation is visible in a few days. At 180° austenite changes to troostite, this transformation reaching a maximum at 245° .

The reaction austenite \rightleftharpoons troostite proceeds from right to left at 110 — 150° , from left to right above 150° , and again from right to left above 1000° . Austenite is regarded as a lower carbide of iron, the composition of which approaches the formula Fe_7C . Troostite and sorbite appear to be solutions of carbon in β - and α -iron respectively.

C. H. D.

Influence of Manganese on the System Iron-Carbon. FRIEDRICH WÜST (*Metallurgie*, 1909, 6, 3—14).—Manganese readily vaporises and attacks the platinum of an electric furnace. A magnesite crucible is therefore placed inside a vertical iron tube, through which a current of nitrogen is passed. The iron tube is coated externally with asbestos and kaolin, and is surrounded by the heating tube of the resistance furnace.

The addition of manganese up to 13% lowers the freezing point of iron saturated with carbon. Further additions raise the freezing point, which is at 1250° in an alloy containing 80% of manganese. The temperature at which the eutectoid, pearlite, is formed is rapidly lowered by the addition of manganese, becoming 580° at 5% Mn, and disappearing at higher concentrations. The difference between the transition points on heating and on cooling is also increased.

Microscopically, the increase in the proportion of manganese is shown by the disappearance of graphite and the increase of cementite. The plates of cementite also increase in size, and the eutectic disappears, its place being taken by a solid solution of carbon in iron and manganese.

The iron-graphite eutectic point is displaced by manganese, being at 4.05% C for an alloy containing 50% Mn. Manganese thus enters into both series of solid solutions, that rich in iron and that rich in carbon.

C. H. D.

Metallic Hydroxides. HERMANN WALDEMAR FISCHER (*Habilitationschrift*, Breslau, 1907).—The red colloidal hydroxide at first obtained by the hydrolysis of ferric chloride solutions is converted by the hydro-

chloric acid also formed into a yellow modification, insoluble in hydrochloric acid. Fresh suspensions of this modification show a green fluorescence. Neutralisation of a part of the acid hinders the formation of the yellow colloid. At 150—170° in a sealed tube, in concentrated solution, a violet-black, dense colloid is also formed, distinct layers of the yellow and black modifications being found together. The black colloid contains only 1.5—3% of water. Similar results are obtained with hydrolysable salts of other metals at 210°.

A study of the dehydration of the mineral ferric hydroxides leads to the conclusion that limonite and xanthosiderite are only colloidal goethite containing various quantities of adsorbed water. Xanthosiderite is thought to be identical with the yellow colloid described above. Goethite is a definite compound, whilst the existence of hydrohæmatite is doubtful.

When sodium hydroxide is added to a solution of chromic chloride, the precipitate formed soon re-dissolves, and a further addition of alkali is necessary to produce a precipitate. This process may be repeated several times. A method is also described of determining, by observations of the conductivity of such solutions, whether basic chlorides are formed. Barium hydroxide is used as the base, being added to solutions of metallic chlorides (0.1*N* chlorine) at 0°. The existence of the compounds $\text{Fe}_2\text{Cl}_5\cdot\text{OH}$ and $\text{Fe}_2\text{Cl}(\text{OH})_5$ is clearly shown by the curves, as is that of $\text{Al}_2\text{Cl}(\text{OH})_5$, $\text{Cr}_2\text{Cl}_5\cdot\text{OH}$, and $\text{Cr}_2\text{Cl}_4(\text{OH})_2$.
C. H. D.

Resistance of Ferrous Solutions to Oxidation by the Air. T. WARYNSKI (*Ann. Chim. anal.*, 1909, 14, 45—47).—Experiments showing that solutions of ferrous sulphate in presence of free sulphuric acid are very stable in contact with the air. Addition of strong hydrochloric acid renders them more liable to oxidation. Traces of certain substances, such as cupric chloride, platinum chloride, and palladium nitrate, greatly favour the oxidation process. L. DE K.

Absorption of Hydrogen by Metallic Nickel. ADOLF SIEVERTS and JOH. HAGENACKER (*Ber.*, 1909, 49, 338—347).—The authors are unable to account for the discrepancy between Sieverts' work (*Abstr.*, 1907, ii, 741) and Mayer and Altmayer's (*Abstr.*, 1908, ii, 950) as to the amount of hydrogen absorbed by nickel at 360° and 560°. They have repeated and confirmed Sieverts' experiments, using about 3 grams, 16.5 grams, and 27 grams of nickel; Mayer and Altmayer's contention that equilibrium was not attained in Sieverts' experiments, owing to the large quantity of nickel used, is thus disproved.

Henry's law does not hold for hydrogen and nickel at 822° and 923°, the amount of hydrogen absorbed being more nearly proportional to the square root of the pressure. C. S.

Alloys of Cobalt and Bismuth. F. DUCELLIEZ (*Bull. Soc. chim.*, 1909, [iv], 5, 61—62).—The author has attempted to obtain alloys of cobalt and bismuth by heating mixtures of the powdered elements to various temperatures in an atmosphere of hydrogen. No development of heat is observed, and malleable products are obtained in which the

cobalt retains its magnetic properties and from which the bismuth can be distilled. R. J. C.

Solubility of Chromic Oxide. MILORAD Z. JOVITSCHITSCH (*Monatsh.*, 1909, 30, 47—50).—The author finds that the statement that strongly ignited chromic oxide is insoluble in acids is incorrect. In two experiments, 2.85 grams and 0.815 gram of chromic oxide, after ignition first by means of a Bunsen flame, and subsequently for ten to fifteen minutes by a blowpipe flame, dissolved in concentrated nitric acid to the extents of 2.585 grams and 0.772 gram respectively; the residue in each case proved highly resistant to the action of the acid and only dissolved in traces.

Evaporation of the acid solution until nearly all odour of nitric acid has disappeared yields a dark brown mass, the absolute alcoholic solution of which gives on evaporation a green, crystalline crust recrystallisable from hot water. On analysis, this crust is found to be a *neutral chromic nitrate*, $\text{Cr}_2(\text{ONO}_2)_3$, which is stable towards light and takes up moisture (maximum, $3\text{H}_2\text{O}$) from the air, becoming a darker green. T. H. P.

Thorium. H. KARSTENS (*Zeitsch. Elektrochem.*, 1909, 15, 33—34).—In reply to Meyer's criticism (this vol., ii, 53) the author gives further details of the chemical part of the work described by Bolton (this vol., ii, 53). The thorium chloride used was a pure white, crystalline substance, which dissolves completely in water and contains thorium and chlorine in the ratio required by the formula ThCl_4 . If the temperature is allowed to rise too high, a yellow, non-crystalline product is obtained which contains oxygen. When the metal is shaken with 5% hydrochloric acid, 85% of it dissolves, but only 10% is present in the solution in the form of the complex acid. Comparison of the acid with meta-thorium chloride showed their properties to be different. T. E.

The Newly Discovered Element of the Tin Group. ANTON SKRABAL and PAUL ARTMANN (*Chem. Zeit.*, 1909, 33, 143).—The metal of the tin group, obtained by Evans (*Trans.*, 1908, 93, 660) from thorianite, and by Ogawa (*Abstr.*, 1908, ii, 953), from molybdenite, closely resembles molybdenum in its reactions. A metal resembling molybdenum, but differing from it in some reactions, was observed in certain specimens of iron and steel in 1897 (Boucher, *Abstr.*, 1898, ii, 73; Ruddock, *Chem. News*, 1897, 76, 118; Jones, *ibid.*, 171).

The authors have obtained from a ferro-vanadium a small quantity of a sulphide resembling that of molybdenum in its reactions, but failing to give the characteristic blue coloration when dissolved in nitric acid and evaporated with sulphuric acid. This metal may be identical with the new metal from thorianite. C. H. D.

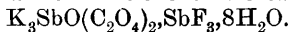
Tetragenic Double Salts of Antimony Fluoride and their Applicability as Mordants. ARTHUR ROSENHEIM and HERBERT GRÜNBAUM (*Zeitsch. anorg. Chem.*, 1909, 61, 187—201).—Tetragenic

double salts are those containing four different elements or radicles, exclusive of water of crystallisation (Meyerhoffer, *Abstr.*, 1903, ii, 292). Salts containing antimony fluoride as a component find application as mordants.

Antimony trifluoride, prepared from antimony trioxide and hydrofluoric acid, is best stored in vessels of white celluloid. Three hundred and eighty-five grams dissolve in 100 grams of water at 0°, and 564 grams in 100 at 30°. There is no appreciable hydrolysis below 30°. The solubility is increased by the addition of alkali salts, but very unequally, potassium sulphate having only a small effect, whilst potassium chloride, oxalate or tartrate increases the solubility greatly. When the quantity of alkali salt exceeds a certain limit, the tetragenic double salt separates.

More dilute solutions have been investigated by means of their conductivity. The conductivity of the mixed solution is compared with the sum of the conductivities of antimony fluoride and of the alkali salt at 0°. The solutions containing potassium nitrate, sulphate, and hydrogen oxalate do not give any evidence of the presence of complex ions, whilst solutions containing normal potassium oxalate and tartrate, ammonium oxalate, and potassium antimony tartrate indicate considerable formation of complex ions, even in dilute solution. The two classes of salts are very sharply distinguished by plotting curves, of which the ordinates are $\lambda_0(\text{SbF}_3 + \text{X}) - \lambda_0\text{SbF}_3$, and the abscissæ, \sqrt{v} . Only those salts the complex ions of which persist in dilute solutions are of use as mordants.

Several of the double salts have been isolated in the crystalline solid state. Potassium nitrate forms the *salt*, $3\text{KNO}_3, \text{SbF}_3$; ammonium oxalate forms large, transparent crystals of $4(\text{NH}_4)_2\text{C}_2\text{O}_4, 3\text{SbF}_3$; sodium oxalate forms $2\text{Na}_2\text{C}_2\text{O}_4, 3\text{SbF}_3$, crystallising unchanged from water; potassium antimony oxalate forms the stable *salt*,



Mercuric chloride and cyanide, like antimony fluoride, have the power of forming tetragenic double salts, and all of these are very weak electrolytes, having also the power of forming complex ions.

C. H. D.

Some New Fluorides. OTTO RUFF, JULIAN ZEDNER, EMIL SCHILLER, and ALFRED HEINZELMANN (*Ber.*, 1909, 42, 492—497).—*Columbium pentafluoride*, CbF_5 , was prepared by the action of fluorine on columbium containing about 3% of aluminium. The roughly-powdered metal contained in a boat was placed in a platinum tube 25 cm. long and 1.2 cm. diameter, the middle portion of which is inserted in an asbestos box; the constricted end of the tube is cooled by a lead worm, and connected to a receiver, from which moisture is carefully excluded. The fluorine when passed over the merely warmed columbium at once combined, and the reaction was finished when the tube began to cool. The box was next heated at 250°, when the pentafluoride distilled into the cooled portion of the tube, the aluminium fluoride remaining behind. On re-distillation in a vacuum at 110°, it is obtained as colourless, strongly refractive, monoclinic prisms, m. p. 72—73° (corr.) and b. p. 236°/760 mm. (corr.). It is very hygroscopic and dissolves in water,

from which sodium hydroxide and ammonia precipitate columbic acid ; yield 75%.

Tantalum pentafluoride, TaF_5 , prepared in a similar manner, and purified by distillation in a vacuum at 90—100°, forms colourless, strongly refractive prisms, m. p. 94° (corr.) and b. p. 225—226.5°/760 mm. (corr.). It is very hygroscopic, dissolving in water, from which alkali and ammonia precipitate tantalic acid containing fluorine. It attacks glass slowly at ordinary temperatures, quickly at higher ; yield 80—85%.

The reaction between uranium and fluorine is a very vigorous one, and the product chiefly consists of tetrafluoride mixed with some oxygenated substance and the hexafluoride in small quantities. *Uranium hexafluoride*, UF_6 , is best prepared from the pentachloride cooled in an alcohol-carbon dioxide mixture. After the reaction is over, carbon dioxide is passed through the apparatus, the tube evacuated, and the product distilled. It forms glistening, colourless, fuming, monoclinic prisms, which do not melt, but sublime at the ordinary temperature under diminished pressure. It is very hygroscopic, is soluble in water, and attacks glass in presence of a trace of water, forming silicon tetrafluoride and uranium oxyfluoride. Its aqueous solution does not decolorise potassium permanganate, and ammonia forms ammonium uranate and fluoride.

W. R.

Alloys of Platinum and Antimony. K. FRIEDRICH and A. LEROUX (*Metallurgie*, 1909, 6, 1—3).—The freezing point of antimony is not appreciably lowered by the addition of platinum. The freezing-point curve rises to a maximum at 1226° and 44.7% Pt, corresponding with the compound $PtSb_2$. A second compound, probably $PtSb$, is formed at 1045°. The curve then falls to a eutectic point at 685° and 77% Pt, and rises to the freezing point of platinum. Two reactions take place in the solid state, the compound $PtSb$ being transformed into one richer in antimony, and a third compound, Pt_5Sb_2 , being formed from alloys rich in platinum at 644°, the eutectic structure disappearing when the alloys are maintained for some hours at this temperature. The compound $PtSb_2$ readily blackens when heated.

C. H. D.

The Platinum Compound Analogous to Purple of Cassius. LOTHAR WÖHLER (*Verh. deut. Naturforsch. Aerzte.*, 1907, ii, 105—106).—The blood-red colour produced by stannous chloride in solutions of platinum salts darkens after a time, more rapidly on warming, and finally the solution becomes black and slightly turbid. The red colour is extracted by shaking with ether or ethyl acetate, and on addition of water a chocolate-brown precipitate forms, consisting of platinum, tin, and oxygen in varying proportions. When freshly precipitated, the substance is soluble in dilute hydrochloric acid, but becomes almost insoluble on drying. It does not diffuse through parchment paper, and is therefore regarded as an adsorption compound of colloidal platinum and colloidal stannic acid. The adsorbed metal does not show the ordinary reactions of colloidal platinum. A similar red solution is obtained by reducing platinum

chloride with an ethereal solution of phosphorus in the presence of gelatin.

When stannous bromide and platinum tetrabromide are brought together, there is a reversible equilibrium: $2\text{SnBr}_2 + \text{PtBr}_4 \rightleftharpoons \text{Pt} + 2\text{SnBr}_4$, which is displaced towards the left by raising the temperature.

G. S.

Mineralogical Chemistry.

Optical Investigation of Sakhalin Naphtha. MICHAEL A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1735—1746. Compare Abstr., 1907, ii, 882, 883).—The author has carried out an optical investigation of the various fractions of Sakhalin naphtha, from the results of which conclusions are drawn as to the geological age of the naphtha. This age is divided into two periods: (1) that during which filtration and distillation occurred, and (2) that of carbonisation. T. H. P.

New Chromium Mineral from Servia. MILORAD Z. JOVITSCHITSCH (*Monatsh.*, 1909, 30, 39—46).—The brooks below one of the branches of the Kopaonik mountains contain a small-grained, glittering sand, from which a magnet removes a dark dull portion, leaving light, shining crystals behind. After purifying from sandy impurities, these two constituents were examined separately.

The shining crystals, D 3·1, to which the author gives the name *chromitite*, give analytical numbers, which, if small proportions of aluminium and magnesium are neglected, correspond with the formula FeCrO_3 , $\text{Fe}_2\text{Cr}_2\text{O}_6$, or $\text{Fe}_2\text{O}_3\cdot\text{Cr}_2\text{O}_3$.

The dull crystals resemble magnetite, both in their appearance and in their magnetic properties, but on separating by means of a magnet placed at varying distances from the sand, three fractions were obtained containing (1) 66·99% Fe and 6·01% Cr; (2) 43—45% Fe and 21·5—25% Cr; (3) 34—38% Fe and 34—36% Cr. Fraction (2) corresponds with a compound having the formula $2\text{Fe}_2\text{O}_3\cdot\text{Cr}_2\text{O}_3$, which the author regards as a transition stage to the chromitite crystals. T. H. P.

Rosasite, a New Mineral from the Mines of Rosas (Sulcis, Sardinia). DOMENICO LOVISATO (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 723—728).—The new mineral occurs sparingly in small veins, associated with malachite and aurichalcite, as compact, apparently fibrous, light green, mammellated masses, D²⁰ 4·074, H 4·5.

CO_2	CuO	ZnO	PbO	H_2O	Total.
30·44	36·34	33·57	trace	0·21	100·56

The analysis corresponds approximately with the formula
 $2\text{CuO}\cdot 3\text{CuCO}_3\cdot 5\text{ZnCO}_3$.

It does not appear to be merely an intimate mixture of malachite and smithsonite.

A dark green mineral was found coating the rosasite, but in quantity insufficient for analysis. C. H. D.

Brugnatellite, a New Mineral Species Found in Val Malenco. ETTORE ARTINI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 3—6).—The asbestos strata of Val Malenco contain a mineral which has not been previously described, and which occurs in the form of flesh-red laminæ or laminar aggregates resembling mica and exhibiting ready cleavage and slight nacreous lustre. This mineral, to which the author gives the name *Brugnatellite*, is a hydrated, ultra-basic carbonate having the composition :

Insol. in HCl.	H ₂ O.	CO ₂ .	Fe ₂ O ₃ .	MnO.	MgO.	Total.
1·03	33·77	7·78	13·20	1·80	42·79	100·37

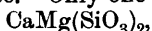
Replacing the small proportion of MnO by an equivalent amount of MgO, the above numbers are in good agreement with those required by the formula $\text{Mg}_6\text{FeCO}_{20}\text{H}_{21}$ or $\text{MgCO}_3, 5\text{Mg}(\text{OH})_2, \text{Fe}(\text{OH})_3, 4\text{H}_2\text{O}$. In its natural position, Brugnatellite is accompanied by asbestos, aragonite, magnesite, artinite, and brucite. T. H. P.

Composition of Warwickite. W. M. BRADLEY (*Amer. J. Sci.*, 1909, [iv], 27, 179—184).—Under I is given the mean of two analyses of material, D 3·342, separated by means of heavy liquids from a metamorphic limestone occurring in contact with granite at Amity, New York. The mineral has the form of minute, slender crystals, showing the characteristic copper-red reflections on the cleavage surfaces.

	B ₂ O ₃ .	TiO ₂ .	SiO ₂ .	MgO.	FeO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	Total.
I.	21·29	24·86	1·39	35·71	9·15	4·76	2·91	100·07
II.	23·87	27·87	1·56	38·63	8·07	—	—	100·00

Spinel and magnetite are intimately associated and intergrown with the mineral, and deducting alumina and ferric oxide, together with equivalent amounts of magnesia and ferrous oxide, the composition of the pure mineral is recalculated under II. This corresponds with the formula $\text{B}_2\text{O}_3, \text{TiO}_2, 3(\text{Mg}, \text{Fe})\text{O}$ or $(\text{Mg}, \text{Fe})_3\text{TiB}_2\text{O}_8$. L. J. S.

Diopside and its Relations to Calcium and Magnesium Metasilicates. EUGENE T. ALLEN and W. P. WHITE, with optical study by FRED. EUGENE WRIGHT and ESPEER S. LARSEN (*Amer. J. Sci.*, 1909, [iv], 27, 1—47).—The thermal and optical relations of calcium metasilicate and of magnesium metasilicate have been previously studied (Abstr., 1906, ii, 683, 865), and the investigation is now extended to mixtures of these. Only one stable compound,



was obtained, this being identical with diopside; it melts at 1380°, and has D 3·275; well-formed crystals were crystallised from molten calcium chloride. Two eutectics with melting points of 1348° and 1375° occur; the former consists of 60% diopside and 40% pseudo-

pyroxene in composition, which is referred to as *clinohypersthene*; this has crystallised out from the fused rhombic pyroxene, and it is identical with the artificially prepared magnesia-pyroxene; its presence has been detected in several chondritic meteorites. Maskelynite and an undetermined mineral resembling monticellite are also present. The felspar has the composition $(Ab, Or)_{10}An_{11}$. The nickel-iron contains: Fe, 81.1; Ni, 17.8; Co, 1.1; P, trace. L. J. S.

Physiological Chemistry.

Influence of Oxygen on Athletes. LEONARD E. HILL and MARTIN FLACK (*Proc. physiol. Soc.*, 1909, xxviii—xxxvi; *J. Physiol.*, 38).—Experiments on athletes designed to show the beneficial effect of oxygen inhalation. W. D. H.

Oxygen Capacity. ARTHUR E. BOYCOTT and C. G. DOUGLAS (*J. Path. Bact.*, 1909, 13, 256—295).—The carbon monoxide method for determining the total oxygen capacity and volume of the blood gives satisfactory results in rabbits. Normal rabbits have about 5.5 c.c. of blood and 0.7 c.c. of oxygen capacity per 100 grams of body-weight; females have more dilute blood than males. About 93% of the total hæmoglobin in rabbits is in the blood. Experiments are given in detail showing the rate of regeneration of the blood after single and multiple hæmorrhages. Apparent anæmia after hæmorrhage and in aniline poisoning may be due to increase in the blood-volume. W. D. H.

The Sugar of the Blood. V. PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1909, 16, 60—67. Compare Abstr., 1908, ii, 117).—By the use of the methods previously described, it is shown that a considerable fraction of the blood-sugar is contained in the corpuscles. W. D. H.

Activation of Hæmolysin by Amino-acids. TAKAOTI SASAKI (*Biochem. Zeitsch.*, 1909, 16, 71—80).—Guinea-pig's serum has very little hæmolytic action on the corpuscles of the goat and horse; the addition of glycine or alanine leads to active hæmolysis. W. D. H.

The Gastric Digestion of Caseinogen. LOUIS GAUCHER (*Compt. rend.*, 1909, 148, 53—56).—The digestion of milk was studied in the case of a dog with a duodenal fistula. Three phases could be distinguished: (I) In the first quarter of an hour after ingestion, the milk could be obtained from the fistula in a practically unchanged state. (II) It was afterwards obtained in a clotted form. (III) In the third phase it was more altered, and coloured with bile. The caseinogen passes the stomach without peptonisation, and clotting is not necessary for the subsequent stages of digestion. S. B. S.

The Part Played by Elementary Hydrogen in Metabolism. CARL OPPENHEIMER (*Biochem. Zeitsch.*, 1909, 16, 45—59).—Elementary hydrogen, like elementary nitrogen, plays no part in metabolism in the animal body. W. D. H.

Protein Metabolism in Development. JOHN A. MURLIN (*Proc. Amer. physiol. Soc.*, 1908, xxxi—xxxiii; *Amer. J. Physiol.*, 23).—In pregnant dogs there is a minus nitrogen balance in the first four weeks, and an increasing plus balance in the last five weeks of gestation. On a creatine-free diet, the creatinine output was constant, but during uterine involution after parturition, creatine appeared in the urine. The differences obtained by subtracting the total resting metabolism of the mother dog from the total metabolism of the mother and puppies after parturition are not quite proportional to the weights, probably because the metabolism in the puppies was reduced as they helped to keep each other warm. In the puppies, immediately after birth, the respiratory quotient was unity; this indicates combustion of carbohydrate (glycogen). W. D. H.

Fate of the Non-hydroxylated Benzene Ring of Protein in the Animal Body. HARALAMB VASILIU (*Bied. Zentr.*, 1909, 38, 46—48; from *Mitt. landw. Inst. K. Univ. Breslau*, 1908, 4, 355—374).—The benzoic acid obtained by oxidising foods with permanganate is derived from the α -phenylaminopropionic acid group of the protein; the benzene ring of the tyrosine group is destroyed.

The benzene ring of α -phenylaminopropionic acid is only to a very slight extent destroyed by herbivorous animals; most of it appears in the urine partly as hippuric acid and partly as α -phenylaminopropionic acid. In the human body, and most probably in the case of carnivorous animals, the greater part is destroyed, and only small amounts of α -phenylaminopropionic acid pass into the urine.

Experiments with sheep showed that 42% of the non-hydroxylated benzene was present in the urine as hippuric acid; the remainder, 58%, is presumably in the form of α -phenylaminopropionic acid or its polypeptide.

The destruction of the benzene ring by carnivorous animals is attributed to the co-operation of acid products, due to animal food. Indications were obtained in experiments with a calf, fed with milk, of the breaking up of the benzene ring. N. H. J. M.

Effect of Carbon Dioxide on the Frog's Pupil. JOHN AUER (*Proc. Amer. physiol. Soc.*, 1908, xvi; *Amer. J. Physiol.*, 23).—In asphyxia the pupils of mammals are dilated. In the frog, exposure to carbon dioxide causes extreme contraction; this also occurs in the isolated eyeball. The gas is, however, unable to overcome fully the opposite effect produced by adrenaline, and adrenaline is unable to exert its full effect when the iris is under the influence of carbon dioxide. W. D. H.

Autolysis. S. YOSHIMOTO (*Zeitsch. physiol. Chem.*, 1909, 58, 341—368).—The commonly used preservatives, boric and salicylic acids, hasten fermentation actions in the liver at certain small "optimum"

concentrations; excess slows or stops the action. The same is true for allylthiocarbimide and alcohol, although the actual figures of optimum concentration are naturally different in all cases. Normal autolysis and that which is produced by carbon dioxide in chloroform water run the same course; there is no lessening of the yield of purine bases, such as is said to occur with other acids. The following table gives the optimum concentrations of the substances mentioned, together with the amount of autolysis as judged by the proportion of the total nitrogen going into solution under similar conditions:

	%.
Chloroform water (taken as the normal)	21.59
Alcohol (concentration 5%)	32.01
Allylthiocarbimide (concentration 1/8%, saturated solution)	38.78
Boric acid (concentration 1%)	40.80
Salicylic acid (concentration, half saturated solution)	47.37

W. D. H.

Heat-coagulation in Plain Muscle. EDWARD B. MEIGS (*Proc. Amer. physiol. Soc.*, 1908, xv—xvi; *Amer. J. Physiol.*, 23).—In both plain and striated muscle of the frog, irritability is lost about 40°; the shortening of striated muscle is marked at 50°, but at this temperature the plain muscle lengthens. In both cases the protein is coagulated, and lactic acid liberated; the swelling of the sarcostyles in the case of striated muscle so produced causes shortening, whereas the swelling of the plain fibre with a different histological structure produces lengthening.

W. D. H.

The Influence of Sodium Chloride and Calcium Chloride in the Potassium Contraction. WILLIAM D. ZOETHOUT (*Amer. J. Physiol.*, 1909, 23, 374—388).—The amount of sodium in a muscle is sufficient to counteract the stimulating effect of a small quantity of potassium salt. The removal of this sodium by immersion in a 6% sugar solution renders the muscle more irritable toward potassium; the same is probably true for calcium. Both sodium and calcium favour the relaxation of a muscle in potassium contraction. Ringer's solution, and 0.7% sodium chloride solution, speedily reduce the irritability of muscle toward potassium. Although such solutions preserve muscular irritability toward electrical stimulation for a long time, they cannot be regarded as altogether inert fluids.

W. D. H.

The Influence of Salts of Strong Organic Bases on the Resting Current and Excitability of Frog's Muscle. RUDOLF HÖBER and HEINRICH WALDENBERG (*Pflüger's Archiv*, 1909, 126, 331—350).—The salts of quaternary ammonium bases, piperidine, guanidine, and trimethylsulphine, that is, of strong organic bases, affect the resting current and excitability of frog's muscle in the same way as do salts of strong inorganic bases, and most closely resemble the effects of cæsium salts. The action is a reversible one. The resting current and excitability are both affected in the same way.

W. D. H.

Cholesterol in Heart Muscle. G. W. ELLIS and JOHN A. GARDNER (*Proc. physiol. Soc.*, 1908, viii—x; *J. Physiol.*, 38).—The amount of cholesterol in heart muscle is approximately the same as in other kinds of muscular tissue. W. D. H.

Cycloses. FRANZ ROSENBERGER (*Zeitsch. physiol. Chem.*, 1909, 58, 369—372).—Polemical. A reply to Starkenstein (this vol., ii, 77). W. D. H.

Black Cephalopod Inks. RAFFAELE PALADINO (*Biochem. Zeitsch.*, 1909, 16, 37—44).—The black excretion of *Eledone moscata* has the following composition: water 40, soluble mineral substances 4·06, soluble organic substances 2·32, insoluble mineral substances 6·67, insoluble organic material 40·6%. The secretion of *Sepia officinalis* has the values: water 20, soluble mineral 8·5, soluble organic 3·5, insoluble mineral 15·0, insoluble organic 34·0%. The composition of the black insoluble pigment, melanin, is C 52·4, H 4·02, N 5·6%, together with sulphur and iron.

The following were shown to be present in the inks: sodium, potassium, calcium, iron, chloride, carbonate, and sulphate. Urea, uric acid, and dextrose could not be detected. J. J. S.

Parent Substance of Hippuric Acid. HARALAMB VASILIU (*Bied. Zentr.*, 1909, 38, 132—133; from *Mitt. landw. Inst. K. Univ. Breslau*, 1908, 4, 374—378. Compare Abstr., 1908, ii, 211).—The hippuric acid produced from clover hay is derived partly (3/5) from proteins and partly (2/5) from a non-nitrogenous substance. In the case of meadow hay the amount produced from non-nitrogenous substances is fifteen times as great as the portion derived from proteins. It seems probable that as regards foods, such as leguminous foods, oil cakes, etc., which give rise to relatively small amounts of hippuric acid, most of the acid is derived from proteins, whilst in the case of foods which furnish large amounts of the acid, its production is mainly from non-nitrogenous substances. The parent substance in the latter case seems to contain a hydroxylated benzene ring; it is possibly quinic acid, which is always present in meadow hay, and yields in the animal body 36% of the theoretically possible amount of hippuric acid.

N. H. J. M.

The Influence of Calcium Chloride on the Formation of Transudates. LEO LOEB, S. M. FLEISCHER, and D. M. HOYT (*Zentr. Physiol.*, 1908, 22, No. 16, reprint).—The addition of calcium chloride to 0·85% salt solution, diminishes the rate of excretion of liquid by the kidneys, and also into the intestine, when the solution is injected intravenously into rabbits. It increases, on the other hand, the rate of transudation into the peritoneal cavity. The latter action is due to two factors, namely, the indirect factor, which results from diminished kidney excretion, and the direct factor, due to the action of the calcium salt on the endothelium of the vessels or peritoneum. The latter can take place when the action of the kidneys is excluded. S. B. S.

Phosphorus of Urine. G. C. MATHISON (*Proc. physiol. Soc.*, 1909, xx—xxii; *J. Physiol.*, 38).—The total phosphorus was estimated by

Bayliss and Plimmer's modification of Neumann's method, and inorganic phosphates by precipitation with magnesia mixture; the difference represents organic phosphorus. The latter represents 5 to 10% of the total, a higher figure than has been previously obtained. W. D. H.

Excretion of Magnesium and Calcium. LAFAYETTE B. MENDEL and STANLEY R. BENEDICT (*Proc. Amer. physiol. Soc.*, 1908, xviii; *Amer. J. Physiol.*, 23).—When magnesium salts are introduced parenterally, elimination occurs through the urine in about forty-eight hours, although some may be retained for two weeks. There is no purgation. There is accompanying this an increased excretion of calcium by the kidney and a lessened excretion of calcium by the bowel. Nitrogen and chlorine are not appreciably altered.

If calcium salts are introduced into the circulation, the calcium, especially in rabbits, is abundantly excreted in the urine; this is accompanied by an increased output of magnesium W. D. H.

Acetone Substances in the Organs of Cases of Diabetic Coma. II. H. CHRISTIAN GEELMUYDEN (*Zeitsch. physiol. Chem.*, 1909, 58, 255—272. Compare Abstr., 1904, ii, 275).—The investigations of the amounts of acetone substances were made in surviving organs; during the life of diabetics, other relationships may prevail. The view put forward is that during life β -hydroxybutyric acid is formed mainly in the liver; it is thence carried by the blood to other organs, and taken up by them; the increase of fat metabolism, owing to the small amount of carbohydrate metabolism, leads to a greater production of the acid than occurs in health; but as it leaves the liver for distribution, the amount remaining in the liver is comparatively small. The formation of the acid and its conversion into acetoacetic acid are oxidation processes. In diabetes, the glycogenic function of the liver is in abeyance, and little or none of the substance is found there. W. D. H.

Experimental Nephritis. JOHN LIGHTERWOOD GREEN (*J. Path. Bact.*, 1909, 13, 296—310).—In nephritis produced in rabbits by potassium chromate the quantity of urine on the first two days sinks to 50% of the normal, and then gradually returns to normal. The protein rises to maximum on the second day, and then gradually disappears. The protein consists of albumin and globulin, in inconstant proportions. In a dog the total nitrogen was reduced by 20%, the chlorides by 50%, the creatinine was slightly reduced, and the phosphates were unaltered. In three cases of the disease in man, the urea nitrogen was found to follow the total nitrogen, but there is no constancy in the reduction of either; in two cases the ammonium excretion was low, and in the third, high; the creatinine was slightly reduced in two cases. In the blood in the experimental cases there was a fall of 14% in the red corpuscles on the onset of nephritis, and a rise of 43% in the colourless corpuscles (especially of polynuclear leucocytes); the return to normal was gradual. W. D. H.

Effect of Calcium on the Cardiac Vagus. JOHN AUER and SAMUEL J. MELTZER (*Proc. Amer. physiol. Soc.*, 1908, xx—xxi; *Amer. J. Physiol.*, 23).—Calcium restores the irritability of the cardiac vagus

in animals poisoned by magnesium salts, but in the normal animal calcium infused in $M/8$ solutions reduces or even abolishes the irritability of the inhibitory fibres of this nerve, leaving its motor fibres unaffected.

W. D. H.

The Behaviour of Phthalic Acid in the Animal Organism. JULIUS POHL (*Biochem. Zeitsch.*, 1909, 16, 68—70).—Porcher states that 75% of isophthalic and terephthalic acids appear in the urine, whilst phthalic acid is almost completely burnt in the organism of the dog. The last statement is in contradiction of work by Pribram. The present experiments confirm the observation of Pribram that the ortho-acid is almost completely recoverable in dog's urine.

W. D. H.

Pressor Substances from Putrid Meat. GEORGE BARGER and GEORGE S. WALPOLE (*Proc. physiol. Soc.*, 1909, xxiii; *J. Physiol.*, 38).—The presence of a substance or substances producing a rise of arterial pressure has been noted by Abelous in putrid meat, and by Dixon, Taylor, and Rosenheim in putrid placenta. Two substances was separated from putrid meat, namely, isoamylamine and *p*-hydroxyphenylethylamine; both are pressor substances, especially the latter. The relation of these two bases to leucine and tyrosine respectively is clear, and the possibility of their formation in the intestine is of interest.

W. D. H.

Physiological Action of Primary Fatty Amines. GEORGE BARGER and HENRY H. DALE (*Proc. physiol. Soc.*, 1909, xxii; *J. Physiol.*, 38).—Barger and Walpole's work (see preceding abstract) suggested the examination of other amines. The following were tested: methylamine, ethylamine, *n*-propylamine, isopropylamine, *n*-butylamine, isobutylamine, isoamylamine, *n*-amylamine, *n*-hexylamine, *n*-heptylamine, and *n*-octylamine. The hydrochlorides were used in all cases in $N/10$ solution. The first to give a pressor effect is isobutylamine; the activity rapidly increases on ascending the series up to hexylamine; those still higher, show a decreasing action.

W. D. H.

Action of Digitalin and Allied Substances on Striated Muscle. AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1908, x—xvi; *J. Physiol.*, 38).—Natroelle's digitalin has no action on muscle; Merck's digitonin cryst., digitalinum pulv. pur. (Merck), digitalinum venum (Schmiedeberg), and digitoxin (Merck) were also employed. The last-named has also no action; the other three vary in degree of activity, but all produce characteristic effects, namely, well-marked contraction and loss of contractility. The action of saponin is very similar.

W. D. H.

Action of Muscarine and Pilocarpine on the Heart. HUGH MACLEAN (*Bio-Chem. J.*, 1909, 4, 66—71).—The effect of these drugs is to be ascribed to their stimulating influence, doubtless by chemical interaction on the nerve endings of the inhibitory nerve fibres of the heart.

W. D. H.

The Passage of Phenolphthalein and of its Disodium Derivative Through the Organism. C. FLEIG (*J. Pharm. Chim.*, 1909, [vi], 29, 55—57. Compare Abstr., 1908, ii, 313).—When given by the mouth, 85% of the phenolphthalein is found in the fæces; it does not appear in the urine unless very large quantities are given *per os*, or unless it is administered hypodermically or intravenously. Phenolphthalein is never hydrolysed in the tissues, but probably passes into the urine in combination with sulphuric or glycuronic acid. G. B.

Atoxyl. III. FERDINAND BLUMENTHAL and ERNST JACOBY (*Biochem. Zeitsch.*, 1909, 16, 20—36).—The introduction of acid radicles (for example, acetyl) into the amino-group of the sodium salt of *p*-aminophenylarsinic acid (atoxyl) lessens its toxicity; the introduction of a methyl group does not. Complete substitution of the amino-group by iodine increases the toxic action; as also does its replacement by hydroxyl (Ehrlich). The toxicity of the mercury salt depends on the amount of mercury given. Reduction products of atoxyl are more toxic than atoxyl itself.

In the body, atoxyl acts directly as an antiseptic. Details are given regarding its deposition in the tissues, and its excretion in the urine.

W. D. H.

The Present State of Chemotherapeutics. PAUL EHRLICH (*Ber.*, 1909, 42, 17—47).—A lecture delivered before the German Chemical Society. C. S.

Chemistry of Vegetable Physiology and Agriculture.

Ammoniacal Fermentation. JEAN EFFRONT (*Compt. rend.*, 1909, 148, 238—240).—The author gives details of some experiments which throw light on the function of butyric ferments in the conversion of atmospheric nitrogen into a form assimilable by plants. Distillery residues sown with an earth culture undergo symbiotic fermentation through the action of aerobic ferments and an anaerobic butyric ferment. The latter has been isolated, and its action studied on dextrose solutions containing various amino-acids. In the case of aminoacetic acid, asparagine, and glutamic acid, the ammonia formed was free from amines, but when betaine was present, pure trimethylamine was obtained. Distillery residues gave ammonia and trimethylamine. The ammoniacal fermentation in each case proceeded at the same rate as the destruction of the dextrose. Analogous results were obtained using ordinary earth in place of the pure culture, but the action was more rapid and complete. W. O. W.

Decomposition of Nitrates by Bacteria. S. A. SEWERIN (*Centr. Bakt. Par.*, 1909, ii, 22, 348—370. Compare Abstr., 1900, ii, 232).—Under anaerobic conditions (in an atmosphere of hydrogen)

the denitrifying power of *Vibrio denitrificans* is increased, whilst in the case of *Bacillus pyocyaneus* there is a still more marked increase. Nitrites are also reduced under anaerobic conditions by both organisms, although less readily than nitrates.

In the reduction of nitrates by *B. pyocyaneus* there is always a production of nitrites, both in aerobic and anaerobic cultures. With *Vibrio denitrificans*, nitrites could not be detected in the majority of cases, and, when present at all, generally showed a less distinct reaction.

The reducing power of both organisms is diminished when hydrogen is replaced by carbon dioxide; and *B. pyocyaneus* failed to grow in broth free from nitrates in an atmosphere of carbon dioxide.

Results of experiments with different soils indicated that a total destruction of nitrates does not take place in soils in their natural condition. Addition of 2% of horse dung and 4% of straw to garden soil and other soils resulted in complete reduction of nitrates by *B. pyocyaneus*. With *V. denitrificans* complete reduction only occurred in one soil, a marl to which 8% of dung had been added. Nitrites were not found in any of the experiments with soils.

N. H. J. M.

Use of Silver Salts in Sterilising Water. F. TRAETTA-MOSCA (*Gazzetta*, 1909, 39, i, 69—109).—The author has examined isotachyol and silver chlorate, perchlorate, and sulphate in regard to their powers of disinfecting water (compare Paterno and Cingolani, *Abstr.*, 1907, ii, 713).

All these compounds exhibit marked germicidal characters, and can be advantageously employed for the sterilisation of drinking water, pathological organisms, such as those of cholera, typhoid, and dysentery, being rapidly destroyed by very small proportions of the disinfectant.

This bactericidal action, which is exhibited to a far greater degree by isotachyol than by the other silver compounds examined, depends principally, although not entirely, on the silver ions. According to D'Anna (*Arch. Farm. sper. sci. affini*, 1904), the acid radicle of a metallic salt influences the disinfecting action of the latter only in so far as it varies the proportion of active metal present. But the author's results are not in agreement with this view, since silver sulphate, containing 69.2% of silver, is inferior as a sterilising agent to the chlorate and perchlorate, containing 56.3 and 52.0% of silver respectively.

T. H. P.

The Rôle of Oxalate in the Germination of Beet Seed. G. DOBY (*Landw. Versuchs-Stat.*, 1909, 70, 155—158).—During germination the alkali oxalate disappeared completely, whilst the amount of calcium oxalate remained unchanged. Only the former substance can therefore be considered as reserve material.

N. H. J. M.

Chemical Nature of Root Secretions. JULIUS STOKLASA and ADOLF ERNEST (*Jahrb. wiss. Bot.*, 1908, 46, 55—102. Compare *Abstr.*, 1905, ii, 607).—Water-culture experiments with maize, oats,

and buckwheat showed that when oxygen is deficient, the roots secrete very marked amounts of fatty acids (formic and acetic acids). In the case of barley there was only a slight production of acids. Sugar beet secreted oxalic and acetic acids. Under conditions of abundant aeration, no acids are secreted, being oxidised to carbon dioxide within the roots; in some cases, traces of hydrogen were given off along with the carbon dioxide. No secretion of mineral acids took place either under conditions of aeration or without aeration.

The amount of carbon dioxide given off by roots varies considerably with different plants. Of the various plants employed, barley produced the greatest amount of dry matter in roots, and also gave off the greatest amount of carbon dioxide. When, however, the amount of carbon dioxide given off in twenty-four hours is expressed in mg. per gram of dry matter, it is seen that barley produces the smallest amount. The quantities for the different plants are as follows: barley, 63.2—74.6; oats, 111.5—135.4; wheat, 87.6—94.8, and rye, 100.7—131.0 mg. CO₂ per gram.

In accordance with these results, it was found that when the four plants were grown in powdered gneiss and in basalt manured with ammonium nitrate, sulphate, and chloride, barley produced the least growth and assimilated the smallest amount of potassium and phosphoric acid, whilst oats produced the greatest amount of dry matter. All the plants, as was also the case with water saturated with carbon dioxide, extracted more mineral matter from basalt than from gneiss.

N. H. J. M.

Significance of the Colloidal Nature of Aqueous Dye-solutions for their Penetration into Living Cells. WILLY RUHLAND (*Ber. Deut. bot. Ges.*, 1908, 26a, 772—782).—A study of the colloidal nature of dyes does not lead the author to modify his criticism of Overton's theory, according to which theory the cell wall is a semi-permeable lipoid membrane. The rate at which various dyes (both basic and acidic) are taken up by living cells bears apparently no relation to the degree of colloidity of their aqueous solutions.

G. B.

Amounts of Iron and Phosphorus in Vegetables. E. HAENSEL (*Biochem. Zeitsch.*, 1909, 16, 9—19).—Determinations of dry matter, ash, iron, and phosphorus in twenty-four vegetables and fruits.

N. H. J. M.

Loss of Nitrates and of Hydrogen Cyanide during the Desiccation of Plants. E. COUPEROT (*J. Pharm. Chim.*, 1909, [vi], 29, 100—102).—Experiments with the leaves and other parts of *Sambucus nigra*, *S. laciniata*, and *S. racemosa* show that when these are allowed to dry by mere exposure to the air at atmospheric temperature, the quantity of nitrates present may be reduced by from 20 to 50%. The first two species also yield hydrogen cyanide, and the quantity of this substance obtainable from the fresh parts of these plants is similarly reduced after air-drying. On the contrary, if the fresh parts of these plants are placed immediately in

a drying apparatus at 60° and maintained at this temperature until dry, there is no loss of nitrates or of hydrogen cyanide. The conclusion is drawn therefore that the losses referred to are due to the utilisation of nitrates and cyanogenetic products by the living cells as reserve materials.

T. A. H.

Composition of *Amapa latex*. A RATHJE (*Arch. Pharm.*, 1909, 247, 49—53).—This latex (sp. gr. 1·0304), which is used by the South American Indians in the Amazon valley as a remedy for consumption, is probably derived from a *Hancornia* sp. It is acid in reaction and taste, and contains neither alkaloids nor glucosides. The resinous product obtained on coagulation has m. p. 45°, saponification number 96·4 (156·7 when saponified under pressure), iodine number (Wys' method) 39·3—53·4, depending on the time the product is left in contact with iodine solution, and Reichert-Meissl number 9·2. It contains gum, sugars, water, formic, acetic, propionic and butyric acids, fatty acids melting at 53—54°, 63—64°, 69—70°, and 78—79°, phytosterol, and other fatty alcohols and hydrocarbons or their near allies, having m. p. 120—121°, 196—197°, 200—201°, and 205—206°.

T. A. H.

Maltase of Maize. R. HUERRE (*Compt. rend.*, 1909, 148, 300—302).—The discrepancies in the observations of various authors are due to the dissimilarity of the ferment in different varieties. The (ungerminated) seeds from one variety of maize from the Landes ("blanc hâtif") have a maltase acting between 0° and 65°, with optimum at 40° (and an amylase with a much lower optimum temperature). Another variety of maize ("jaune hâtif") has a maltase acting between 20° and 80°, with optimum at 60—62°.

G. B.

Pentosans of *Soja hispida*. G. BORGHESANI (*Bied. Zentr.*, 1909, 38, 141; from *Staz. sper. agrar. ital.*, 1907, 40, 118).—The following percentage results are given:

	Furfuraldehyde.	Pentose.	Pentosan.
<i>Soja hispida tumida</i> , var. <i>pallida</i>	1·67	3·25	2·86
" " <i>platycarpa</i> , var. <i>pallida</i>	1·74	3·38	2·97
" " " " <i>melanosperma</i>	2·26	4·39	3·86
" " " " <i>castanea</i>	2·15	4·17	3·67
" (green)	2·11	4·09	3·60

N. H. J. M.

Is the Omission of Magnesium in Soil Analysis Justifiable? OSCAR LOEW (*Chem. Zeit.*, 1909, 33, 118—119).—Attention is called to the importance of determining magnesium in soil in addition to potassium, calcium, phosphoric acid, and nitrogen. Experiments on the effect of magnesium manures have frequently been made without ascertaining the amount already present in the soil. A large number of soils in the Rhine Palatinate were found by Kling to contain only 0·04—0·06% MgO, whilst more than half contained only traces, and some none at all. On the other hand, a soil near Munich contains over 10% MgO (as dolomite).

The frequently discordant results of experiments on the relative values of sodium and calcium nitrates are attributed, in part, to varying relations of the amounts of calcium and magnesium in the soil. Soil already containing a high relation of calcium to magnesium would be injured by further applications of calcium, especially when in a readily available form such as nitrate.

N. H. J. M.

Decomposition of Soil-producing Rocks. EMIL HASELHOFF (*Landw. Versuchs-Stat.*, 1909, 70, 53—143).—Gramineous and leguminous plants are able to produce more or less growth in freshly-broken unweathered rocks, such as basalt, muschelkalk, etc. Of the two groups, the leguminous plants, owing to their greater range of roots and their power of utilising atmospheric nitrogen, have a much greater power of obtaining nutrients from the minerals than gramineous plants. The different plants of the two groups also vary in this respect among themselves.

Addition of nitrogenous manures distinctly increased the yields and also the amounts of nitrogen in the plants; there was, however, no increase in the amounts of other constituents.

N. H. J. M.

Diffusion of Manurial Salts in Soil. ACHILLE MÜNTZ and H. GAUDECHON (*Compt. rend.*, 1909, 148, 253—258).—When soluble salts, such as sodium nitrate and potassium chloride, are applied to air-dried soils in small patches, the soil gradually darkens in the places containing the salt, owing to deposition of moisture from the surrounding portions. Determinations of moisture after a week or ten days showed that the parts of the soil to which the salts were applied contained more, whilst the intermediate portions contained less, moisture than was originally present. In the case of potassium chloride it was found that in ten days no lateral diffusion had taken place to a distance of 20 mm., whilst the soil of the spot to which the salt had been applied contained 1·48%. These results are considered to explain the failure of crops when the seed and manure have been sown about the same time in dry weather; some of the seeds become surrounded by concentrated solutions of salts, whilst the remaining seeds fail to germinate because of the diminished amount of water.

Similar experiments with a wet soil (containing 15·6% water), which received at different points 2 grams of sodium nitrate and potassium chloride at a depth of 1 cm., showed that in six days no appreciable lateral or vertical diffusion had taken place at a distance of 25 mm. In another experiment in soil containing 16·1% of water, a slight diffusion at a distance of 20 mm. was detected at the end of a month, but not at 40 mm.

When rain falls, the solutions of the particles are carried straight down without appreciable lateral diffusion of the salts. It is only during very prolonged falls of rain that a gradual distribution of the salts occurs.

Under ordinary conditions, the diffusion of salts in the soil is extremely slow.

N. H. J. M.

Physiological Characterisation of Ammonium Salts. DMITRI PRIANISCHNIKOFF (*Ber. Deut. bot. Ges.*, 1908, 26a, 716—724).—The

partial replacement of sodium nitrate by ammonium sulphate in sand cultures has a beneficial effect on the absorption of crude phosphates, but when the whole of the nitrogen is supplied as ammonium sulphate the "physiological acidity" of the latter salt acts unfavourably, and calcium carbonate must be added in order to neutralise the sulphuric acid set free. The calcium carbonate can be replaced by sodium nitrate, but only partly by ammonium nitrate. G. B.

Properties and Action of Ammonium Sulphate Containing an Excess of Sulphuric Acid. OTTO LEMMERMANN (*Bied. Zentr.*, 1909, 38, 15—17; from Fühling's *Landw. Zeit.*, 1908—9).—The two chief varieties of ammonium sulphate contain excess of sulphuric acid amounting to 1—1.5 and 0.5% respectively. The presence of hydrogen ammonium sulphate, even when the excess of sulphuric acid reaches the amount of 3%, does not render the manure appreciably more hygroscopic, whilst the results of pot experiments with barley failed to show any injurious action. N. H. J. M.

Manurial Experiments with the Two Commercial Forms of Calcium Cyanamide and with Calcium Nitrate. BR. STEGLICH (*Verhandl. Ges. deut. Naturforsch. Aertze.*, 1907, II, 147—150).—Experiments on various crops from 1903 to 1907, in which the action of the three manures is compared with that of sodium nitrate and in most cases with ammonium sulphate as well.

The results vary considerably in different years. The averages over the whole period indicated that "kalkstickstoff" has a value of 96 as compared with sodium nitrate=100 and ammonium sulphate=95. "Stickstoffkalk," which was only included in the experiments of 1906 and 1907, and calcium nitrate (1907) showed values of 94 and 101 respectively.

The percentage of nitrogen in a sample of "kalkstickstoff" which was kept for three years fell from 18.5 to 12. N. H. J. M.

Manurial Experiments with Calcium Cyanamide. JOHANNES BEHRENS (*Bied. Zentr.*, 1909, 38, 67; from *Ber. landw. Versuchsstat. Augustenberg*, 1906, 40).—Field experiments with barley, in which calcium cyanamide was applied a week before the seed was sown, showed an increase of about 20% of grain as compared with the unmanured plot, whilst sodium nitrate more than doubled the yield.

When applied as a top-dressing to buckwheat and barley, the former was injured beyond recovery, whilst the latter, although injured at first, recovered later on. N. H. J. M.

Action of Calcium Cyanamide on Carrots, Kohl-rabi, and Mangolds under Damp Climatic Conditions. ALBERT STUTZER (*Bied. Zentr.*, 1909, 38, 104—106; from Fühling's *Landw. Zeit.*, 1908).—Sodium nitrate, ammonium sulphate, and calcium cyanamide applied to carrots gave similar results as regards total dry matter, whilst the relations of roots to leaf varied, sodium nitrate producing the greatest amount of leaf and cyanamide the most root (both as dry matter). The cost of producing an increase of 10 kilos.

of dry matter (roots) of carrots, kohlrabi, and mangolds was less when calcium cyanamide was employed than with sodium nitrate.

The rainfall had been excessive in June, July, and August, and August was cold and windy.

N. H. J. M.

Action of Calcium Nitrate and Calcium Cyanamide on Peat Soils. HJALMAR VON FEILITZEN (*Mitt. Ver. Förd. Moorkultur*, 1909, Heft. 1 and 2; and *Svenska Mosskulturför. Tidskr.*, 1909, No. 1).—Calcium nitrate applied to oats, potatoes, and hemp grown in peaty soil deficient in nitrogen and in sandy soil gave results equal to those obtained with sodium nitrate; in some cases calcium nitrate produced higher yields than sodium nitrate.

Calcium cyanamide yielded good results when applied to different peaty soils. As compared with sodium nitrate the yields were sometimes higher and sometimes lower. When used for grass, it should be applied some time before the commencement of growth to avoid injurious action.

N. H. J. M.

Manurial Experiments with Calcium Nitrate on Potatoes. ALBERT STUTZER (*Bied. Zentr.*, 1909, 38, 138—139; from *Mitt. deut. landw. Ges.*, 1908, St. 4, 19).—Equal amounts of nitrogen as sodium and calcium nitrates gave equally increased yields of tubers. The greatest amount of starch was produced by 50 kilos. of nitrogen per hectare as sodium nitrate, and the next largest amount by 25 kilos. of nitrogen as calcium nitrate. Larger amounts of calcium nitrate reduced the amount of starch.

In experiments with tobacco, calcium nitrate acted very favourably on leaf development, and the burning quantity of the leaf was better than with sodium nitrate.

N. H. J. M.

Amount and Composition of the Drainage Waters Collected during the Year 1907-8. B. C. BURT (*Rep. Cawnpore Agric. Stat.*, for the year ending June 30, 1908, 18—19. Compare *Abstr.*, 1908, ii, 890).—The total amounts of rain and drainage, and of nitrogen as nitrates in the drainage, from June 1 to October 31, were as follows:—

No.	Depth of soil in inches.	Rainfall, inches.	Drainage, inches.	Nitrogen as nitrates.	
				Per million.	lb. per acre.
1.....	72	17·15	3·645	11·70	9·65
2.....	72	17·15	4·844	12·61	13·83
3.....	36	17·15	5·920	24·26	32·49
4.....	36	17·15	6·756	24·30	37·15

N. H. J. M.

Use of Ferrous Arsenate against Insect Parasites of Plants. VERMOREL and DANTONY (*Compt. rend.*, 1909, 148, 302—304).—A 4% solution of crystallised ferrous sulphate is slowly added to a 4% solution of sodium arsenate until a potassium ferro- or ferri-cyanide test-paper is turned blue; the mixture is then diluted with four volumes of water, so that it contains about 0·2% of ferrous arsenate,

and is used as a spray. It is much less toxic to plants than the alkali arsenates, and adheres better than Scheele's or Schweinfurth's green.

G. B.

Analytical Chemistry.

Automatic Sampler and Mixing Apparatus. O. BINDER (*Zeitsch. anal. Chem.*, 1909, 48, 32—35).—For fairly uniform samples the apparatus consists of a channel or gutter provided with a number of funnels; the sample is placed in a separate funnel, the stem of which is closed with the finger, and, by moving the finger, the sample is allowed to run into the channel and thence through the funnels into bottles placed below the funnels. If the sample is large and consists of pieces of widely varying sizes, it should be introduced into a chamber divided into four compartments by means of diagonal partitions; two of the "quarterings" thus obtained are mixed, re-distributed over the apparatus, and so on, until a conveniently small average sample has been obtained. This sample may then be divided into smaller parts by means of a funnel and dividing plates.

W. P. S.

Weighing Hygroscopic Substances in the Open. R. HOTTINGER (*Zeitsch. anal. Chem.*, 1909, 48, 73—78).—It is shown that the weight of hygroscopic substances may be obtained in open vessels by weighing the substance, dried previously, several times at regular intervals. By plotting a curve showing the increase of weight at definite intervals of time, the correct weight of the dry substance may be obtained by extrapolation.

W. P. S.

Gravimetric Estimation of Halogens by means of Silver Nitrate. ERNST ALEFELD (*Zeitsch. anal. Chem.*, 1909, 48, 79—80).—A precipitate which filters readily and is free from turbidity is obtained if about 5 c.c. of ether be added to the halogen solution acidified with nitric acid before the addition of the silver nitrate solution. The precipitate should be collected on a Gooch filter moistened previously with ether.

W. P. S.

Iodine Compounds and Gold Solutions. C. J. REICHARDT (*Pharm. Zeit.*, 1909, 54, 58).—If a few drops of 1% auric chloride are added to a little of a very dilute solution of potassium iodide, iodine is liberated, particularly on heating to boiling. If, when cold, the liquid is shaken with chloroform, this turns violet. If potassium bromide is present, yellow crystals will be found floating on the chloroform. The process is suitable for the detection of traces of iodides in commercial bromides; a 1% sodium aurichloride solution is then employed.

If to a few drops of a 1% sodium aurichloride solution are added 8 c.c. of water and then a drop of a freshly-prepared 0.5% potassium

iodide solution, the liquid on heating shows a yellow opalescence, but remains clear in transmitted light. If now are added substances capable of reducing gold, and the heating is continued for about half a minute, characteristic colorations are noticed. It is remarkable that lactose, unlike dextrose, gives no reduction. A list is given of some homeopathic compounds which give colorations varying from violet to dark blue. The colours should be observed in transmitted and also in incident light, and compared with a similar liquid to which lactose has been added.

L. DE K.

Colorimetric Estimation of Dissolved Oxygen in Water.

GEORGE B. FRANKFORTER, G. W. WALKER, and A. D. WILHOIT (*J. Amer. Chem. Soc.*, 1908, 31, 35—43).—An apparatus is described with which the colorimetric estimation of dissolved oxygen by means of ammoniacal cuprous chloride, according to Ramsay and Homfray (*Abstr.*, 1902, ii, 171), can be made with considerable accuracy. The essential parts of the apparatus are constructed entirely of glass, and the mixing of the cuprous chloride and ammonia is effected in the apparatus itself. A few experiments have been made on the rate at which oxygen is absorbed by water.

G. S.

Estimation of Sulphur in Urine. EMIL ABDERHALDEN and

CASIMIR FUNK (*Zeitsch. physiol. Chem.*, 1909, 58, 331—333).—The statement of Osterberg and Wolf that Schulz's method gives too low results is confirmed. Good results are obtained if the oxidation of the urine is effected with sodium peroxide.

W. D. H.

Estimation of Total Sulphur in Urine. F. W. GILL and

HARRY S. GRINDLEY (*J. Amer. Chem. Soc.*, 1909, 31, 52—59).—Experiments showing that there is a loss of sulphur attending the estimation of this element in urines when the sodium peroxide methods or other alkaline fusion methods are resorted to. The loss may amount to 10%, or even more, of the total sulphur present.

L. DE K.

Estimation of Total Sulphur in Urine. OTTO FOLIN (*J. Amer.*

Chem. Soc., 1909, 31, 284—285).—A reply to Gill and Grindley's criticism (preceding abstract) on the author's sodium peroxide method for the estimation of the total sulphur in urine (*Abstr.*, 1906, ii, 124).

E. G.

Estimation of Sulphide in Alkali Cyanides. THOMAS EWAN

(*J. Soc. Chem. Ind.*, 1909, 28, 10—13).—A critical examination of several methods of estimating small quantities of sulphide in solid cyanides. (1) Ten grams of the cyanide are dissolved in 15 c.c. of water and the sulphide titrated by a standard lead nitrate solution until a drop of the solution no longer gives a brown stain when brought in contact with a drop of the lead solution on filter paper. This is a rapid works' method; the chief error is due to oxidation of the sulphide by atmospheric oxygen, which is much accelerated by the lead. The results when multiplied by 1.25 are sufficiently accurate.

(2) Colorimetric methods, using lead sulphide, are only correct when the two solutions compared are of identical composition, and when oxidation is avoided or made to affect both solutions equally. A method described by G. W. Williams fulfils these conditions (*J. Chem. Metall. Min. Soc. S. Africa*, 1905, 6, 170). W. Feld's method, in which the sample is distilled with excess of magnesium chloride in a current of carbon dioxide, the hydrogen sulphide evolved being collected in standard iodine solution, is also accurate, but somewhat troublesome.

T. E.

Titration of Sulphites with Permanganate. JAROSLAV MILBAUER (*Zeitsch. anal. Chem.*, 1909, 48, 17—24).—Owing to the fact that sulphurous compounds are not completely oxidised to sulphuric acid by means of permanganate, the estimation of sulphites by direct titration with permanganate solution is untrustworthy. Results may be obtained, however, which agree well with those found on titration with iodine, if a very dilute solution of the sulphite is added to ten times the required quantity of permanganate solution, acidified with more than 20% (by volume) of concentrated sulphuric acid, and the excess of permanganate then titrated with standard oxalic acid, ferrous sulphate, or hydrogen peroxide solution. The excess of permanganate cannot be titrated with thiosulphate solution after the addition of potassium iodide. The addition of a trace of iodine or bromine has a favourable influence on the oxidation.

W. P. S.

Qualitative Analysis of Sulphates, Sulphites, and Thio-sulphates. WLADIMIR ALEXANDROFF (*Zeitsch. anal. Chem.*, 1909, 48, 31—32).—The method described for the separation and identification of sulphates, sulphites, and thiosulphates in the presence of each other depends on the different solubilities of barium sulphate, sulphite, and thiosulphate, and on the fact that silver thiosulphate decomposes at the ordinary temperature with the formation of silver sulphide, whilst silver sulphite remains unaltered. About 0.1 gram of the mixed salts is dissolved in water, and the boiling solution is treated with an excess of barium nitrate solution; when quite cold, the precipitate, consisting of barium sulphate and a little barium sulphite, is collected on a filter, washed, and tested in the usual way for sulphite. The filtrate is treated with silver nitrate solution, and the mixture is set aside for about forty minutes or until the silver thiosulphate has decomposed. Ammonia is then added, the silver sulphide is removed by filtration, and the filtrate is acidified with hydrochloric acid. The silver chloride is collected on a filter, and the filtrate is treated with bromine after the addition of ammonium chloride. The sulphite is thus oxidised, and a precipitate of barium sulphate is formed.

W. P. S.

Simple Method of Estimating the Nitrogen as Nitrates and Nitrites in Mixtures and in Presence of Organic Matter. T. ZELLER (*Landw. Versuchs-Stat.*, 1909, 70, 145—154).—The solution containing nitrates and nitrites is boiled with a measured amount of a solution of ammonium chloride of known strength

(3—4%) in a 100 c.c. flask until about 2 c.c. remains. The residue is diluted to 100 c.c. The nitrogen as ammonium chloride still remaining is determined in 40 c.c. by boiling with magnesia. The difference between the initial amount of ammonium chloride and the amount of ammonium recovered represents the nitrogen as nitrites. A second 40 c.c. is reduced with sulphuric acid and iron, and distilled with sodium hydroxide. The result obtained less the first result gives the amount of nitrogen as nitrate.

Carbonates, when present, must be precipitated with barium chloride before treatment with ammonium chloride.

Results of a considerable number of estimations in weighed amounts of sodium nitrite, both alone and in presence of other substances, inorganic and organic, show that the method is trustworthy.

N. H. J. M.

Gravimetric Estimation of Nitric Acid. A. HES (*Zeitsch. anal. Chem.*, 1909, 48, 81—98).—In order to obtain trustworthy results by the method described by Busch (Abstr., 1905, ii, 282), the solution should contain about 0.1% of nitrate; the nitrate solution under examination should, therefore, be concentrated or diluted until this concentration is attained. Dextrin, gelatin, and possibly other organic compounds hinder the crystallisation of nitron nitrate, but the presence of aluminium sulphate, magnesium sulphate, ammonium sulphate, potassium phosphate, magnesium chloride, tartaric acid, citric acid, sucrose, and dextrose is without influence on the estimation. When oxalic acid is present, the results obtained are too high. Chloric acid precipitates nitron quantitatively as nitron chlorate if the solution contains about 0.25% of chloric acid, but nitric and chloric acids may be estimated together in the same solution if the amount of one of the acids is known. W. P. S.

Detection of Phosphorus. J. PESET (*Zeitsch. anal. Chem.*, 1909, 48, 35—36).—From the experiments carried out by the author, it is seen that Mitscherlich's process is capable of detecting the presence of as little as 0.0000021 gram of phosphorus, whilst the phosphorescence produced by 0.0000085 gram is very visible. In carrying out the test, it is recommended that the liquid or substance suspected of containing phosphorus should be placed in a flask of about 400 c.c. capacity and connected with a glass tube some 60 cm. long and 6 mm. in diameter. If the contents of the flask are heated to boiling, then cooled slightly, and again boiled, the phosphorescence is more readily seen, not only in the glass tube, but also in the flask. W. P. S.

Detection of Phosphatic Compounds in Cereals. P. CARLES (*Ann. Chim. anal.*, 1909, 14, 57—58).—The substance (flour, bran, etc.) is mixed with its own weight of nitre and a tenth of its weight of sodium hydrogen carbonate, and introduced by degrees into a platinum crucible heated to redness. When cold, the mass is powdered and again heated. The mass is then heated with dilute nitric acid, and should there remain any char, this may be readily burnt. After boiling the acid liquid for half an hour, adding more nitric acid if

necessary, the phosphoric acid is present in its normal form, and may be precipitated by magnesium mixture and finally titrated with uranium solution. By means of this method, the results of the analyses will be perfectly concordant.

L. DE K.

Colorimetric Estimation of Phosphoric Acid. ISIDORE POUGET and D. CHOUGHAK (*Bull. Soc. chim.*, 1909, [iv], 5, 104—109).—The method depends on the formation of an insoluble precipitate of strychnine phosphomolybdate when a solution containing sodium molybdate, strychnine sulphate, and nitric acid is added to a solution of a phosphate in nitric acid. The opalescent liquids produced in this way show in the colorimeter tints varying from yellow to brown, depending on the intensity of the opalescence. The exact conditions of working and the precautions to be observed in presence of excess of calcium, iron, or arsenic are described in detail in the original.

T. A. H.

Colorimetric Estimation of Phosphates in Solution with Other Salts. CLARENCE ESTES (*J. Amer. Chem. Soc.*, 1909, 31, 247—250).—Veitch (*Abstr.*, 1903, ii, 329) has shown that ammonium salts and certain chlorides affect the colour of phosphomolybdate solutions. It has now been observed that, in estimating phosphorus in meat by the colorimetric method, the salts introduced into the solution with the phosphates from the oxidising agents used interfere very seriously with the intensity of the colour. A study has therefore been made of the influence of several reagents on the coloration. The results of the experiments show that sodium nitrate and probably potassium ethyl sulphate at first decrease the colour in proportion to the quantity of salt present, but that as the amount is increased a certain intensity is reached, beyond which further addition of the salt does not produce any change. Sodium sulphate, potassium hydrogen sulphate, magnesium sulphate, sodium chloride, and an excess of nitric acid all greatly diminish the intensity of the colour, and, if present in large quantities, reduce it to a mere trace. When calcium or magnesium nitrate is added to the solution, the colour is at first reduced, but, on adding a larger quantity, the colour is gradually restored, until it becomes nearly normal. Tables are given which express the percentage error caused by these salts in the colorimetric estimation of phosphates, and also the quantity of each salt which will produce an error of approximately 5% in the readings.

E. G.

Volumetric Estimation of Phosphoric Acid, Mono-alkali and Di-alkali Phosphates. JOHN M. WILKIE (*J. Soc. Chem. Ind.*, 1909, 28, 68—69).—The method is based on the fact that when silver nitrate is added to an orthophosphate the precipitate always consists of trisilver phosphate; the precipitation is rendered complete by addition of sodium acetate, and the amount of acetic acid liberated, which, of course, varies according to the nature of the phosphate used (phosphoric acid, mono-sodium hydrogen phosphate, di-sodium hydrogen phosphate) is then titrated with *N*/10 barium hydroxide, using phenolphthalein as indicator. By way of a check, a definite quantity of *N*/10

silver solution having been used, the excess of silver may be titrated by Volhard's method.

If carbonates are present, the silver titration should be applied after expelling the carbon dioxide by means of *N*/10 sulphuric acid.

L. DE K.

Detection of Small Quantities of Arsenic and Preparation of Arsenic-free Chemicals. GEORG LOCKEMANN (*Verh. Ges. deut. Naturforsch. Aertze.*, 1907, ii, 143—145).—The organic matters are destroyed by heating with nitric and sulphuric acids and subsequent fusion with nitre. The neutral or faintly acid solution finally obtained is mixed with a little iron-alum, and enough ammonia is added to completely precipitate the ferric hydroxide, which, in the cold, carries down the arsenic. After half an hour, the precipitate is collected, washed with cold water, and then redissolved in dilute sulphuric acid and tested in the Marsh apparatus. According to the author, iron salts do not retard the reaction.

Sulphuric acid may be freed from arsenic by heating it at 250° and passing a current of hydrogen chloride. Arsenic-free chlorides and nitrates may be obtained by treating their solutions with excess of ferric hydroxide; even ammonia may be thus purified. From the purified chlorides and nitrates, the corresponding arsenic-free acids may then be prepared.

L. DE K.

Estimation of Carbon Dioxide in Blood. W. DIBBETT (*Chem. Zentr.*, 1909, i, 49; from *Arbb. Geb. Path. Anat. Bact.*, 1908, 6, 228—235).—A weighed quantity of blood (about 5 c.c.) is mixed in a special apparatus with 10 c.c. of strong oxalic acid solution, and the carbon dioxide evolved is absorbed in standard barium hydroxide solution. When the barium carbonate has subsided, the excess of hydroxide is titrated with standard oxalic acid.

L. DE K.

Estimation of Calcium Oxide in Presence of Calcium Carbonate, etc. HEYER (*Chem. Zeit.*, 1909, 33, 102—103).—2.5 Grams of the sample are placed in a half-litre flask with 125 c.c. of water, and, after shaking, 125 c.c. of 2% ammonium chloride solution are added. The stopper is inserted, and the whole well shaken at intervals for some time. Water is then added up to the mark (or a trifle over to compensate for undissolved matter), the whole is again well shaken, and then allowed to subside. An aliquot part is withdrawn and titrated with *N*/10 acid. The ammonia found represents the calcium oxide, for calcium carbonate does not act on ammonium chloride in the cold.

L. DE K.

Volumetric Estimation of Barium. ARTHUR E. HILL and WILLIAM A. H. ZINK (*J. Amer. Chem. Soc.*, 1909, 31, 43—49).—A quantity of barium salt containing about 0.1 gram of barium is dissolved in water and rendered faintly alkaline with ammonia. After diluting to 60—70 c.c., *N*/6 potassium iodate is added to the extent of 25 c.c. more than is required theoretically. When, after stirring, the barium iodate has settled, it is collected on a filter and washed three times with strong ammonia and then with alcohol. The precipitate,

and afterwards also the filter, is transferred to a flask, 50 c.c. of 10% potassium iodide and 10 c.c. of hydrochloric acid are added, and the iodine liberated is titrated with $N/10$ thiosulphate. One mol. of this = $1/12$ at. of barium; sodium salts do not interfere. When potassium or ammonium compounds are present, the barium must be precipitated from a hot solution. In presence of magnesium a little ammonium chloride should be added, and the liquid heated before precipitation. Calcium or strontium should be absent. L. DE K.

Estimation of Lead as Oxalate. WILHELM BÖTTGER [and K. POLLATZ] (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1907, ii, 175—177).—The acid solution is neutralised with ammonia, and acetic acid is added so as to get an $N/2$ acid solution. The lead is then precipitated with a slight excess of oxalic acid.

After washing with cold water, the lead oxalate is dried at 100° and weighed, or it may be titrated with permanganate. L. DE K.

Electrolytic Estimation of Lead and of Manganese by the Use of the Filtering Crucible. FRANK A. GOOCH and F. B. BEYER (*Amer. J. Sci.*, 1909, [iv], 27, 59—63; *Zeitsch. anorg. Chem.*, 1909, 61, 286—292. Compare Abstr., 1908, ii, 529).—Good results may be obtained in the case of lead with the filtering crucible as an electrolytic cell if nitric acid is present in the proportion of 30 c.c. of the strong acid in 100 c.c. of the solution. The liquid should be kept in continuous filtration until the lead has completely deposited as peroxide, and the acid liquid must then be displaced gradually by solution of ammonium nitrate, and all the while the current must be kept up. After washing with water, the peroxide is dried at 200° and weighed.

Manganese is deposited from a solution containing free sulphuric acid as hydrated peroxide, which is then converted into the anhydrous condition by cautious heating, first at 200° , and then in the spreading flame of a large burner. L. DE K.

Analysis of Red Lead. ALFRED PARTHEIL (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1907, ii, 159).—The estimation of the insoluble constituents of red lead by the extraction of the latter with hot nitric and oxalic acids is inaccurate, since the resulting solution of lead nitrate yields a sparingly soluble precipitate of oxalate and oxal-nitrate of lead. Good results are obtained by treating the red lead (2.5 grams) with 10 c.c. of water, 5 c.c. of lactic acid, and 10 c.c. of 25% nitric acid; the insoluble portion is washed, dried, and weighed.

The value of a technical red lead can be determined by its colour, or by an estimation of the lead peroxide by Topf's method (Abstr., 1887, 997).

Of the samples examined, only a few approximated to the composition Pb_3O_4 ; several gave values approaching Pb_4O_5 . C. S.

Action of Permanganate on Ferrous Salts in Presence of Hydrochloric Acid. W. COLET BIRCH (*Chem. News*, 1909, 99, 61—63, 73—74).—Fresenius' method of titrating iron with permanganate in presence of hydrochloric acid by adding an equal

amount of the ferrous solution after the first titration and re-titrating, this process being repeated several times, is inaccurate. The addition of various salts, recommended by several authors, is usually without effect, ammonium sulphate even making the results less accurate. Manganese sulphate gives fairly good results, preventing chlorine from escaping, but is troublesome (compare Harrison and Perkin, *Abstr.*, 1908, ii, 228).

The brown compound, which obscures the end-point, is MnCl_3 , as is shown by its isolation as $\text{MnCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$. C. H. D.

Precipitation of Cobalt by Potassium Nitrite. LUCIEN L. DE KONINCK (*Bull. Soc. chim. Belg.*, 1909, 23, 11—13).—The author states that cobalt is effectually precipitated by adding to the solution, which should contain free nitric acid, a solution of potassium nitrite far more than sufficient to neutralise the acid. The precipitation is then more complete than when working, as usual, in a solution containing free acetic acid. Traces of cobalt, often present in commercial nickel salts, may thus be isolated. L. DE K.

Procedure for the Oxidation of Chromic Acid to Perchromic Acid. WILLIAM J. KARSLAKE (*J. Amer. Chem. Soc.*, 1909, 31, 250—251).—In the detection of chromium by the oxidation of chromic acid to perchromic acid, it is usual to acidify the solution, then to add ether, and finally a little hydrogen peroxide. When this procedure is followed, it often happens that the reduction of the perchromic acid to a chromium salt is so rapid that the blue colour is not produced. If, however, the hydrogen peroxide is added first and thoroughly mixed with the neutral or alkaline chromate solution, and the mixture is then treated with dilute sulphuric or nitric acid, a good blue coloration is produced, even in the absence of ether. The addition of ether is not necessary, except for the detection of traces of chromium. E. G.

Iodometric Estimation of Vanadic Acid, Chromic Acid, and Iron Oxide in the Presence of One Another. GRAHAM EDGAR (*Amer. J. Sci.*, 1909, [iv], 27, 174—178; *Zeitsch. anorg. Chem.*, 1909, 61, 280—285).—A process for the estimation of vanadic and chromic acids in presence of each other, and based on the differential reducing action of hydrobromic and hydriodic acids, has been described previously (*Abstr.*, 1908, ii, 989). The author now states that this is also available in presence of ferric iron, which is also reduced by boiling with hydriodic acid.

In order to obtain the necessary data for calculation, it is necessary to determine one of the constituents separately; the author prefers estimating the chromic acid in a portion of the original solution as follows. A slight excess of sulphuric acid and a few c.c. of syrupy phosphoric acid are added, and then an excess of standard arsenious acid. After about twenty minutes, the solution is made alkaline with sodium hydrogen carbonate, and the excess of arsenious acid is titrated by adding excess of standard iodine and titrating this, after the lapse of half an hour, with standard thiosulphate, using starch as indicator. L. DE K.

Volumetric Estimation of Bismuth. RICHARD EHRENFELD and A. INDRA (*Zeitsch. anal. Chem.*, 1909, 48, 24—26).—The phosphate method for the volumetric estimation of bismuth (Abstr., 1908, ii, 72) yields trustworthy results if the cochineal indicator, described by Repiton (Abstr., 1908, ii, 320), is employed in the final titration. Results of experiments are recorded which show that the average error of the process amounts to 0.6% of the bismuth present, which is less than the error observed in the process as described originally.

W. P. S.

Elementary Analysis of Organic Substances. KENZŌ SUTŌ (*Zeitsch. anal. Chem.*, 1909, 48, 1—17).—Several modifications of the apparatus usually employed are suggested. A drying tube is inserted between the air or oxygen purifying tubes and the combustion tube in order to prevent any moisture yielded by the indiarubber connexions finding its way into the weighed calcium chloride tube. The outlet end of the combustion tube is surrounded by a small steam-jacket, so that the water resulting from the combustion cannot collect at the end of the tube, and this end may be connected directly with the calcium chloride tube by means of a glass adapter fitting closely to the end of the combustion tube. The joint is rendered air-tight by means of a piece of rubber tubing.

W. P. S.

Combustion of Compounds Containing Nitrogen by the Simplified Method. MAX DENNSTEDT and F. HASSLER (*Chem. Zeit.*, 1909, 33, 133).—The lead peroxide used in the authors' simplified process should be mixed with half its bulk of pure red lead in order to absorb the nitric fumes given off in the combustion, which otherwise would affect the carbon and hydrogen determination.

L. DE K.

New Potash Apparatus. M. S. LOSANITSCH (*Ber.*, 1909, 42, 237).—The apparatus is a modification of the Geissler bulb. The gas passes first into a glass vessel, in which are three small wash-bottles in series, all being half full of potassium hydroxide. It is thus exposed to a considerable surface of the absorbent before passing into the wash-bottles. A drying tube of the usual pattern is fused to the glass vessel. The apparatus weighs about 25 grams empty and 50—60 grams when filled.

E. F. A.

Estimation of Carbon by means of the Bomb Calorimeter. J. AUGUST FRIES (*J. Amer. Chem. Soc.*, 1909, 31, 272—278).—A modification of the bomb calorimeter is described, which is recommended for determining both the heat of combustion and the carbon content on the same material, or can also be used for the estimation of carbon alone. The top of the calorimeter is provided with two openings and valves, an inlet terminating on the inside of the cover, and an outlet extending by means of a fine platinum tube to within about $\frac{5}{8}$ -inch of the bottom of the bomb. After ignition, the gas in the bomb is led by means of an aspirator through four U-tubes, of which the first and last contain pumice stone and sulphuric acid, whilst the other two

contain soda-lime, to absorb the carbon dioxide. Results of carbon estimations by means of this apparatus are quoted, and show that the method is trustworthy and accurate.

It is suggested that hydrogen could also be estimated with the bomb calorimeter, but for this purpose the bomb would have to be lined with platinum or other non-corroding material, as otherwise the escaping acids would attack the apparatus. E. G.

Estimation of Essential Oils. MARTIN KLASSERT (*Zeitsch. Nahr. Genussm.*, 1909, 17, 131—132).—It is pointed out that during the evaporation of the ethereal solution of the essential oil, obtained as described by Reich (Abstr., 1908, ii, 1075), moisture may condense on the ethereal solution, and also that ether itself contains water; consequently, the residue of essential oil in many cases contains small quantities of water. The author recommends that the evaporation of the ether should be carried out in a basin, which is placed under a bell-jar. A current of dry air is drawn in at the top of the bell-jar by means of a water pump attached to a tube passing through a tubulure near the bottom of the side of the jar; this tube is bent inside the bell-jar so that its end is just above the surface of the solution contained in the basin. The air current is regulated to about 60 bubbles per minute, a drying bottle being placed between the tube and the pump for this purpose, and when the ether has been evaporated, the opening at the top of the bell-jar is closed while the pump is kept working. The reduced pressure thus produced in the bell-jar causes any condensed water to evaporate quickly, and the essential oil remaining in the basin is then weighed, after the basin and its contents have been allowed to attain the ordinary temperature. During the evaporation of the ether, the temperature is so reduced that there is but little, if any, loss of essential oil. W. P. S.

Precipitation of Reducing Sugars with Basic Lead Acetate. A. HUGH BRYAN (*Zeitsch. Ver. deut. Zuckerind.*, 1909, 1—4. Compare Pellet, Abstr., 1906, ii, 400; Watts and Tempny, Abstr., 1908, ii, 236; and Prinsen-Geerligs, Abstr., 1908, ii, 991).—To determine the effect of various clarifying agents (lead salts) on reducing sugars, solutions of dextrose and lævulose were prepared containing 5 grams of the sugar and 1 gram each of magnesium sulphate and ammonium tartrate; the lead salt was added to 50 c.c. of the solution, and the whole diluted to a volume of 100 c.c. After filtration, the excess of lead was removed by means of potassium oxalate, and the sugar estimated by Allihn's method. The results obtained show that normal lead acetate precipitated practically no sugar, but that basic lead acetate, whether added as a solution or in the dry state, and basic lead nitrate removed very large amounts of sugar; in every case more lævulose was precipitated than dextrose. It was also found that the polarisation of mixed solutions of sucrose, dextrose, and lævulose was affected by clarification with lead salts in the presence of optically inactive substances precipitable by lead, a portion of the reducing sugars being removed by the precipitate formed. W. P. S.

A Method to Show the Presence of Pentoses in the Presence of Ketoses. HERBERT E. ROAF (*Proc. physiol. Soc.*, 1908, v; *J. Physiol.*, 38).—If ketoses are present, the reaction of pentoses with phloroglucinol or orcinol and hydrochloric acid is obscured by the occurrence of a brown precipitate. But if the solution is distilled with 6% hydrochloric acid, the distillate gives characteristic reactions; phloroglucinol and hydrochloric acid give first a brown and then a dark green colour, or if orcinol is used, there is first a grey and then a bluish-green. These results are not masked by the presence of ketoses. W. D. H.

Seliwanoff's Test for Sugars of the Lævulose Group. JOSEPH PIERAERTS (*Bull. Assoc. chim. suc. dist.*, 1909, 26, 560—562*).—The author states that Seliwanoff's reagent (resorcinol and hydrochloric acid) does not afford a ready means for the recognition of lævulose and its anhydrides in sugar mixtures. L. DE K.

Apparatus for Reversed Filtration and its Application to the Estimation of Fibre. WATZLAFF IWANOWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1753—1756).—The disadvantages of the various apparatus which have been described for reversed filtration, such as that of Blümmer (*Chem. Zeit.*, 1908, 32, 232), lie in the limited choice of filtering material, which must be paper or fine cloth, and in the readiness with which the filter, when of paper, tears.

The apparatus devised by the author to remove these disadvantages consists of a tube widened at one end, into which fit two perforated disks of glass, porcelain, etc., holding between them the filtering material, and retained in position by means of a rubber band. The tube is immersed in the solution to be filtered and connected with an exhausted flask.

The estimation of fibre in food materials can be readily carried out by means of the apparatus. The material is boiled with dilute sulphuric acid, which is then sucked through the filter fitted with a cloth disk, and the residue washed twice with water, the latter being sucked off in each case; "dickes Crème-Tuch" is the best material for the filter. The cloth filter and the residue are then boiled together with dilute alkali, which dissolves the cloth quantitatively. One quantitative filter and four disks of quick-filtering paper having been previously dried and weighed, the alkaline liquid, cooled to 40—30°, is drawn off through the filter fitted with one of the quick-filtering papers. The residue is boiled with water, which is sucked through another of the papers. Finally, the residue and the two used papers are boiled with water, and the whole filtered through the two remaining filters, which are then washed, dried, and weighed. This method is found to give accurate results. T. H. P.

Colour Reactions of Dihydroxyacetone. GEORGES DENIGÈS (*Compt. rend.*, 1909, 148, 172—173).—In presence of concentrated sulphuric acid, dihydroxyacetone develops intense and permanent colorations when added to phenols or to certain opium alkaloids. 0.1 c.c. of a solution of the phenol or alkaloid (1 gram + 28 c.c.

* and *Bull. Soc. chim.*, 1909, [iv], 5, 248—250.

alcohol, 90—95%) is mixed with 0.4 c.c. of a solution of dihydroxyacetone containing not more than 1 gram per litre; exactly 2 c.c. of sulphuric acid (D 1.84) are then added, and the coloration appears in one or two minutes. Codeine gives a blue tint even with 0.0001 mg. of dihydroxyacetone.

Morphine and heroine give violet or sepia tints, whilst thymol gives a blood-red, and β -naphthol a green, coloration, the solution in the latter case showing a green fluorescence. Resorcinol gives a colour resembling that of the alkali dichromates.

W. O. W.

New Reactions of Dihydroxyacetone. GEORGES DENIGÈS (*Compt. rend.*, 1909, 148, 282—283. Compare preceding abstract).—The reactions previously ascribed by the author to dihydroxyacetone are not specially characteristic of the pure compound, but are partly due to the presence of bromine. To obtain the reactions with pure dihydroxyacetone, it is necessary to add 0.1 c.c. of a 4% solution of potassium bromide to the other reagents employed. Under these conditions, guaiacol gives a blue coloration, salicylic acid a raspberry-red, and gallic acid a deep violet coloration.

W. O. W.

Detection of Benzoic and Salicylic Acids in Fermented Beverages and in Milks. LUCIEN ROBIN (*Ann. Chim. anal.*, 1909, 14, 53—54).—*Wines, Ciders, Beers.*—Fifty c.c. of the liquid are mixed with a little ferric chloride and a little hydrochloric or sulphuric acid, and shaken with 40—50 c.c. of ether. After washing the ether twice, one-half is taken and used for the detection of salicylic acid; the other portion is shaken with 25 c.c. of a weak alcoholic solution of sodium hydrogen carbonate, and the alkaline liquid is evaporated to dryness and examined for benzoic acid by the nitration test described previously (*Abstr.*, 1908, ii, 1078).

Milk.—This must be deprived first of its fatty matter and casein. Fifty c.c. of the sample are slowly added with stirring to a mixture of 10 c.c. of 5% sulphuric acid and 20 c.c. of strong alcohol, and the filtrate, which must be quite clear, is then treated with ether as directed. If an emulsion forms, some more water may be added, and the ether should be washed with water containing a very little alcohol.

L. DE K.

Microscopical Detection of Lichen Acids. EMANUEL SENFT (*Verh. Ges. deut. Naturforsch. Aertze.*, 1907, ii, 161—164).—A particle of the thallus is put on an object glass and covered with a large drop of bone oil. After breaking it up with a lancet as much as possible, a thick covering glass is placed on it, but by means of a second covering glass, or a thin strip of paper, it is raised slightly at one side.

The glass is now heated over a small flame for some time to extract the acids, and the cover is then gently pressed with a lead pencil and moved so as to collect the liquid on one spot. After the lapse of about one day, the slide is examined under the microscope. Sometimes it is advisable to extract a larger quantity of the lichens with a suitable solvent (chloroform, benzene, alcohol, etc.), and to recrystallise the residue left on evaporation from bone oil as directed.

In this manner, the author has obtained characteristic crystals of *calycin*, *chrysocetraric acid*, *pinastric acid*, *oxypulvic acid*, *rhizocarpic acid*, *vulpic acid*, *methylpulvic acid*, *callopismic acid*, *physcianin*, and *parietin*.

L. DE K.

Characterisation of Fish Oils by the Bromine Addition Products. HENRIK BULL and J. C. F. JOHANNESSEN (*Chem. Zeit.*, 1909, 33, 73—74).—A modification of Hehner and Mitchell's gravimetric method so as to render it suitable for the testing of dorse liver oil. One gram of the fatty acids obtained from the sample is dissolved in 5 c.c. of glacial acetic acid and 25 c.c. of ether, and 0.5 c.c. of bromine is added very slowly with continual cooling and shaking.

The precipitate is collected in a weighed tube containing asbestos, washed thrice in succession with 5 c.c. of the ether-acid mixture, and then twice with 5 c.c. of dry ether. The tube is then dried at 100° and weighed. Genuine dorse liver oil yields about 34% of brominated product, but on altering the proportions of the reagents, or on adding the bromine carelessly, quite different figures are obtained.

L. DE K.

Detection of Aniline. J. PESET (*Zeitsch. anal. Chem.*, 1909, 48, 37—40).—Several characteristic colour reactions produced by the action of oxidising agents on aniline are given. If two drops of aniline are treated with 0.5 c.c. of concentrated nitric acid and 0.2 gram of potassium chlorate, a blue coloration is produced, which quickly changes to yellowish-red; after a short time, an odour of benzaldehyde is noticed, and a gas is evolved containing hydrogen cyanide. On diluting the mixture with water, a yellow precipitate forms, which is insoluble in benzene, light petroleum, and chloroform, but soluble in amyl alcohol and acids. The blue solution and the amyl alcohol solution exhibit absorption spectra. If the aniline solution tested is dilute, heat must be applied in order to obtain the colorations. One part of aniline in 102,400 parts of water shows a feeble yellow coloration; if ammonia is added and the mixture shaken with amyl alcohol, 0.000009 gram of aniline may be detected. Concentrated nitric acid and sodium hypochlorite give a blue coloration with aniline; the colour changes to red, and becomes brown on the addition of ammonia. Both colours are soluble in amyl alcohol. Nitric acid and sodium nitrite, manganese dioxide or lead peroxide, give a green coloration with aniline, changing to red, whilst nitric acid and potassium dichromate yield an intense red colour, which gradually becomes green, then blue, and finally red with the evolution of gas. If permanganate is employed with nitric acid, a green coloration changing to blue is observed. When aniline is treated with 10% acetic acid and sodium peroxide, a yellow coloration is obtained on boiling the solution. All these colours are soluble in amyl alcohol in the presence of ammonia, and the solutions show absorption bands.

W. P. S.

Detection of Methylaniline and Dimethylaniline in Presence of Each Other. HERMANN EMDE (*Arch. Pharm.*, 1909, 247, 77—79).—Several grams of the substance under examination are dissolved in

strong hydrochloric acid, and the solution added drop by drop to excess of platinum tetrachloride dissolved in water. By careful crystallisation of the precipitate from alcohol containing hydrogen chloride, the two platinichlorides can be separated. Methylaniline platinichloride, m. p. 199° (decomp.), forms compact, orange-red crystals. *Dimethylaniline platinichloride*, m. p. 173° (decomp.), crystallises in orange-red needles, and decomposes when warmed in water, forming an inky fluid. Instead of separating the two platinichlorides, the original precipitate may be boiled with water, when, if dimethylaniline platinichloride is present, an inky liquid is formed. From this, methylaniline platinichloride crystallises out on cooling.

T. A. H.

Estimation of Urea. F. HAESLER (*Chem. Zeit.*, 1909, 33, 110).—The urine, representing not more than 0.1 gram of urea, is added slowly from a burette to 25 c.c. of sodium hypobromite solution (200 grams of sodium hydroxide free from carbonate in 750 c.c. of water; when cold, 50 c.c. of bromine, and then water up to a litre), and the carbon dioxide formed in the reaction is estimated gravimetrically in Henriques and Meyer's apparatus (*Abstr.*, 1900, ii, 687). Before liberating the carbon dioxide, it is necessary to reduce the excess of hypobromite, and this is done effectually by means of zinc or aluminium powder. The reduction is carried out in a flask furnished with a Bunsen valve, so as to exclude atmospheric carbon dioxide, and is complete after three hours. A blank experiment should be made once for all to determine any carbon dioxide present in the hypobromite itself. $\text{Carbon dioxide} \times 15/11 = \text{urea}$. L. DE K.

Estimation of Urea. ADOLF JOLLES (*Zeitsch. anal. Chem.*, 1909, 48, '26—30).—In the process described, the urea is decomposed by alkaline sodium hypobromite, the excess of hypobromite decomposed by nascent hydrogen, and the carbon dioxide, resulting from the decomposition of the urea, is then liberated by the addition of acid, collected, and weighed. The urea solution, containing not more than 0.25 gram of urea, is placed in a flask, and 100 c.c. of sodium hypobromite solution (prepared by dissolving 30 grams of bromine in 500 c.c. of 10% sodium hydroxide solution) are added. The flask is closed by a Bunsen valve, and the contents are shaken for five minutes. Three grams of Devarda's mixture (45 parts of aluminium, 50 parts of copper, and 5 parts of zinc) are then added, and, after two hours, the flask is connected with an upright condenser, the upper end of which is connected in turn with drying tubes and a weighed potash bulb. A current of air free from carbon dioxide is drawn through the whole apparatus, and hydrochloric acid is added gradually through a tapped funnel to the contents of the flask. The latter is eventually heated, and the current of air continued until the whole of the carbon dioxide has been absorbed in the potash bulb. The increase of weight of the latter is a measure of the urea, as 44 parts of carbon dioxide are equivalent to 60 parts of urea. A blank estimation is necessary, in order to allow for the carbon dioxide which is invariably present in the reagents employed. The method yields trustworthy results in the case of pure urea.

W. P. S.

A New Ureometer. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1909, 14, 52—53).—The decomposition flask containing 1 or 2 c.c. of the urine is fitted with a cylindrical reservoir filled with the hypobromite solution. By gently turning a stopcock, a desired volume of the reagent is made to flow into the urine. The nitrogen evolved escapes through a side-tube, and is collected over water and measured with the usual precautions.
L. DE K.

Estimation of Alkaloids in Coca Leaves. ANNE W. K. DE JONG (*Rec. trav. Chim.*, 1908, 27, 419—421).—12.5 Grams of the finely-powdered leaves, moistened with 5 c.c. of 25% ammonia, are extracted in a Soxhlet apparatus with light petroleum of low b. p. After ten to fifteen hours' extraction, the petroleum is poured into a separating funnel, and, after rinsing the flask with some light petroleum, the leaves are extracted a second time for three hours. The mixed petroleum extracts are then shaken, first with 50 c.c. and then 25 c.c. of 0.5% hydrogen chloride solution. The acid extracts are passed through a small filter, which is then washed twice with water. The filtrate is shaken once with ethyl ether, which is rejected, and the liquid is then rendered alkaline with ammonia and shaken, first with 50 c.c. and then with 25 c.c. of ether. The ethereal solution is then introduced into a flask, and when it has become quite clear, it is carefully decanted into a weighed flask, and the other flask is rinsed twice with a little ether. The ether is then recovered by distillation, and the last traces are removed by placing the flask in boiling water and passing a current of air. After cooling in a desiccator, the flask is re-weighed.
L. DE K.

Estimation of Creatinine in Urine. G. EDLEFSEN (*Chem. Zentr.*, 1909, i, 108; from *Münch. med. Woch.*, 1908, 55, 2524—2527).—The creatinine is precipitated by means of dilute sulphuric acid in presence of alcohol and ether; the precipitate is collected and redissolved in water, and then titrated with barium hydroxide with phenolphthalein as indicator; $0.396 \text{ SO}_4 = 0.604 \text{ creatinine}$. The urine should be first freed from phosphates and sulphates by the usual barium mixture. According to another process, after removing urea with mercuric nitrate, 10 c.c. of the urine are mixed with 5 c.c. of a 1% solution of salicylic acid, and the excess of this is extracted by shaking with pure ether and titrated with $N/2$ sodium hydroxide. Twenty-two parts of salicylic acid combine with seventy-eight parts of creatinine.
L. DE K.

Estimation of Tannins. LUIGI ERMANNOCAVAZZA (*Chem. Zentr.*, 1908, ii, 2045; from pamphlet, 4 pp.).—The tannin solution is precipitated with calcium hydroxide solution, and the calcium tannate is introduced into a narrow tube graduated for the purpose. After settling, the volume is read off, and this calculated into the corresponding weight of tannin.
L. DE K.

General and Physical Chemistry.

New Proof of the Existence of Molecules. THE SVEDBERG (*Zeitsch. physikal. Chem.*, 1909, 65, 624—633).—The absorption of light in solutions is proportional to the concentration, c , of the solute and to the length, l , of the absorbing layer. In the present paper the limiting value of the absorption constant, $\lim.k = cl$, has been determined by measurements under such conditions that the absorption is just visible.

The apparatus consists of two tubes of Jena glass, A and B , each two metres long and 15 mm. in diameter, placed parallel to one another and illuminated at one end by a flame and screen. The tube A contains distilled water, and B the solution to be tested; in front of A is placed a glass trough with parallel sides, containing a known volume of distilled water. From a burette a concentrated solution of the substance contained in B is dropped into the distilled water in the trough until the colours of the two tubes appear the same. It is shown by experiments with copper sulphate and with magenta that $\lim.k$ can be determined with considerable accuracy in very dilute solution; in the case of magenta, at a dilution of 1×10^{-7} normal.

The method has been used to investigate the solutions of colloidal gold obtained by reduction with hydrazine hydrochloride and with an ethereal solution of phosphorus respectively. The concentration of the gold solution was varied, and in each case the value of $\lim.k$ was determined, and, when practicable, the size and number of the colloidal particles determined by means of the ultramicroscope. The results show that the particles become progressively smaller the greater the dilution. The curve obtained by plotting the values of $\log(1/\lim.k)$ as ordinates against the values of $\log(1/\text{concentration})$ rises at first, attains a maximum, and then falls continuously as far as the observations can be carried. The observations show that the specific absorption in the colloidal region is at first nearly independent of the concentration, but in less concentrated solution decreases rapidly. As the fall in absorption runs parallel with a diminution in the size of the particles, as far as the latter can be observed with the ultramicroscope, it may be assumed that the steady diminution of the absorption in still more dilute solution indicates a further diminution in the size of the particles in regions inaccessible to the ultramicroscope. G. S.

Importance of Refractometric Investigations in Pharmacy. ENDRE VON KAZAY (*Chem. Zentr.*, 1909, i, 309; from *Pharm. Post*, 1908, 41, 993—994).—Examples are given which show the importance of determining the molecular refraction of substances as a means of ascertaining the nature of their internal structure. With pyridine it is experimentally found that $n_D = 1.50468$, $D = 0.979$, hence $M(n-1)/D = 40.7$; thus supporting the structure assigned by Reidl and Dewar (which gives a calculated value 40.0).

When extended to the consideration of two rings, similar accord is

observed between the observed and the calculated values for molecular refraction, thus: Naphthalene, $n_D = 1.5245$, $D = 0.962$ (98°), $M(n-1)/D = 76.45$ (calc. 76.4). β -Naphthol, $n_D = 1.6114$, $D = 1.1$ (99°), $M(n-1)/D = 79.2$ (calc. 79.2); also with quinoline the Reidl-Dewar structure is valid, $n_D = 1.6093$, $D = 1.0947$, $M(n-1)/D = 71.78$ (calc. 71.8). The refractive index found for thiophen from $n_D = 1.5237$, $D = 1.0643$, $M(n-1)/D = 41.32$, is in agreement with the structure

$$\begin{array}{c} \text{HC} - \text{CH} \\ | \quad | \\ \text{HC} - \text{CH} \end{array} > \text{S}.$$

The fact of being able to differentiate between molecular structures by molecular-refraction measurements makes it possible to decide whether an artificially prepared substance is identical in all respects with the natural substance. For instance, the refractive index of artificial camphor is $(n-1)/a = 0.4873$, whilst that of natural camphor is 0.5036, showing that the more highly refractive natural substance contains a double linking in the ring, $M(n-1)/a = 76.54$ (calc. 76.6).

J. V. E.

Resolution of Racemic Substances Prepared by Chemical Synthesis. Effect of Circularly-polarised Light. A. COTTON (*J. Chim. Phys.*, 1909, 7, 81—96. Compare Cotton, *Ann. Chim. Phys.*, 1896, [vii], 8, 373; Byk, *Abstr.*, 1905, ii, 70).—The author discusses the possibility of resolving a racemic mixture into its components by physical means, and draws the conclusion, in agreement with P. Curie, that the resultant of the physical agents employed must also possess enantiomorphous dissymmetry, and must influence the chemical change in a definite way. These requirements should be satisfied by circularly-polarised light.

Experiments are described in which an alkaline solution of copper racemate was exposed in vessels for several days to solar light circularly polarised to right and left respectively. The conditions in this case appear particularly favourable to resolution, because the *d*- and *l*-tartrates absorb right and left rays unequally, and the solutions undergo reduction on exposure to light. The solutions, however, showed no optical activity at the end of the experiment. Among other causes of this failure it is suggested that the solutions may have been too concentrated, and therefore the salt was not sufficiently split up into its *d*- and *l*-components.

The possible mode of formation of optically active substances in nature is briefly discussed.

G. S.

Formation of [Optically] Active Compounds by P. Curie's Method. PHILIPPE A. GUYE and G. DROUGININE (*J. Chim. Phys.*, 1909, 7, 97—100. Compare Curie, *J. Phys.*, 1894, [iii], 3, 641; Cotton, preceding abstract).—Curie has suggested that the formation of one of the optical antipodes ought to be favoured if the chemical change which ordinarily gives rise to a racemic mixture is carried out in a dissymmetric medium constituted by the superposition of a magnetic on an electrostatic field. In order to test this theory, the authors have examined the reaction in which bromine combines with methyl fumarate to form methyl dibromosuccinate, and the analogous reaction

in which bromine combines with methyl cinnamate, but the products showed no sign of optical activity.

The investigation is being continued with more powerful fields.

G. S.

Dispersion of Light in Gases. I. Dispersion of Acetylene and Methane. STANISLAS LORIA (*Bull. Acad. Sci. Cracow*, 1908, 10, 1059—1067).—The refractive indices of methane and acetylene have been measured for a series of wave-lengths by the interferometer method. The methane was prepared from magnesium methyl iodide, and the acetylene from calcium carbide, the primary product being purified by fractional distillation. The values of a and b in the dispersion formula $n - 1 = a(1 + b/\lambda^2)$ are for methane: $a = 0.00042607$, $b = 1.441 \times 10^{-10}$, and for acetylene, $a = 0.00054242$, $b = 1.453 \times 10^{-10}$.

H. M. D.

A New Bunsen Spectroscope for the Investigation of Absorption Spectra of Liquids. OTTO SCHUMM (*Zeitsch. physiol. Chem.*, 1909, 59, 54—56).—The instrument which is described in full, with diagrams, gives sharp results.

W. D. H.

Connexion between Band and Line Spectra of the same Metallic Elements. W. NOEL HARTLEY (*Sci. Trans. Roy. Dubl. Soc.*, 1908, ii, 9, 85—138).—Experiments have been made to ascertain the connexion between the bands and lines which characterise the spectra of certain elements. Calcium spectra were obtained from (1) solid calcium salts ignited in the oxyhydrogen flame, (2) metallic calcium in the flame of a Mecke burner, (3) lime in the same flame, (4) the condensed spark between electrodes of metallic calcium, and (5) the spark, without condenser, taken from solutions. The flame spectra of the elements rubidium, caesium, calcium, strontium, barium, silver, copper, tin, lead, and thallium were obtained when gradually diminishing quantities of salts of the metals were introduced into the oxyhydrogen flame. The quantities were varied by dropping determinate volumes of solutions of known strength on to ashless filter papers, which were then dried and introduced into the flame. The observations lead the author to the conclusion that the banded flame spectra are the spectra of the atoms, and that the monatomic metallic elements, which exhibit two spectra, one of lines and the other of bands, can exist in two different conditions, the difference being due to the larger amount of energy associated with the atom which exhibits a line spectrum. The acquisition of energy by the primitive or normal atom arises from its chemical properties and from the excess of energy, which is transferred to it in the flame or arc, over that which is necessary to liberate the atom from its compounds.

H. M. D.

Spectroscopic Investigation of the Behaviour of Metallic Salts in Flames of Different Temperatures. HERBERT AUERBACH (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1909, 7, 41—66).—The apparatus used in the experiments was described in the first part of the paper (this vol., ii, 105). The author records the spectral lines and bands which were obtained when the alkali and alkaline

earth metals, copper, manganese, iron, nickel, and cobalt in the form of chlorides and thallium and lead in the form of nitrates were introduced into (1) the Bunsen flame, (2) the coal-gas air blow-pipe flame, and (3) the coal-gas oxygen blow-pipe flame. Except in the case of manganese, iron, nickel, and cobalt, all the spectra show an increase in the number of lines and bands as the temperature rises. The increase takes place for the most part towards the ultra-violet end. This indicates that rise of temperature causes a displacement of the energy of emission towards the ultra-violet end of the spectrum. The photographs show lines in the ultra-violet down to $\lambda = 2380$; this result is contradictory to the statement made by Eder and Valenta that flame spectra do not give rise to lines of smaller wave-length than $\lambda = 3000$.

In the third section of the paper the various theories of spectral emission are discussed, and an explanation of the abnormal behaviour of manganese, iron, cobalt, and nickel is given. The chlorides of these metals are volatile in the Bunsen flame, and give rise to spectra without undergoing chemical change. In the coal-gas air blow-pipe flame they are transformed into oxides, which are not sufficiently volatile at this temperature to give rise to emission spectra. In the coal-gas oxygen blow-pipe flame, on the other hand, the oxides are volatile and emission spectra are observed, which, however, differ somewhat from the Bunsen flame spectra.

H. M. D.

Normal Lines from the Arc Spectrum of Iron in the Definite System of Rowland. JOHANNES HARTMANN (*Physikal. Zeitsch.*, 1909, 10, 121—124).—A plea for the retention of Rowland's system as the basis of wave-length measurements of spectral lines. Although the absolute value given by Rowland for the standard red line of cadmium has been shown by recent measurements to be inexact, it is maintained that this is not sufficient to warrant a change in the basis of the vast collection of wave-length data. The author has recalculated the data recently obtained by Buisson, Fabry and Perot, Eversheim and Pfund, and these are recorded in the definite Rowland system for which the red cadmium line has the value $\lambda = 6438.7098$.

H. M. D.

Dissymmetrical Separations in the Zeeman Effect in Tungsten and Molybdenum. ROBERT JACK (*Proc. Roy. Soc. Edin.*, 1909, 29, 75—83).—The spark spectra of salts of the metals in question were used, and the light of the spark was focussed on the slit of the grating apparatus by means of a quartz lens. The wave-length, distance from middle component, and intensity of many lines are quoted, and it is shown that cases both of normal and abnormal asymmetry occur, that is, the middle component of the triplet may be nearer the component towards the red or violet end of the spectrum respectively. It appears that there is some connexion between the rotation of the plane of polarisation produced by the quartz and the type of dissymmetry, but this rule does not hold in all cases.

The theory of the subject has been developed by Voigt on the

assumption that besides coupling between electrons of the same vibration frequency, couplings between electrons of different frequencies may also occur.
G. S.

Radiation of Various Spectral Lines of Neon, Helium, and Sodium in a Magnetic Field. JOHN E. PURVIS (*Proc. Camb. Phil. Soc.*, 1909, 15, 45—52).—Measurements have been made of the constituents of various spectral lines of neon, helium, and sodium, using a Rowland grating and field strengths of 24000 and 26100 units. The author finds far fewer constituents than were obtained by Lohmann, who used an echelon of 32 plates and a field of 11000 units, and, in connexion with this, points out the great difficulty in distinguishing the real constituents of a divided line from those of the adjacent images of other orders when an echelon grating is used for the observations. The distances between the constituents of several triplets and the sextriplet ($\lambda=6383$) are recorded. The shifts of the constituents of various neon lines towards the red end of the spectrum under the influence of the magnetic field have also been measured; the amounts of the shifts are different for different lines. The intensities of the unaltered lines were found to be less than those of the strongest constituents when the neon was subjected to the action of the magnetic field.
H. M. D.

Question in Absorption Spectroscopy. ROBERT A. HOUSTON and ALEXANDER S. RUSSELL (*Proc. Roy. Soc. Edin.*, 1909, 29, 68—74).—The question whether on mixing two coloured solutions which do not act on one another chemically the absorption spectrum of the components remains unchanged has been investigated. The measurements were made with a special form of spectrophotometer, provided with two slits, one vertically above the other, and the instrument could also be used as a spectroscope. The arrangement was such that the absorption effect when the light passed through the two solutions in succession could be compared with that observed when it passed through the mixed solutions.

For certain salt solutions no effect was observed, but in the case of mixtures of uranyl nitrate with copper sulphate and with nickel sulphate a shifting of certain bands on mixing is observed, and it is shown that this is due to chemical action. There appears to be a slight shifting when a solution of copper sulphate is mixed with an ammoniacal solution of carmine, but there is no evidence as to whether it is physical or chemical. Formánek (*Zeitsch. Farb. Text. Chem.*, 1902, 1, 505) has stated that on mixing solutions of certain dyes there is a displacement of certain bands, but the authors find by the spectroscopic method no displacement or any alteration of intensity in four of the cases investigated by Formánek. No well-defined case of a physical action between molecules has therefore been observed.
G. S.

Selective Reflection and Molecular Weight of Minerals. W. W. COBLENTZ (*Jahrb. Radioaktiv. Elektronik*, 1907, 4, 132—136).—As a result of the examination of the absorption and reflection spectra of the sulphates and carbonates of magnesium, calcium,

strontium, barium, and lead, it has been found that the maxima of the characteristic bands are displaced towards the red end of the spectrum as the atomic weight of the metallic element increases. When the maxima of the bands are plotted as a function of the atomic weight, the points corresponding with the metals in the above series lie approximately in a straight line.

H. M. D.

Decline of Low-temperature Phosphorescence. JOSEPH DE KOWALSKI (*Compt. rend.*, 1909, 148, 280—282).—The phosphorescence exhibited by certain organic compounds which have been subjected to a strong light at the temperature of liquid air quickly dies out on removing the source of illumination. In the case of the alcoholic solutions of benzene and its derivatives which the author has examined, the phosphorescence extends in an unbroken spectrum from the violet end more or less towards the red, except in the case of coloured substances, which exhibit the usual absorption bands. On removing the source of light, the longer wave-lengths of the phosphorescence spectrum decay much more quickly than the shorter wave-lengths. Thus, in the case of alcoholic aniline, orange persisted three seconds, green twenty-seven seconds, and violet fifty seconds. It is possible that a particular wave-length in the ultra-violet would exhibit a maximum of persistence.

R. J. C.

Colour of Fluorescence and Solvent. HANS STOBBE (*Ber.*, 1909, 42, 790—797).—An investigation on the influence of the solvent on the colour and intensity of the fluorescence of 1-phenylnaphthalene-2:3-dicarboxylic anhydride.

A detailed description and sketch of the apparatus employed to observe the fluorescence of the solutions is given.

The behaviour of eighty-five solvents was investigated, and the following results obtained: (1) Solutions of the anhydride in alkyl iodides, ethers, and esters are not fluorescent. (2) Solutions in aliphatic hydrocarbons, alcohols, and acids exhibit a slight blue fluorescence. (3) The fluorescence is far more intense in brominated and chlorinated solvents, and is either dark blue or violet. Solutions in chlorinated solvents, as a rule, have an intense violet fluorescence. (4) A relationship between the dielectric constant of the solvent and the intensity of the fluorescence does not exist.

The author suggests that the change in the colour of the fluorescence is probably connected with the formation of molecular complexes, produced by the combination of the anhydride with the chlorinated or brominated solvent through the agency of the residual affinities of the halogen and anhydride.

W. H. G.

Influence of Impurities on the Photo-electric Effect in Liquids. EUGÈNE BLOCH (*Compt. rend.*, 1909, 148, 621—622).—Water and aqueous solutions of sodium chloride, potassium chloride, and potassium nitrate have been examined for the Hertz-Hallwachs photo-electric effect. The positive result which is obtained when the liquids are illuminated by sparks passing between aluminium electrodes, or by a mercury arc light in a quartz vessel, has been

traced to the presence of impurities. If the surface of the liquid is perfectly clean, neither water nor the aqueous solutions show the photo-electric effect.

It is suggested that the electrical conductivity of the atmosphere is in part due to the photo-electric action of solar rays on the earth.

H. M. D.

Photo-electric and Actino-dielectric Action in the Phosphorescence of the Alkaline Earth Sulphides. PHILIPP LENARD and SEM SAELAND (*Ann. Physik*, 1909, [iv], 28, 476—502).—The electrical phenomena which are observed when the sulphides of the alkaline earth metals are exposed to light have been examined in detail. It is found that the photo-electric action is intimately connected with the phosphorescence of the sulphides and is localised in certain centres which are also the centres of light emission. The excitation of a phosphorescent substance by light or cathode rays is supposed to consist in the polarisation of these emission centres. The centres are characterised by the presence of the metallic "impurity," and the polarisation consists in the loss of electrons from the atoms of the foreign metal. The phosphorescence which follows the excitation is a result of the recombination of the electrons with the metal.

What is termed actino-dielectric action is observed when the phosphorescent substance is exposed to red light while under the influence of an electric field. It is attributed to a displacement of ions under the influence of light and is not characteristic of phosphorescent substances.

H. M. D.

Calculation of Photochemical Reactions. CHR. WINTHER (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1909, 7, 66—70).—Two equations have been deduced to express the velocity of a non-reversible photochemical change, one on the assumption that the velocity is proportional to the intensity of the light at each point of the reacting system, the other on the assumption that the velocity is proportional to the light absorbed. The author compares the two equations, and shows that they are identical in the case where the photochemical change is unimolecular. The changes investigated experimentally up to the present are unimolecular; it is therefore impossible to decide whether the velocity is determined by the absorbed light or not.

H. M. D.

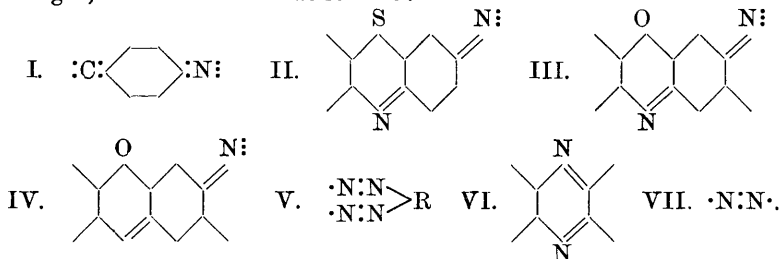
Colloidal Symbiosis. RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 63—64).—A discussion of the difference in the behaviour of silver bromide dry plates on developing. The greater readiness with which large molecular complexes of silver bromide are developed in comparison with small molecular complexes is examined in the light of two theories. A comparison is made between the granules of silver bromide in a photographic plate and the cells of a living organism. The fact that the protoplasmic molecular aggregates of a cell respond as a whole to the action of many chemical reagents is further supposed to be analogous to the response of complex granules of bromide to the action of the developer. This analogy leads to the conception of a colloidal symbiosis.

H. M. D.

Retarding Action of Bromides in Photographic Developers as a Colloido-chemical Process. LUPPO-CRAMER (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 92—94).—The addition of soluble bromides to the developer in order to reduce the effect of over-exposure has been found to have a considerable influence on the character of the reduced silver. If large quantities of bromide are present, the velocity of the developing process is greatly reduced, and instead of the ordinary black silver gel, a light grey-coloured form of silver is obtained. The adsorption capacity of the grey silver is very much less than that of the black variety, and this difference shows itself in the behaviour of the two forms towards ammonium persulphate when this is employed to reduce intensities. The grey silver is acted on much more quickly than the black. This has been shown by parallel experiments with two negatives, one of which was developed without addition of bromide, whilst the other was first over-exposed and then developed with the addition of bromide to counteract the effect of the over-exposure.

H. M. D.

Relation between the Constitution of Dyes and their Sensitiveness to Light. KURT GEBHARD (*Zeitsch. angew. Chem.*, 1909, 22, 433—435).—The sensitiveness of a dye to light stands in close relation to the presence of definite groups in the molecule. An examination of about sixty dyes in aqueous solution leads to the conclusion that these groups, arranged in the order of increasing stability to light, can be tabulated as follows:



The chief factor in causing sensitiveness to light appears to be quinonoid structure; a comparison of I. and IV. shows, however, that the stability is increased when one of the groupings, $\cdot\text{C}:\text{C}\cdot$, forms part of a ring. Dyes, such as Martius' Yellow, containing single linkings, are particularly stable to light.

The presence of substituents is also of great importance in determining the sensitiveness of a dye to light. These substituents have either an accelerating or a retarding influence. The most important accelerator is the hydroxyl group, its influence being well illustrated by the increasing sensitiveness of the series: Alizarin-blue-R, Alizarin-orange, Purpurin, and Alizarin-indigo-blue-J; it appears, however, that the hydroxyl groups must all be in the same benzene nucleus, Alizarin-SX, for example, being more stable to light than the isomeric Purpurin. Another important accelerator is the substituted, and particularly the monosubstituted, amino-group; Rhodamine-B and Rhodamine-G differ only in that the former contains a diethylamino-

group where the latter has an ethylamino-group. The latter is the more sensitive to light.

Of substituents exerting a retarding influence, the hydrogen ion is the most important. Gallein, as the acid, is more stable to light than its salts, whilst in Diamond-yellow and Diamond-flavine the retarding influence of the hydrogen ion overpowers the accelerating influence of the hydroxyl group. The sulphate, bromine, and chlorine ions also exert a retarding influence to the action of light, which is well seen in the great stability of Victoria-green as against that of Malachite-green.

Dyes which contain accelerating substituents become more stable by the introduction of retarding groups, and vice versa. Instances of the first case are Victoria-green and Malachite-green, Rose-Bengal and Tetraiodofluorescein, Rhodamine-B and Rhodamine G; an example of the second case is Methyl-violet, which, by the introduction of the methyl group, becomes more sensitive to light than Malachite-green.

C. S.

Charges on Ions produced by Radium. C. E. HASELFOOT (*Proc. Roy. Soc.*, 1909, *A*, 82, 18—22).—Townsend has described a method for the direct determination of N_e , where N is the number of molecules in 1 c.c. of a gas at normal temperature and pressure and e the charge on an ion, and has shown that the positive ions produced by secondary Röntgen rays have in some cases a single and in others a double atomic charge, whereas the charge on the negative ions is always the same. The same method has been applied by the author to the ions produced by radium. Observations under different conditions lead to the conclusion that the positive and negative ions have the same electric charge. As in the case of the ions produced by Röntgen rays, it was found that the negative ions produced by radium do not obey the simple laws of diffusion when the air is very dry.

H. M. D.

Atmospheric Radiation of High Penetrating Power. THEODOR WULF (*Physikal. Zeitsch.*, 1909, 10, 152—157).—The results of observations of the diurnal variation of intensity of the penetrating atmospheric radiation are communicated. During October, 1908, the hourly measurements showed two maxima and two minima. In November the mid-day minimum disappeared, and in December no periodicity could be detected. The observations indicate a complete parallelism between the variation of the air potential and that of the γ -radiation.

Comparative measurements in the chalk mines of Valkenburg (15 metres below the surface) gave values for the intensity of the γ -radiation which were on the average 42% smaller than those obtained at the surface.

H. M. D.

Penetrating Radiation. DOMENICO PACINI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 123—129).—A cylinder of polished zinc was used as recipient for the air, the internal electrode being a copper cylinder. The apparatus was established in the Apennines at a height

of 1090 metres in August and September. The minimum value found for the ionisation of the air was 6.3 ions per c.c. per second. The minimum value found by McLennan in Toronto (Abstr., 1908, ii, 648) was 6.0. The ionisation has a double diurnal period. The conclusion is drawn that the source of the penetrating radiation capable of ionising the air inside a metallic cylinder is not in the soil.

C. H. D.

Distribution of the Radiation of Radioactive Substances. HEINRICH GREINACHER (*Physikal. Zeitsch.*, 1909, 10, 145—152).—The author has already shown (compare Abstr., 1908, ii, 551) that the radiation from plane geometrical figures, cut from hardened masses of uranium compounds, shows a peculiar distribution. A similar distribution is observed if prismatic figures of a phosphorescing substance are brought into contact with a photographic plate. By comparison of the images yielded by a solid prism of gypsum mixed with phosphorescent paint and by an aluminium prism coated superficially with the phosphorescent material, it has been found that the "angle effect" is due to rays which proceed from the interior of the active substance.

The same angle effects are obtained when a radium preparation is enclosed in a cube of lead placed in contact with a sensitive plate. They are also produced when radium, enclosed in a cylinder of lead sufficiently thick to cut off the α - and β -rays, is brought up close behind a photographic plate in front of which a cube of lead is placed. In these circumstances, the action must be due to the secondary rays generated in the lead by the primary γ -rays from the radium. Whether the "angle effect" is, in general, due to primary or secondary rays cannot be decided, but a mathematical consideration indicates that the peculiar distribution is essentially due to the operation of Lambert's cosine law.

H. M. D.

Radioactivity and Pleochroic Halos. OTTO MÜGGE (*Centr. Min.*, 1909, 65—71, 113—120, 142—148).—The radiations of radium produce changes in the optical characters of certain minerals similar to those observed in the pleochroic halos. A detailed description is given of pleochroic halos seen in several minerals (cordierite, biotite, etc.), these halos occurring around enclosed grains of zircon, orthite, etc. The effects produced by radium bromide placed in contact with various rock-forming minerals for periods extending over several months are recorded. The most sensitive mineral is rock-salt: after three days there is a marked change in colour, and after fourteen days a dark brownish-yellow spot is produced; on heating, this spot passes through a series of colours, and finally the colour disappears. Cordierite is also readily affected, with a change in the colour and pleochroism and a diminution in the strength of the double refraction. Finally, the photographic activity of some radioactive minerals (zircon, orthite, thorite, thorianite, etc.), namely, those minerals around which pleochroic halos occur in nature) was compared with the activity of uranium and of radium bromide.

L. J. S.

Comparison of the Radium Emanation Spectra Obtained by Different Observers. T. ROYDS (*Proc. Roy. Soc.*, 1909, *A*, 82, 22—25. Compare this vol., ii, 206; Rutherford and Roysds, *Abstr.*, 1908, ii, 787; Cameron and Ramsay, 1908, ii, 786).—A comparison of the author's table of the spectral lines of radium emanation with that of Ramsay and Cameron shows that there are differences which are too large to be explained as errors in measurement or variations of intensity due to impurities. After eliminating the well-marked emanation lines, the spectrum of Cameron and Ramsay is found to be almost identical with the xenon spectrum obtained by the discharge from a Leyden jar with spark gap. The author draws the conclusion that the emanation examined by these observers was contaminated with xenon.
H. M. D.

Measurements of the Active Emanation of Sea-Water from the Atlantic Ocean. W. KNOCH (*Physikal. Zeitsch.*, 1909, 10, 157—158).—During the course of a voyage across the Atlantic, twelve measurements of the amount of emanation in sea-water were made. Except in one instance, a positive result was obtained, the average activity of the samples being equal to 0.1 Mache unit.
H. M. D.

Relative Ionisation Produced by Röntgen Rays in Different Gases. J. ARNOLD CROWTHER (*Proc. Camb. Phil. Soc.*, 1909, 15, 38—39).—A comparison has been made of the ionisation effects produced by "soft" and "hard" Röntgen rays in passing through various gases and vapours. The beam of rays was passed between two parallel plate electrodes, care being taken to prevent any portion of the beam falling on either electrode so as to eliminate secondary radiation effects.

Compared with air as a standard, methyl iodide, methyl acetate, and carbon dioxide show a decrease in the relative ionisation on passing from soft to hard rays; hydrogen and ethyl bromide show an increase, whilst the relative ionisation in the case of ethyl chloride and carbon tetrachloride remains nearly constant.

For the very soft rays used in the author's experiments, the ionisation in hydrogen is only 1% of that in air at the same pressure.

H. M. D.

Secondary Radiation Excited by γ -Rays. F. E. HACKETT (*Sci. Trans. Roy. Dubl. Soc.*, 1909, 9, 201—218).— γ -Rays from radium bromide were allowed to fall at an angle of 45° on the lower surface of plates of different metals, and the intensity of the secondary rays, emitted from the upper surface of the plate in the plane of incidence and in a direction at right angles to the incident γ -rays, was measured by means of an ionisation chamber. The secondary radiation measured in this way is nearly constant for metals the atomic weight of which lie between 27 and 120; it is greater for tungsten, gold, platinum, mercury, lead, and bismuth, and still greater for uranium. The experimental numbers indicate that the secondary radiation per atom is approximately proportional to the atomic weight when this is less than 120, but increases more rapidly than the atomic weight when

this exceeds 120. The hardness of the secondary rays diminishes with increase of atomic weight for soft γ -rays, but increases for hard γ -rays. For metals of low atomic weight the penetrating power of the secondary rays is nearly independent of the hardness of the primary rays; on the other hand, for metals of high atomic weight the hardness of the secondary rays changes in a corresponding manner with that of the primary rays. H. M. D.

Slow Cathode Rays. O. VON BAEYER (*Physikal. Zeitsch.*, 1909, 10, 168—176).—The properties of the slowly moving cathode rays which are emitted by a glowing Wehnelt cathode have been examined. Experiments were made to determine the velocity and the ionising power of the rays. When the rays come into contact with metal surfaces, they give rise to a diffuse secondary radiation. H. M. D.

The Influence of Cathodic on Canal Rays. JEAN BECQUEREL (*Le Radium*, 1908, 5, 329—330).—Partly polemical in reply to Bestelmeyer (*Abstr.*, 1908, ii, 799). The author again refers to his observation that the canal rays are affected by the electrical charges carried to the walls of the tube by the cathode rays, and are thus displaced to a certain limited extent in the same sense as the latter. G. T. M.

Existence of Positive Electrons in Vacuum Tubes. A. DUFOUR (*Compt. rend.*, 1909, 148, 622—625).—Further experiments are described which confirm the author's view that the beam of rays examined by Becquerel (compare *ibid.*, 546) is a secondary beam which has its origin in the canal rays. The experimental arrangement adopted by the author agrees so closely with that used by Becquerel that there can be no doubt that the rays examined in the two series of experiments are identical. H. M. D.

A New Radioactive Product of the Uranium Series. JACQUES DANNE (*Compt. rend.*, 1909, 148, 337—339).—In the course of preparing a quantity of uranium-*X*, a new substance has been isolated intermediate between uranium and uranium-*X*; it is the immediate parent of the latter. This substance, *radiouranium*, is less active than uranium when fresh, but gradually increases to a maximum activity 3.35 times that of uranium in forty-four days. At the end of this time some uranium-*X* can be separated from it, when its activity falls again to the initial low value.

In order to separate radiouranium from uranium and uranium-*X*, the mixed active nitrates from 22 kilos. of uranium nitrate were treated with acetone to dissolve uranium nitrate and then with freshly precipitated ferric oxide in acetone to absorb uranium-*X* nitrate. The insoluble residue of radiouranium nitrate, calcined and converted into chloride, weighed 0.4 gram, whereas the uranium-*X* chloride obtained weighed 0.5 gram. The former was half and the latter sixty-three times as active as uranium. R. J. C.

Radioactivity of Rubidium. NORMAN CAMPBELL (*Proc. Camb. Phil. Soc.*, 1909, 15, 11—12).—With the object of comparing the

radioactivities of potassium and rubidium, the author has made measurements of the ionisation produced by layers of finely powdered rubidium sulphate of different thicknesses. The rubidium sulphate was specially prepared by Kahlbaum.

Denoting by α the ionising power of the total radiation from one gram of the substance when the whole of the radiation is absorbed in air, the author calculates for the two metals: potassium, $\alpha = 2.003 \pm 0.0376$; rubidium, $\alpha = 14.47 \pm 0.365$. On the other hand, the values of λ/ρ (where λ is the coefficient of absorption of the material for the rays it emits and ρ is the density of the material) for the metals are: potassium, $\lambda/\rho = 8.23 \pm 0.1$; rubidium, $\lambda/\rho = 53.2 \pm 2.1$.

From this it follows that, although for infinitely thick layers the activity for potassium is slightly greater than for rubidium, the intrinsic activity of the latter is at least seven times as great as that of the former.

H. M. D.

Electrical Condition of Gases in the Nascent State. J. A. CUNNINGHAM and SATISH CHANDRA MUKERJI (*Jahrb. Radioaktiv. Elektronik*, 1907, 4, 370—375).—The electrical condition of the oxygen evolved by heating various oxygen compounds has been investigated. The oxygen, generated by heating the substances in a hard glass tube, was made to pass through a cylinder along the axis of which an insulated rod was supported, this being connected with one of the pairs of a quadrant electrometer. The rod and the inside of the cylinder were silver plated, and the cylinder was connected with one or other of the poles of a battery of 280 volts. From the movements of the electrometer needle, the approximate number of ions per c.c. of gas has been calculated. The conductivity of the oxygen depends on the substance from which it is evolved, and diminishes in the series: potassium chlorate, potassium perchlorate, potassium permanganate, sodium peroxide, mercuric oxide. In the case of potassium chlorate and sodium peroxide the conductivity of the oxygen was found to vary according as the cylinder was positively or negatively charged.

H. M. D.

Conduction of Electricity. JOHANN KOENIGSBERGER (*Zeitsch. Elektrochem.*, 1909, 15, 97—105).—Metallic conductivity is distinguished from electrolytic conductivity by (1) absence of products of electrolysis; many metallic oxides and sulphides conduct electricity without decomposition. (2) Absence of polarisation. Pure adularia, KAlSi_3O_8 , at temperatures below 1070° exhibits an apparent polarisation of a few millivolts, but this is shown to be of thermoelectric origin, due to differences of temperature at the junctions produced by the Peltier effect. A true electrolyte, such as solid barium sulphate, gives a polarisation of more than 1 volt. (3) From Nernst's law of partition it appears probable that a substance which dissolves (without decomposition) in water to a solution containing ions will be an electrolytic conductor in the solid state. (4) The resistance of a pure solid conductor has a minimum value at some temperature, whereas the resistance of a solid electrolyte always diminishes as the temperature rises. (5) Electrolytic conductors exhibit selective

absorption and emission in the ultra-violet and infra-red, whereas with metallic conductors the absorption and emission are continuous.

The resistance, w , of a metallic conductor at t° is given by the expression: $w_0(1 + at \pm \beta t^2)e^{-q \frac{t}{(t+273)(273)}}$, where w_0 is the resistance at 0° , a and β the temperature-coefficients of pure metals, 0.003 and 0.000002 respectively, and q is one-half of the heat of dissociation of a negative electron. In addition to the oxides and sulphides of many metals, cuprous iodide and a number of silicates at temperatures below 1000° exhibit metallic conductivity. The effect of impurities in diminishing the conductivity is much smaller for substances with a large value of q than for those with a small value.

The heat evolved by the combination of a negative electron with a gram-atom of an element is evaluated approximately. For the alkali metals it is under 50, for the alkaline earth metals under 100, for hydrogen greater than 500, for graphite 700, silicon 600, titanium 300, zirconium 100, boron 100, aluminium less than 40, and for most of the remaining metals under 20; the electronegative elements, nitrogen, chlorine, etc., have very large values, probably larger than 10,000. The values for some sulphides and oxides are also given. T. E.

Electro-capillary Action and Discharge in Rarefied Gases. G. REBOUL (*Compt. rend.*, 1909, 148, 617—618).—Experiments are described which show that the formation of drops of mercury in an exhausted tube facilitates electrical discharge. The apparatus used consisted of a tube provided with two electrodes, the upper one being an ordinary disk electrode, the lower one a nickel tube perforated at its upper extremity by a small hole at which drops of mercury could be formed. The two electrodes were connected by a battery of accumulators.

When the potential difference is approximately equal to that required for discharge, it is found that the formation of the drops of mercury facilitates the discharge whether the mercury is positively or negatively charged. If the mercury is negatively charged, the formation of the mercury drops permits disruptive discharge to take place when the potential difference is 10 or 20 volts lower than that required for the discharge under ordinary conditions. It is supposed that the drop formation is accompanied by the liberation of ions, and the greater effect observed when the mercury is negatively charged is attributed to the greater mobility of the negative ions. The variation in the superficial area of the drops may also diminish the difference of potential at the air-mercury surface, and this action appears to be the dominant one at low pressures. If, when the pressure is sufficiently low, the phosphorescent stage has been reached, the formation of drops at the cathode inhibits the phosphorescence effect. H. M. D.

Carriers of the Positive Charges of Electricity Emitted by Hot Wires. SIR JOSEPH J. THOMSON (*Proc. Camb. Phil. Soc.*, 1909, 15, 64).—The value of e/m has been determined for the positively charged particles emitted by a heated strip of platinum wire which had been

kept for several days in a high vacuum and heated repeatedly to incandescence. The number obtained shows that the mass of the particles was about twenty-seven times the mass of a hydrogen atom. The gas given off by the hot wire after prolonged heating gave a bright carbon monoxide spectrum, whilst that of nitrogen could not be detected. From this observation the author draws the conclusion that the carriers of the positive electricity are carbon monoxide molecules.

After heating the platinum to a red heat in an atmosphere of hydrogen, the value of e/m showed that the average mass of the carriers was only eight or nine times that of the hydrogen atom. This is in agreement with the view that the carriers of the positive electricity given out by hot metals are, for the most part, the molecules of gas absorbed by the metal.

H. M. D.

Tables of Molecular Conductivities. PHILIP BLACKMAN (*J. Physical Chem.*, 1909, 13, 144—153).—Tables are given of the molecular conductivities of a large number of salts at 18° and 25°, calculated by the method already described (*Abstr.*, 1906, ii, 647).

G. S.

Piezochemical Studies. ERNST COHEN and L. R. SINNIGE (*Zeitsch. Elektrochem.*, 1909, 15, 76—77).—The increase of $E.M.F.$ of a galvanic cell with the pressure (at constant temperature) $(dE/d\pi)\tau$ has been shown by Willard Gibbs to be equal to $-(dV/de)\tau$, where dV is the change of volume of the cell due to the passage of a quantity of electricity, de .

For the cell $\text{Cd} \mid \text{CdSO}_4 \text{ solution} \mid 12.5\% \text{Cd amalgam}$ the quantity dV/de is a constant; the authors find that $dE/d\pi$ is constant, and equal to 0.0000196 volt per atmosphere between 0 and 1000 atmospheres.

The authors show further that it is possible to determine the effect of pressure on the solubility of a salt by measuring the effect of pressure on the $E.M.F.$ of cells containing electrodes reversible with respect to the anion and cation of the salt and a saturated solution of the salt, in one case with the solid salt, in the other case without it. The experimental results are reserved for a later communication.

T. E.

Calculation of Electromotive Forces from Thermal Data. WALTHER NERNST (*Sitzungsber. K. Akad. Wiss. Berlin*, 1909, 247—267).—In a previous paper (*Abstr.*, 1907, ii, 153), the author has deduced the following expressions for condensed systems: $Q = Q_0 + \beta T^2 + \gamma T^3 + \dots$ (1) and $A = Q_0 - \beta T^2 - \gamma/2 T^3$ (2), where Q represents the heat of reaction and A the available energy. β and γ are constant for any one system, and can be calculated by means of the equation $dQ/dT = C_1 - C_2 = 2\beta T + 3\gamma T^2 + \dots$, where $C_1 - C_2$ represents the difference of the heat capacity before and after the transformation of one gram-equivalent. At temperatures not too far from the absolute zero, A is approximately equal to Q , and therefore the $E.M.F.$ of a galvanic combination may be calculated from purely thermal data as follows. The thermal data obtained at the ordinary temperature are extra-

polated to as low a temperature as possible, then the *E.M.F.*, *E*, is calculated from the value of *Q* by means of the equation $Q = A = FE$, where $E = Q/23,046$, when the *E.M.F.* is expressed in volts. Then, by means of equation (2) above, the value of the *E.M.F.* is calculated for any required temperature and compared with the experimental value.

The theory is tested by application to a number of reactions, including some in which gases are concerned, and it is shown that, in general, there is good agreement between the observed and calculated values of *E*. The equations do not apply in the first instances to gas elements, but it is shown that the *E.M.F.* of the latter may be calculated from thermal and vapour-pressure data. G. S.

Asymmetry due to the Passage of a Continuous Current through a Chain of Aqueous Solutions of Electrolytes with a Common Ion. M. CHANOT (*Compt. rend.*, 1909, 148, 618—621).—The author has examined the potential differences which are set up at the liquid interfaces when a continuous current is passed through a series of solutions arranged according to the scheme $MR \mid M'R' \mid MR$. The potential differences, which are opposite in sign, are due to the changes in concentration which are brought about by the electrolytic conduction. When the two different solutions contain a common anion, the middle electrolyte increases in concentration at the surface at which the current enters, and at the opposite surface if the solutions contain a common cation. H. M. D.

Heat of Ionisation and the Ionisation Constant of Water. ADOLF HEYDWEILLER (*Ann. Physik*, 1909, [iv], 28, 503—512).—The new data for the mobilities of the hydrogen and hydroxyl ions and for the influence of temperature on the mobility of these ions as well as on the heat of neutralisation and on the electrical conductivity of solutions of acids, bases, and salts have been utilised for a recalculation of the heat of ionisation of water and of the ionisation constant.

The heat of ionisation (*s*) and its variation with the temperature (*t*) is given by the equation $s = 14617 - 48.5t$. This agrees very well with the equation recently obtained by Noyes. The quantity of ionised water in 1 c.c. of the liquid at different temperatures is given by $\log \alpha = 30.2339 - 3047.3/T - 12.125 \log T$. For the ionisation constant $K_w = (\alpha')^2/1 - \alpha'$, in which $\alpha' = 1000\alpha$, the following values have been calculated.

Temperature	0°	10°	18°	25°	50°	100°	150°	200°
$K_w - 10^{14}$	0.116	0.281	0.59	1.04	5.66	58.2	234	525

These are about 25% larger than the values obtained by Noyes.

H. M. D.

Reducing Action of Electrolytic Hydrogen on Arsenious and Arsenic Acids when Liberated from the Surface of Different Elements. WILLIAM THOMSON (*Proc. Roy. Soc. Edin.*, 1909, 29, 84—95).—The apparatus used has already been described (*Abstr.*, 1904, ii, 777). Thirteen different elements were used as cathodes, and the order of their efficiency in removing arsenious acid

from solution as arsenic trihydride is as follows : lead, zinc, cadmium, tin, silver, graphite, iron, platinum, aluminium, gold, cobalt, nickel, and palladium. The order for the removal of arsenic acid is not quite the same. These results disprove the suggestion of Chapman and Law (Abstr., 1906, ii, 196) that the efficiency of hydrogen with respect to arsenious and arsenic oxides depends largely on the supertension of the cathode. For example, silver, with a very low supertension, liberates arsenic as the trihydride from arsenious acid with about the same velocity as lead or zinc, which have very high supertensions. Further, palladium, which has a comparatively high supertension, is at the bottom of the series as regards efficiency in decomposing either arsenious or arsenic acids.

The rate at which arsenic is removed from solution in the presence of the different metals has also been determined, and the results are given in tables and curves. In the case of lead, zinc, cadmium, tin, and silver, the reduction proceeds as a unimolecular reaction when arsenious acid is employed. G. S.

Migration Constants of Dilute Solutions of Hydrochloric Acid. C. CHITTOCK (*Proc. Camb. Phil. Soc.*, 1909, 15, 55—63).—The experiments were undertaken with the object of throwing light on the cause of the abnormally low electrical conductivity of very dilute aqueous solutions of strong acids and bases. The apparatus used was so arranged that a comparatively small volume of the solution in the neighbourhood of each electrode could be separated from the rest. This volume of solution was large enough to contain the whole region in which any change of concentration had taken place, and, after stirring to obtain homogeneity, the concentration of the electrode solutions was ascertained by measuring the electrical conductivity by means of two subsidiary electrodes. In all the experiments the electrolysing current was kept small enough to prevent any evolution of chlorine at the anode.

The transport ratio of the chlorine ion was found to increase from 0.171 at a concentration of 0.001405 equivalent per litre to 0.275 at a concentration of 0.0001006. The change in the migration constant is much greater than that which was observed by Whetham and Paine in the case of dilute solutions of sulphuric acid.

The author concludes that the change is too great to be explained by a decrease in the mobility of the hydrogen ion. On the other hand, if the water used as solvent contained a trace of ammonia, the observed results may probably be explained, for the effect of the presence of ammonia would be to replace the hydrogen ion by the much less mobile ammonium ion, the extent of the replacement increasing with the dilution. H. M. D.

Electrolysis of Alkali Chlorides. Electrical Conductivities, Densities, and Specific Heats of Solutions of Potassium Chloride and of Potassium Hydroxide. ADRIEN JAQUEROD (*J. Chim. Phys.*, 1909, 7, 129—151).—The electrical conductivities and densities of solutions of potassium chloride containing 70.4, 140.8, 211.2, and 281.6 grams of the salt per litre, of solutions containing

about 50, 100, 150, and 200 grams of potassium hydroxide per litre and of solutions containing mixtures of these salts in varying proportions, have been measured at intervals of temperatures from 20° to 80°. Specific heat measurements with the same solutions were made at room temperature.

The conductivity measurements were made by Kohlrausch's method, and the results are given in tabular form. The results of the measurements of the density of solutions containing known amounts of potassium chloride and of potassium hydroxide are represented at temperatures from 20° to 80° by means of the formula

$$\alpha_t = \frac{0.9957 + 0.000616P_{\text{KCl}} - 0.00000013P^2_{\text{KCl}} + 0.000855P_{\text{KOH}} - 0.00000038P^2_{\text{KOH}}}{1 + 0.00045(t - 30)}$$

where P represents the weight of solute in grams per litre at room temperature.

The measurements of specific heat were made in a silver calorimeter by dropping a ball of silver warmed to 100° into the solution in question. The results for potassium chloride are represented by the formula $C = 1 - 0.001264p + 0.00000111p^2$, and those for the hydroxide by the analogous formula $C = 1 - 0.00142p + 0.0000021p^2$, where p represents the concentration of the solution in grams per litre.

G. S.

Influence of Foreign Substances on the Thermo-electric Properties and the Resistivity of Aluminium. H. PÉCHEUX (*Compt. rend.*, 1909, 148, 627—628).—The thermo-electric properties and the resistivity of three samples of commercial aluminium containing small quantities of iron, silicon, and carbon have been examined. The thermo-electric force of the aluminium copper couple is diminished by the presence of small quantities of iron and silicon in the aluminium. The variation of the *E.M.F.* with the temperature corresponds approximately with a parabolic curve.

The resistance measurements indicate that the resistivity of aluminium is increased by the presence of small quantities of iron and aluminium, and that the temperature-coefficient of the resistivity increases as the proportion of impurities increases. H. M. D.

Magnetic Properties of Several Easily Liquefied Gases. P. PASCAL (*Compt. rend.*, 1909, 148, 413—415).—The magnetic susceptibilities of a number of liquefied gases were determined by observing the difference in level when one arm of the quartz U-tube containing the liquid was placed in a powerful magnetic field. The values obtained were: SO_2 , $-2.97.10^{-7}$; NH_3 , $-11.15.10^{-7}$; C_2N_2 , $-4.32.10^{-7}$; N_2O_3 , $-3.03.10^{-7}$; N_2O_4 , $-2.75.10^{-7}$; $\text{CH}_3\cdot\text{NH}_2$, $-9.06.10^{-7}$; CH_3Cl , $-6.67.10^{-7}$; Cl_2 , $-5.90.10^{-7}$.

It was assumed that molecular susceptibility, like rotatory power, is the same in liquid and gaseous states, and the magnetic susceptibilities of the gases at 0° and 760 mm. were calculated. They are all of the order 10^{-9} .

The molecular susceptibility (susceptibility \times molecular weight) of the various gases is roughly a linear function of the number of

atoms in the molecule ; thus magnetic susceptibility appears to follow a law similar to that of Dulong and Petit for specific heats.

R. J. C.

Determination of Melting Points. SIDNEY W. BUNKER (*Pharm. J.*, 1909, [iv], 28, 324).—In order more readily to determine the melting point of substances which are not easily introduced into a narrow tube—for instance, benzoic acid and, more especially, waxes—the following apparatus has been devised. Fig. 1 represents in section the receptacle for the substance the m. p. of which is to be determined.

a is a brass ring, upon which rests a rubber washer, *b*, and then comes a $\frac{3}{4}$ " circular, microscopic cover-glass, *c*, which is separated from a second cover-glass, *e*, by a platinum disk, *d*. In the centre of this platinum disk a hole is cut, in which is placed the substance to be examined, and above the second cover-glass, *e*, a rubber washer, *f*, is placed. These all rest on the flange of *a*; the brass top, *g*, is then screwed down tightly to prevent the entrance of water or oil, or whatever the heating-bath consists of. Fig. 2 indicates the manner in which this arrangement is attached to the thermometer by means of rubber rings, *r*, round the side screws, *h*, the whole being supported in a beaker containing the liquid constituting the bath.

Below 190° rubber bands may be used to attach the apparatus to the thermometer, and above 100° thin leather or kid washers must be substituted for the rubber washers *b* and *f*.

The advantages claimed for this method of determining m. p.'s are that in many cases (especially with waxes) it is more rapidly carried out; the thickness of the layer experimented on is always equal to the thickness of the platinum disk, *d*; the cover-glasses are almost uniform in thickness; and it is easier to observe a flat surface than the rounded sides of a capillary tube.

J. V. E.

Dependence of the Melting Point of a Solid Substance on its Surface Energy. P. PAWLOFF (*Zeitsch. physikal. Chem.*, 1909, 65, 545—548).—In continuation of previous work (this vol., ii, 19), a formula connecting the melting point of a particle and its radius is deduced, and the three cases in which, at the melting point of the particle, the vapour pressure over the plane surface of the liquid is respectively greater than, less than, or equal to, the vapour pressure

FIG. 1.

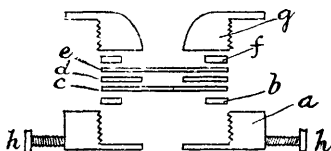
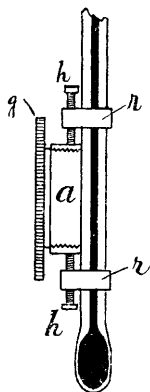


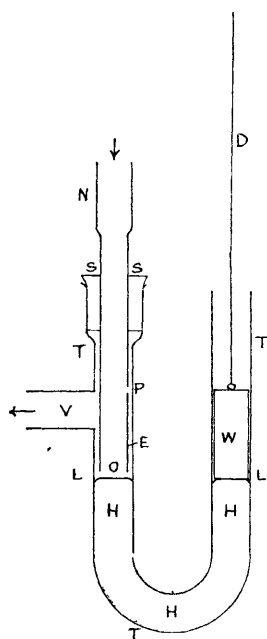
FIG. 2.



over the plane surface of the solid are discussed and represented graphically. Only the first case has been experimentally realised.

G. S.

An Electrically-controlled Gas Regulator. E. EMMET REID (*Amer. Chem. J.*, 1909, 41, 148—152).—The new regulator consists



of a U-tube, *TT'*, provided with a side-tube, *V*, and having one limb enlarged at the top to receive an india-rubber stopper, *SS*, through which passes the tube *NO*, with an external diameter 1 mm. less than the internal diameter of the U-tube. The latter is filled with mercury (*HHH*) to a level about 1 mm. below the end of the tube *NO*. *W* is an iron weight 15—20 mm. long and 1 mm. less in diameter than the U-tube; it is suspended from a lever attached to the armature of an electro-magnet. The armature is ordinarily held up by a spring, but when attracted by the magnet the weight falls 1—2 mm. The passage of the gas is shown by the arrows. If the coils of the electro-magnet are in series with any form of electrical regulator in which contact is made when a certain temperature is exceeded, then, in the latter event, *W* falls, drives the mercury up to close the end of *NO*, and so prevents the passage of all gas except that which can pass through a by-pass, *P*. The latter acts as a by-pass. The high surface-tension of mercury prevents the latter rising between the weight, *W*, and the walls of

the U-tube. Another form of regulator based on the same principle is described, in which the entire apparatus is made of metal, thus avoiding all danger of fire.

E. H.

Thermo-dynamic Equilibrium and Stability. JOSEPH E. TREVOR (*J. Physical Chem.*, 1909, 13, 154—156).—A mathematical discussion of the conditions that must be satisfied to ensure that a given *r*-phase state of an *n*-component substance shall be a stable thermo-dynamic state.

G. S.

Heat of Formation of Aniline and Some of its Derivatives. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1909, 43—59).—The differences between the values obtained by Petit (*Abstr.*, 1888, 1239) for the heats of combustion of *o*-, *m*-, and *p*-toluidine [964.7 cal., 965.6 cal., and 958.8 cal. (solid) respectively] and that obtained by the same author for aniline (818.5 cal.) are about 10 cal. less than the mean difference (157 cal.) between the heats of combustion of two immediate homologues. For the heat of combustion of aniline,

Stohmann (Abstr., 1897, ii, 359) found the value 810.2 cal., Thomsen 829.9 cal., whilst Lemoult (Abstr., 1907, ii, 10) obtained 815.3 cal. Moreover, Stohmann has formulated the rule that the heats of combustion of isomeric compounds are the greater the greater the reactivity of the isomeride, and according to the results of Bredig (Abstr., 1894, ii, 229) and of Farmer and Warth (Proc., 1904, 20, 244), the affinity constants of *o*-, *m*-, and *p*-toluidine increase in the order named, whence their heats of combustion should, contrary to Petit's results, lie in the same order. In order to fix the heat of combustion of aniline and determine whether the toluidines form an exception to Stohmann's rule, the author has determined the heats of combustion of these compounds and some of their derivatives, and has obtained the following results: Aniline, 816.76 cal. (-9.46 cal.); *o*-toluidine, 969.93 cal. (0.7 cal.); *m*-toluidine, 965.72 cal. (4.9 cal.); *p*-toluidine (solid), 969.31 cal. (+1.3 cal.); (liquid) 973.5 cal. (-2.9 cal.); aceto-*o*-toluidide, 1174.61 cal. (53.6 cal.); aceto-*m*-toluidide, 1174.72 cal. (53.5 cal.); aceto-*p*-toluidide, 1174.31 cal. (53.9 cal.). The first figure refers to the heat of combustion at constant pressure; the second, in brackets, to the heat of formation. Thus the author's value for the heat of combustion of aniline accords well with the mean (816.9) of Petit and Lemoult's results adopted by the latter as correct. The value obtained for *m*-toluidine makes this substance an exception to Stohmann's rule unless the value is invalidated by the substance used being impure, but those for the other two isomerides differ from Petit's results and accord with the affinity constants. It is pointed out that the suppression of the basic function of the toluidines by acetylation has removed the difference between their heats of combustion.

E. H.

Heat of Formation of Some Organic Fluorine Compounds.

III. FRÉDÉRIC SWARTS (*Bull. Acad. Roy. Belg.*, 1909, 26—42. Compare Abstr., 1907, ii, 9; 1908, ii, 354).—By combustion in a calorimetric bomb, the author has determined the heats of formation of the following compounds. The first value following the name of the compound is the heat of combustion at constant pressure, and the second, in brackets, its heat of formation. $\beta\beta$ -Difluoroethylamine, 326.01 cal. (66.69 cal.); tetrafluorodiethylamine, 566.04 cal. (116 cal.); tri- ω -fluoro-*m*-toluidine, 830.7 cal. (83.5 cal.); tri- ω -fluoroaceto-*m*-toluidide, $\text{CF}_3\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, 1042.81 cal. (128.99 cal.); fluoroacetamide, 249.55 cal. (92.8 cal.); difluoroacetamide, 208.39 cal. (115.11 cal.); difluoroacetanilide, 944.82 cal. (82.7 cal.). The values given are the mean of from three to seven experiments with each substance. *Difluoroacetanilide*, $\text{CHF}_2\cdot\text{CO}\cdot\text{NHPh}$, prepared by heating equal molecular quantities of difluoroacetic acid and aniline in sealed tubes at 170° for forty-eight hours, crystallises in spangles, m. p. 52.4°, b. p. 259.8°.

Difluoroacetamide, prismatic crystals, m. p. 51.8°, b. p. 108.63°/35 mm., is prepared by acting on ethyl difluoroacetate with concentrated ammonia at -10°.

Comparison of the heats of formation thus determined with the values for the compounds in which fluorine has been replaced by

hydrogen shows that the decrease corresponding with the replacement of a fluorine by a hydrogen atom varies from a minimum of 17.3 to a maximum of 26.2 cal. It is found also that the differences between the heats of formation of the fluoroamines and the amines, and between those of the fluoroamides and the amides themselves, are of the same order as those between the alcohols and acids and their fluoro-derivatives.

E. H.

Compressibility of Gases between 0 and 3 Atmospheres at all Temperatures. ANATOLE LEDUC (*Compt. rend.*, 1909, 148, 407—410).—The author shows that the equation he put forward (*Abstr.*, 1897, ii, 133) to express the deviation of a gas from Boyle's law in terms of the pressure is not contradicted by Rayleigh's researches, since, according to the equation, if the pressure is very small the deviation will be infinitesimal and the gas will appear to obey Boyle's law as perfectly as Rayleigh found.

The deviation from Boyle's law ($1 - pv/p_0v_0$) is equal to $(mp + np^2)$, where m and n are constants for each gas. In gases which obey the law of corresponding states, m and n should be functions of the critical constants. Ether, hydrogen phosphide, and hydrogen sulphide are less compressible, and ammonia is more compressible than the theory demands.

R. J. C.

A Means of Holding the Weighed Tube Used in the Determination of Vapour Density by the Displacement Method. ROBERT BRANDENBURG (*Chem. Zeit.*, 1909, 33, 192).—The small tube containing the weighed sample of substance to be examined is placed in a suitable iron or nickel jacket, and by means of a small electro-magnet or permanent magnet it is retained in the upper part of the inner vapour tube until the operator has closed the apparatus. By this means no loss is occasioned by the weighed sample falling quicker than the vapour tube can be closed, and on removing the magnet the small tube falls to the bottom.

J. V. E.

Simple Method for Determining Vapour Densities. PHILIP BLACKMAN (*Chem. News*, 1909, 99, 87—88).—A more accurate formula is given for the calculation of vapour densities determined by the author's method (compare *Abstr.*, 1908, ii, 157, 564; this vol., ii, 21).

G. S.

Simple Method for Determining Vapour Densities. III. PHILIP BLACKMAN (*Zeitsch. physikal. Chem.*, 1909, 65, 549—552. Compare preceding abstract).—A discussion of some details of the apparatus, and the precautions to be observed, particularly with reference to the manometer, in determining vapour densities by the author's method.

G. S.

Simple Method for Determining Vapour Densities. VI. PHILIP BLACKMAN (*J. Physical Chem.*, 1909, 13, 138—143. Compare preceding abstracts).—The density and hence the degree of dissocia-

tion of phosphorus pentachloride, chloral hydrate, and aldehyde ammonia have been determined by the author's method. The following are the degrees of dissociation under certain experimental conditions described in the paper: phosphorus pentachloride, 24.2% at 170°, 54% at 210°, and 79.2% at 250°; chloral hydrate, 10.89% at 107° and 56.41% at 120°; aldehyde ammonia, 72% at 103° and 98% at 106°. G. S.

Regulation of Temperature in the Measurement of Osmotic Pressure. HARMON N. MORSE and W. W. HOLLAND (*Amer. Chem. J.*, 1909, 41, 92—117).—The importance of keeping the temperature of the osmotic cell as nearly constant as possible during the measurement of the osmotic pressure lies in the fact that the cell, being filled with a liquid having a high coefficient of expansion, and being attached to a manometer of small bore, acts as a sensitive thermometer, and "thermometer effects" caused by fluctuating temperature cannot possibly be distinguished from true osmotic effects. Moreover, since after the development in a cell of the maximum osmotic pressure of a solution the transference of the solvent through the membrane becomes very tardy, full recovery from a change in temperature occupies a very long time. Further, it is important that the cell should be filled at the same temperature as that at which the osmotic pressure of the contained solution is to be measured, otherwise the concentration of the solution will be altered.

The present paper is devoted to a description of the successive attempts to secure a constant temperature in the baths employed in the work described previously (Abstr., 1901, ii, 543; 1902, ii, 553; 1903, ii, 272; 1904, ii, 651; 1905, ii, 575; 1906, ii, 600, 601; 1907, ii, 439, 440, 553; 1908, ii, 671, 759, 1019, 1020; this vol., ii, 216). The apparatus finally adopted, which is based on the principle of causing the water in the bath to pass rapidly first over a continuously cooled surface, second, over a heated surface controlled by a thermostat, and third, over the cooled surface again, is described in detail with diagrams. Although this apparatus prevented the temperature of the water in the bath from varying more than 0.01°, the variation in temperature of the supernatant air was much greater; accordingly, similar apparatus was provided to keep also at a constant and similar temperature the air in the room in which the bath was situated.

A new form of thermostat is described.

E. H.

Laws of Mobility and Diffusion of the Ions Formed in Gaseous Media. E. M. WELLISCH (*Proc. Camb. Phil. Soc.*, 1909, 15, 1—10).—Expressions are deduced for the coefficient of diffusion of an ion through a gas, and also for its mobility; these involve only known physical constants. An ion is supposed to consist of two elements: (1) a mass nucleus surrounded by a sphere of force; (2) an electric charge, the effect of which is to increase the radius of the sphere of force without altering the mass. As the ion moves through the gas, its charge attracts the neutral molecules, resulting in an increase in the frequency of the collisions and a diminution of the mean free path.

The calculated mobility agrees with that observed for several gases, but in the case of ammonia, ethyl alcohol, ethyl chloride, and carbon tetrachloride there are considerable differences. The calculated coefficients of diffusion for air, hydrogen, oxygen, and carbon dioxide agree only moderately with Townsend's experimental values.

H. M. D.

Coefficient of Diffusion of the Emanation of Actinium. G. BRUHAT (*Compt. rend.*, 1909, 148, 628—631).—Experiments have been made which show that the diffusion of the emanation of actinium into air and other gases is regulated by the same laws as those which determine the diffusion of ordinary gases and vapours. The rate of diffusion into air is inversely proportional to the pressure of the air, and varies as the square of the absolute temperature. From a comparison of the rate of diffusion of the emanation with that of ethyl ether, ethyl alcohol, water, and carbon dioxide, the author concludes that the molecular weight of the emanation is about 70. H. M. D.

Reaction-Velocity and Diffusion. FERENCZ JÜTTNER (*Zeitsch. physikal. Chem.*, 1909, 65, 595—623).—In connexion with the Noyes-Whitney-Nernst theory as to the dependence of the velocity of reaction in heterogeneous systems on the rate of diffusion, the author deduces some very complicated equations which are intended to represent the course of the reaction in certain special cases. G. S.

Diffusion through Membranes. CASIMIR JABŁCZYŃSKI (*J. Chim. Phys.*, 1909, 7, 117—128).—The apparatus consists of a flat, circular dish divided into two equal portions by a vertical partition, part of which consists of a circular piece of cigarette paper. Each compartment is provided with a stirrer. The dish is supported horizontally in a thermostat at constant temperature; the solution to be examined is placed in one compartment and water in the other, and the stirrers started. After a few minutes, portions of the solutions are removed simultaneously with a special form of double pipette and analysed.

Experiments were made with solutions of sodium chloride, of potassium chloride, and of hydrochloric acid of different concentrations. The results appear to be accurate to about 2%, and the advantages of the method are its rapidity and the fact that the results are not disturbed by shaking, which is a drawback of the usual methods. On the other hand, the method only gives comparative results. G. S.

Free Pressure in Osmosis. L. VEGARD (*Proc. Camb. Phil. Soc.* 1909, 15, 13—23).—Measurements have been made of the velocity with which water passes through a semi-permeable membrane under different hydrostatic pressures, and also of the velocity of osmosis for aqueous solutions of sucrose of different concentrations. In the first case the velocity is proportional to the pressure. In the osmotic flow, the initial velocity is abnormally high, and gradually falls until a steady state is reached. This state sets in more quickly and is more pronounced for dilute than for more concentrated solutions; it is also

dependent on the soundness of the semi-permeable membrane. If the frictional and osmotic velocities are plotted on the same diagram as a function of the hydrostatic and osmotic pressures respectively, it is found that the friction line is a tangent to the osmotic curve at the zero point. From this relationship the conclusion is drawn that the work required for the osmotic passage of water through the membrane is equal to that required for pressing the pure solvent through with a velocity equal to the osmotic velocity. It follows from this that in osmosis there is a motion of pure water through by far the greatest part of the membrane. In passing through the membrane from the side of the pure solvent, the pressure falls to a minimum value and then increases to the pressure of the solution. In the latter region the motion takes place against the pressure fall and cannot be a motion of the fluid in bulk, but is an inter-molecular motion maintained by the energy which becomes available when the two liquids are brought into contact. The difference between the pressure on the solvent and the minimum pressure is called the free pressure of osmosis. For small velocities this free pressure is equal to the osmotic pressure.

H. M. D.

Osmotic Studies. LOUIS KAHLENBERG (*J. Physical Chem.*, 1909, 13, 93—113).—In reply to the criticisms of Cohen and Commelin (Abstr., 1908, ii, 811) on his earlier work (Abstr., 1906, ii, 337), the author maintains that they have failed to show that stirring is unnecessary in measuring osmotic pressures; the criterion is not that fairly concordant results may be obtained without stirring, but that, in comparable experiments, higher pressures are always obtained when the solution is stirred.

Three additional observations of the osmotic pressure of a 0.125 normal solution of sucrose in pyridine at 0° have been made by the previous method. The highest pressure observed was only 23 cm. of the osmotic liquid; this developed within ten hours, remained constant for three days, and then began to diminish. This supports the author's previous statement that the osmotic pressure of such solutions is very much smaller than the gas pressure.

The osmotic apparatus used by Cohen and Commelin is adversely criticised, and the author maintains the validity of his previous results in all respects.

G. S.

Solutions in Mixtures of Alcohol and Water. ERNST CUNO (*Ann. Physik*, 1909, [iv], 28, 663—664. Compare Abstr., 1908, ii, 160).—In reference to the author's previous paper, it is pointed out that the miscibility of ethyl alcohol and water in presence of potassium carbonate has been also examined by J. M. Bell (compare Abstr., 1905, ii, 684). The two series of observations agree satisfactorily.

H. M. D.

Ultramicroscopic Observations on Crystalline Liquids. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 59—62; *J. Russ. Phys. Chem. Soc.*, 1909, 41, 28—33).—*p*-Azoxyanisole, anisaldazine, cholesteryl propionate, and cholesteryl benzoate have

been examined by means of the ultra-microscope during the transition from the isotropic liquid through the anisotropic liquid to the crystalline, solid condition. The observations made confirm the author's view that the crystalline, liquid condition is characterised by the presence of very small, crystalline particles, in which the forces which determine crystalline form are developed to only a relatively small extent.

H. M. D.

Spontaneous Crystallisation. RENÉ MARCELIN (*Compt. rend.*, 1909, 148, 631—633).—The author's observations on the spontaneous crystallisation of solutions of lead acetate lead to the conclusion that, other things being equal, the power of spontaneously crystallising decreases with increase in the time during which the system has been maintained in the liquid condition, and is independent of the number of times the solution has been crystallised. With increase in the temperature at which the liquid has been heated, the power of crystallising spontaneously diminishes. The observed facts cannot be explained on a molecular kinetic hypothesis, or on the assumption that the crystallisation is due to the presence of crystalline nuclei in the supercooled liquid. On the other hand, the view that the crystallisation is due to particles of foreign suspended matter, is in agreement with the observations.

It has been found in the case of supercooled solutions of potassium nitrate that finely-powdered substances are much more effective in inducing crystallisation than the same substances in the form of larger particles. The action of the small particles is supposed to be similar to the action of these in the condensation of supersaturated vapours.

H. M. D.

Gaps in Isomorphous Mixtures. WLADIMIR I. VERNADSKY (*Bull. Acad. Sci. St. Pétersbourg*, 1909, 139—149).—Denial of the existence of gaps in isomorphous mixtures is not in accord with observed facts, such gaps being especially marked in the case of minerals, and also existing in other cases (compare Stortenbeker, *Abstr.*, 1903, ii, 470; Muthmann and Kunze, *Abstr.*, 1895, ii, 7; Gossner, *Abstr.*, 1908, ii, 366).

T. H. P.

Adsorption (Dyeing) and Cohesion (Felting) of Woollen Fibres and Swelling Affinity. ED. JUSTIN-MUELLER (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 64—70).—The adsorption phenomena which are observed with adsorbents, such as animal and wood-charcoal, are not comparable with those which are met with in the case of absorbents, such as cotton and wool fibres, which undergo a process of gelatinisation in contact with the medium containing the adsorbable substance. Comparative measurements of the extent to which wool fibres stick together after heating for several hours at 100° in distilled water, dilute solutions of sulphuric acid, and in a natural water containing a large proportion of lime, have been made. Both acid and alkali accelerate the gelatinisation process. Measurements were also made of the amounts of various colouring matters absorbed by blood-charcoal, wood-charcoal, and wool from aqueous solutions. The

variation of the adsorption with the temperature, and the influence of acids and alkalis on the adsorption, indicate that the adsorption process in the case of woollen fibres is quite different from that of the charcoal. Whereas the cause in the latter case is to be found in capillary affinity, the adsorption by wool fibres is due to what the author terms "swelling affinity."

H. M. D.

The Borderland between Colloidal Chemistry, Mineralogy, and Geology. CORNELIO DOELTER and FELIX CORNU (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 89—92).—A collection of notes relating to the structure of naturally-occurring substances from the standpoint of colloidal chemistry. The relationship pointed out by Cornu (this vol., ii, 222), that for every simple mineral colloid there is a corresponding crystalloid, is termed the "homoisochemite" law. Mineral colloids which correspond in composition with such crystalloids are called pseudo-stoicheiolites. A sub-division of mineral colloids is suggested, depending on the number of adsorbed compounds.

H. M. D.

Extension of the Notion of Solubility to Colloids. JACQUES DUCLAUX (*Compt. rend.*, 1909, 148, 295—297).—Colloidal solutions can be concentrated by filtering out the solvent under pressure through collodion. An increasing pressure will remove more and more solvent, until a limit is attained where the colloid solidifies. This limiting pressure is termed the "maximum osmotic pressure" of the colloid, and the limiting concentration the "solubility" of the colloid.

The solubility so defined of gelatin is about four parts in one hundred of water, of gelose less than one in one hundred, and of some kinds of ferric oxide more than sixty in one hundred of water. The osmotic pressure of Bredig's colloidal platinum is less than 20 mm. of water, whereas that of ferric hydroxide is more than 20 metres of water.

The author proposes to employ this conception of solubility in defining the relative stability of various colloids, in describing the modifications of a colloid through added substances, etc., and also in separating colloids from one another as salts are crystallised.

Experiment has shown that the solubility of a colloid is very closely related to the size, composition, and electric charge of the molecular clusters which compose it.

R. J. C.

Theory of Reversible Sols. H. WALDEMAR FISCHER and O. BOBERTAG (*Jahrsb. Schles. Ges. vaterländ. Cult. Naturwiss. Sek.*, 1908, Reprint 1—15. Compare Abstr., 1908, ii, 1024).—For the study of reversible colloids it is necessary to have as a standard substance one which is perfectly free from electrolytes, is a simple chemical substance of known constitution having a minimum reactive power, of great stability, and of high molecular weight. It is found that myricyl alcohol, $C_{30}H_{61}\cdot OH$, and the paraffin, $C_{60}H_{122}$, prepared therefrom sufficiently fulfil these requirements.

The behaviour of myricyl alcohol towards chloroform, amyl alcohol, ether, alcohol, and benzene is practically identical, it being almost

insoluble in the cold, the solubility increasing rapidly with rise of temperature.

A hot saturated solution when suddenly cooled changes to a semi-solid, gelatinous mass. The temperature at which gelatinisation takes place is to a great measure dependent on the concentration of the solution; a critical point is reached as in the case of two incompletely miscible liquids.

From this it follows that the concentration of the Gels varies with the temperature, and, therefore, the chloroform, etc., that is present is neither as chloroform of crystallisation or in molecular combination, nor is it simply absorbed. When a 0.01% ethereal solution of myricyl alcohol is suddenly cooled to -60° , a reversible sol is obtained, an opalescent liquid from which a drop of cold alcoholic solution of carbon dioxide causes a flocculent precipitation.

Smaller values are obtained for the solubility of myricyl alcohol in chloroform and amyl alcohol when the temperature is increased than when the temperature is decreased. If very slowly cooled, myricyl alcohol separates from solution in small, rhombic crystals, which readily lose the chloroform when exposed to the air.

J. V. E.

Apparent Colloidal Diffusion. Porosity of Collodion Membranes. RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 62—63).—A case of apparent diffusion of colloidal silver chloride is described. A silver chloride-collodion emulsion, which had been prepared from silver nitrate and lithium chloride and contained a very slight excess of lithium chloride, was spread in a thin layer on a glass plate and dried at the ordinary temperature. The silver chloride was distributed through the layer of collodion in a finely divided granular condition. After some weeks the silver chloride was found to have become quite coarse-grained and non-transparent, and instead of being uniformly distributed through the collodion, it was now found to lie entirely on the surface of the collodion membrane. This apparent diffusion of the colloid is attributed to the solvent action of the small excess of lithium chloride on the silver chloride. The collodion film is supposed to exert a pressure on the salts present, and silver chloride separates on the surface. The lithium chloride thus set free dissolves more of the fine-grained silver salt in the interior, and further separation of the dissolved colloid takes place at the surface.

Unsuccessful attempts to obtain partly porous collodion films are described.

H. M. D.

Freezing of Jellies. GIUSEPPE BRUNI (*Ber.*, 1909, 42, 563—565).—The results obtained by Lottermoser (this vol., ii, 27) confirm those published by the author some time ago (*Rend. Soc. chim. Roma*, 1905, 3, 1). Analyses of the crystalline substance obtained by freezing the gel of silicic acid show that its composition is not definite, but lies between $\text{SiO}_2 \cdot 0.788\text{H}_2\text{O}$ and $\text{SiO}_2 \cdot 3.67\text{H}_2\text{O}$. A constant relationship between the quantity of water in the hydrogel and in the crystalline silicic acid could not be discovered.

W. H. G.

Mechanism of Agglutination. LEONOR MICHAELIS (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 55).—The author points out that Loeb's

view (*ibid.*, 1908, 3, 113) of the process of agglutination involves the conclusion that the surface tension not only diminishes, but, indeed, becomes negative; this is contradictory to the generally accepted view that coagulation phenomena are accompanied by a diminution of the total surface. Loeb's observations can be explained quite readily in terms of the latter view.

H. M. D.

Passivity in Acid Solutions. OTTO SACKUR [with J. ALVARES] (*Zeitsch. Elektrochem.*, 1908, 14, 607—613).—A current is passed through a cell containing a nickel anode immersed in sulphuric acid and a copper cathode in copper sulphate contained in a porous pot. With small currents, the *E.M.F.* at the terminals of the cell is proportional to the current; when a certain current strength is exceeded, the *E.M.F.* rises suddenly, indicating that the nickel has become passive. The critical current is approximately proportional to the area of the anode and to the concentration of the hydrogen ions in the solution. It increases rapidly with the temperature, and with the quantity of halogen ion in solution. The nickel is dissolved quantitatively below the critical current density, but, above it, small quantities still go into solution. It is shown that the current density which would be sufficient to reduce the concentration of the hydrogen ions at the surface of the anode to 10^{-7} , and so permit of the separation of nickel hydroxide, is very much smaller than the critical current density observed. The explanation of passivity by the formation of an insoluble skin of hydroxide is therefore rejected.

T. E.

Passivity in Acid Solutions. II. J. ALVARES (*Zeitsch. Elektrochem.*, 1909, 15, 142—144).—Iron is investigated in the same way as nickel (preceding abstract). The critical current is higher when the anode is rotated than when it is at rest; it increases with the concentration of the sulphuric acid to a maximum (at $1N\text{-H}_2\text{SO}_4$) and then diminishes again. The addition of halogen ions makes no difference to the critical current; a rise of temperature increases it. In the active condition the iron is covered with a black skin, which disappears when it becomes passive, the metal assuming a matt, metallic appearance.

The critical current for chromium increases continuously with the strength of the acid, as is the case with nickel; chromium also becomes passive in hydrochloric acid. In the active state the chromium dissolves as the green chromic ion, whereas in the passive state it dissolves as chromic acid.

T. E.

Formation of Esters. ANTON KAILAN (*Zeitsch. Elektrochem.*, 1909, 15, 106—110). RUDOLF WEGSCHEIDER (*ibid.*, 111).—Polemical papers referring to a criticism of Kailan's work by Goldschmidt (this vol., ii, 129).

T. E.

Atomic Weights. JULIEN DELAUNEY and MAURICE GARNIER (*Mon. Sci.*, 1909, [iv], 23, 27).—An attempt to deduce a connexion between the atomic weights of related elements.

H. M. D.

Forms of Matter. II (continued). P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 123—139. Compare this vol., ii, 132, 221).—The absence of precipitation on the addition of a dilute solution of aluminium chloride to concentrated ammonia solutions is not always due to the formation of a true solution, but is determined by the formation of a hydrosol. Such a hydrosol results as a consequence of the peptisation of the very finely divided precipitate of aluminium hydroxide. The conditions for the formation of the aluminium hydroxide hydrosol in ammonia solutions are discussed in detail. There are two limiting concentrations below and above which the peptisation does not occur, and an intermediate concentration for which the hydrosol formation reaches a maximum.

Other special cases are considered, and the author then gives the general conditions which are necessary and sufficient for the occurrence of peptisation phenomena. These conditions differ somewhat from those given by Lottermoser (compare Abstr., 1907, ii, 851).

Although barium sulphate and aluminium hydroxide have been examined in very great detail, numerous observations have been made on the precipitation phenomena in the case of a very large number of other insoluble substances. A list of substances which have been obtained in all possible forms of fine-grained, crystalline (so-called colloidal amorphous) precipitates is given. For the investigation in any particular case of the influence of concentration on the nature and structure of the precipitated substance, it is necessary that the product VC should be kept constant in the experiments, V being the volume of the solution and C its concentration.

From a consideration of the factors which determine the nature of the crystallisation process, it is shown that the order of magnitude of the solubility of a substance can be ascertained from the form of the precipitate, which is obtained under given conditions. H. M. D.

Apparatus for Rapidly Obtaining a Stream of Water at Constant Temperature for Refractometers and Polarimeters. VON HEYGENDORFF (*Chem. Zeit.*, 1909, 33, 244).—A reservoir of about one litre capacity is fitted with an outlet at the bottom and an overflow tube which can be readily adjusted so as to maintain any required constant head of water. By this means a constant flow of water from the outlet is made to pass through a copper coil heated by a Bunsen burner to the temperature necessary to raise the temperature of the outflowing water to that required. The adjustment of the water flowing into the reservoir keeps the head of water constant, and by raising or lowering the waste tube the water may be caused to flow through the hot copper coil at a more rapid or a less rapid rate, thus decreasing or increasing the temperature. With this arrangement it is possible to maintain a current of water through jacketed tubes, etc., at temperatures between 20—40° by using an ordinary Bunsen burner. J. V. E.

New Forms of Condenser. H. STOLTZENBERG (*Zeitsch. angew. Chem.*, 1909, 22, 351. Compare Abstr., 1908, ii, 938).—A double

cylinder condenser, Fig. 1, and a spiral condenser with water-jacket, Fig. 2, have been devised so as to present maximum cooling surface, and have the advantage of being readily detachable for cleaning. They are modifications of those described previously by the same author.

J. V. E.

An Apparatus for Decanting and Filtering.

J. HUDIG (*Chem. News*, 1909, 99, 112—113; *Chem. Zeit.*, 1909, 33, 298—299).—The

apparatus described and figured in detail consists of a horizontal shaft fixed rigidly on a stand; on this shaft rotate several holders made of wood, each carrying an adjustable spring clamp to hold a flask. Besides this spring clip each holder is fitted with a clamping spring for the purpose of attaching a glass rod to serve as a guide for the outflowing liquid. At the side of each holder a wooden cog-wheel is fitted which engages with a worm spindle moving in a guide that is rigidly fixed to the shaft. The worm spindle can be clamped by means of a small nut. A flask may therefore be held in any desired position or may be slowly tipped by turning the worm spindle by means of a milled head.

By means of this arrangement the operation of washing a precipitate by decantation and finally transferring it to a filter may be considerably facilitated and hastened. It is claimed for this method that the fluid may be decanted absolutely free from precipitate; the filter may be kept constantly filled; the precipitate may be completely washed; and several filtrations may be simultaneously effected.

J. V. E.

Demonstration of the Expansions of Gases and Vapours.

H. REBENSTORFF (*Zeitsch. physikal.-chem. Unterr.*, 1908, 21, 378—383).—A series of experiments, illustrated by figures of the apparatus, employed in demonstrating the alteration in the volumes of gases and vapours as induced by changes of pressure.

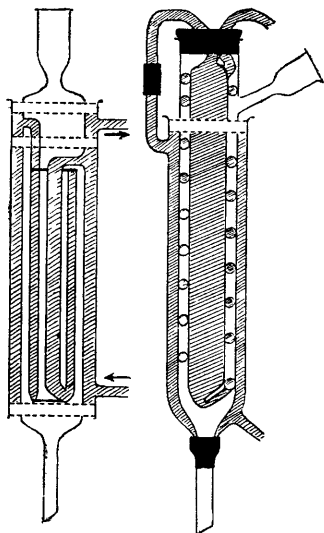
G. T. M.

Supercooling of Water.

V. KUMMERELL (*Zeitsch. physikal.-chem. Unterr.*, 1908, 21, 391).—A basin containing ether is placed on a layer of water, and as the ether evaporates, a stage is reached when the evaporating liquid froths up suddenly in a manner quite distinct from its superficial evaporation. This phenomenon is due to the supercooling of the underlying water, which finally freezes, generating a considerable amount of heat, and thus causing the more rapid frothing

FIG. 1.

FIG. 2.



up of the ether. At this point the basin is found to be frozen to the moistened surface. G. T. M.

A Demonstration of Atmospheric Humidity and Cold produced by Evaporation. H. STROMAN (*Zeitsch. physikal.-chem. Unterr.*, 1908, 21, 390—391).—Two small Erlenmeyer flasks, one containing a little water and the other a similar amount of concentrated sulphuric acid, are each fitted tightly with a cork carrying a test-tube in which ether is placed. A stream of ordinary air is blown through the two test-tubes so that the ether evaporates. The tube over water becomes encrusted on its exterior with ice, whilst the tube over the strong acid remains unchanged. The interiors of the tubes leading in the air current will both become encrusted with ice, showing the humidity of ordinary atmospheric air. G. T. M.

A Lecture Demonstration of Lime-burning. KARL SCHEID (*Zeitsch. physikal.-chem. Unterr.*, 1908, 21, 393—394).—A steel or platinum tube with an obliquely truncated closed end is used for heating various forms of calcium carbonate. When the open end is fitted with a glass tubulure, a large amount of carbon dioxide can be quickly collected and tested. The inverse change can be observed by connecting the tube with a manometer and gently heating the platinum tube with a very small flame, when the recombination of the gas with the residue is readily indicated. G. T. M.

Inorganic Chemistry.

Quadrivalency of Oxygen. H. STANLEY REDGROVE (*Chem. News*, 1909, 99, 109—110. Compare Abstr., 1908, ii, 564).—The recent work of Miss Smedley on the constitution of the carboxyl group (*Trans.*, 1909, 95, 231), the formulation of which is considered to be

$-\text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{OH} \end{smallmatrix}$, has prompted the author to consider this question in the

light of its thermo-chemical properties. Arguments for and against this constitution of the carboxyl group are given, in which it is assumed that when oxygen becomes quadrivalent the thermal value of the two primary valencies remains unaltered. It is, however, far more probable that when oxygen functions as a quadrivalent atom the thermal value of its two primary valencies will be decreased. If this be so, all the arguments from the thermal point of view in support of the above formulation entirely break down. From the thermal data available, the conclusion is drawn that the quadrivalent oxygen formula for the carboxyl group cannot be justified. J. V. E.

Concentration of Hydrogen Ions in Sea-Water. WILHELM E. RINGER (*Chem. Weekblad*, 1909, 6, 113—123. Compare Ringer and Klingen, Abstr., 1908, ii, 320; Salm and Friedenthal, Abstr., 1907, ii, 389; Neumann, Abstr., 1894, ii, 373; Smale, Abstr., 1894, ii, 436; Bose, Abstr., 1900, ii, 704; 1901, ii, 589; 1902, ii, 58; Wilmore, Abstr., 1901, ii, 2, 142; Coggeshall, Abstr., 1895, ii, 377; Richards, Abstr., 1898, ii, 7; Jahn, Abstr., 1900, ii, 522; Sauer, Abstr., 1904, ii, 307; Palmaer, Abstr., 1907, ii, 424; Abegg and Bose, Abstr., 1900, ii, 127; Sackur, Abstr., 1902, ii, 121; Tower, Abstr., 1896, ii, 142).—Reference is made to the work of the authors cited, and the results of a number of determinations of the concentration of the hydrogen ions in various parts of the North Sea are given. C_H varies between 0.58 and 1.40×10^{-8} . The water is slightly alkaline, and there is not any appreciable difference between samples from the northern and southern parts of the ocean. In those from Bømmelfjord the acidity increases with the depth and with increase in the percentages of salts and carbon dioxide. No definite relation between the percentage of salts and the concentration of hydrogen ions was observed. It is possible that increase in acidity is associated with fall in temperature. A. J. W.

The Molecular Magnitude of Sulphur in Bromoform Solution. ALESSANDRO BORGO and M. AMADORI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 138—141. Compare Paternò, this vol., ii, 118).—Sulphur in bromoform solution gives cryoscopic results corresponding very exactly with the formula S_8 .

Pure bromoform, distilled in a vacuum and repeatedly frozen, is best preserved in the solid state in the dark, being thawed immediately before use. C. H. D.

Equilibrium in the System Colloidal Sulphur—Solution of Crystalloid. THE SVEDBERG (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 49—54).—Colloidal sulphur was prepared by slowly adding a concentrated solution of sodium thiosulphate to concentrated sulphuric acid, the temperature not being allowed to rise above 25° ; after the addition of water, the mixture was washed, filtered, and the resulting solution precipitated by addition of sodium chloride; the separated sulphur was then decanted, centrifuged, dissolved in water, and again precipitated, these operations being repeated until the sulphur was quite free from sulphate.

The solubility of this colloidal sulphur in 0.2, 0.3, 0.4, and 0.5 molar sodium chloride, 0.2 molar sodium bromide, and 0.2 molar sodium sulphate solutions was measured for a series of temperatures. In all cases the variation of the solubility (c) with the temperature (t) is given by the equation $\log c = k.t$, in which k is a function of the concentration of the dissolved crystalloid. For equimolar solutions, k appears to be independent of the anion of the dissolved electrolyte.

H. M. D.

The Absorption of Sulphur Dioxide in Water. W. FULDA (*Arb. Kais. Gesund. Amt.*, 1909, 30, 81—86).—A theoretical paper
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dealing with the deviation from Henry's law of the solubility of sulphur dioxide in water, as determined by earlier investigators.

S. B. S.

Pyrosulphuryl Chloride, $S_2O_5Cl_2$. WILHELM PRANDTL and PAUL BORINSKI (*Zeitsch. anorg. Chem.*, 1909, 62, 24—33).—The pyrosulphuryl chloride described by previous observers, with the exception of Konowaloff (Abstr., 1883, 553, 782, 900), has been a mixture containing sulphuryl hydroxychloride, $SO_2Cl \cdot OH$. The pure compound, prepared by the action of sulphur trioxide on carbon tetrachloride, the crude product being repeatedly subjected to very slow fractional distillation, boils at $150.7^\circ/730$ mm. The presence of the hydroxyl compound in most preparations is due to the presence of some sulphuric acid in the sulphur trioxide used. The crude product is best purified by the cautious addition of ice, which decomposes the sulphuryl hydroxychloride rapidly, the lower layer, which may be separated, then consisting of nearly pure pyrosulphuryl chloride, D^{20}_D 1.876, D^{18}_D 1.844. The vapour density at 205° is normal, moisture being excluded.

Pyrosulphuryl chloride reacts very slowly with water. In moist air it becomes turbid, owing to the separation of drops of sulphuric acid, which disappear on warming and reappear on cooling.

C. H. D.

Catalytic Oxidation of Hypophosphorous Acid by Copper. J. BOUGAULT (*Compt. rend.*, 1909, 148, 415—417).—On adding a solution of sodium hypophosphite to a large excess of copper sulphate, a brownish-yellow precipitate is formed, which, on boiling, is gradually converted into a well-crystallised powder, consisting of extremely pure copper. If, however, excess of hypophosphite is used, a granular, brown precipitate, probably Würtz's hydride, Cu_2H_2 , is obtained, which, on heating, gives a large volume of hydrogen and a frothy, reddish-brown precipitate of copper. This precipitate has a very powerful catalytic action on solutions of sodium hypophosphite, whereby hydrogen is evolved, and the hypophosphite becomes oxidised into phosphite and phosphate. The action is stopped by the accumulation of acidic products, but on neutralising the liquid or taking a fresh portion of hypophosphite, more hydrogen can be obtained.

By placing 0.35 gram of the copper powder in four solutions of hypophosphite successively, 4 litres of hydrogen were obtained.

Copper precipitated by zinc has a similar, but much feebler, catalytic activity.

R. J. C.

[Preparation of Colloidal Arsenic.] CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 202561).—A stable colloidal solution of arsenic may be obtained by reducing its compound in an alkaline medium in the presence of a protective colloid. White arsenic dissolved in aqueous sodium hydroxide containing some protein material, such as white of egg, lysalbic acid or gelatin, is reduced by alkaline pyrogallol. The solution is dialysed or the colloidal arsenic precipitated by acid, washed, and again dissolved in water. The colloidal arsenic may be precipitated from solution by acetone, alcohol, or a mixture of the latter with ether. On evaporating the

solution, it is obtained in black, lustrous lamellæ, which dissolve in water to a deep brown solution,
G. T. M.

The Growth of Quartz Crystals. GIORGIO SPEZIA (*Atti R. Accad. Sci. Torino*, 1909, 44, 95—107).—Quartz hexagonal prisms, cut from crystals in directions perpendicular to the axes, were suspended in heated solutions of sodium silicate in which fragments of quartz were placed. Each experiment lasted several months, the temperature being as high as 340° in the neighbourhood of the solution. Sodium chloride in the solution modifies the growth, causing greater limpidity, striations on the prism faces, and a different development of the rhombohedral faces. The greatest growth takes place when the principal axis of the prism is vertical, that is to say, parallel with the diffusion currents.
C. H. D.

Thermal Effects of the Musical Arc. [Probable Crystallisation of Carbon.] LA ROSA (*Compt. rend.*, 1909, 148, 616—617).—By a suitable modification of the experimental arrangement previously described (*ibid.*, 475), the author has obtained from sugar carbon, transparent, crystalline particles, which fall in bromoform and methylene iodide, and are sufficiently hard to scratch a ruby.
H. M. D.

Combustion of Gases without Flame and the Conditions in Incandescent Lighting. JEAN MEUNIER (*Compt. rend.*, 1909, 148, 292—294. Compare this vol., ii, 463).—A platinum wire was substituted for the fork and mantle of an ordinary Welsbach burner with a glass chimney, and by careful manipulation of the gas supply the platinum could be maintained in incandescence, although there was no flame at the burner or the wire. Local combustion could thus go on at the surface of the wire, although the whole chimney was filled with an explosive mixture, but a sudden disturbance of the gas supply or outer air caused the burner to light up with a mild explosion. Combustion of gases without flame is similar to the combustion of solids like carbon, being attended by a convergence of molecules to the ignition point.
R. J. C.

Argon in Association with Radioactive Zirconium Minerals. ANDREAS VON ANTROPOFF (*Zeitsch. Elektrochem.*, 1909, 15, 144—145).—O. Hahn suggests (*ibid.*, 50) that the argon found in a zirconium mineral (Abstr., 1908, ii, 943) was derived from the atmosphere. The author states that the quantity was far larger than could be accounted for in this way.
T. E.

Some Corroded Metals. WILLEM P. JORISSEN (*Chem. Weekblad*, 1909, 6, 150—153).—An account of the corrosive action of light and air on certain metals and alloys.
A. J. W.

Laboratory Preparation of Sodium or Potassium Hydroxide Free from Carbonate. WILLEM P. JORISSEN and H. FILIPPO, jun. (*Chem. Weekblad*, 1909, 6, 145—149).—The authors describe a method of preparing sodium or potassium hydroxide free from carbonate by

a modification of the Castner-Kellner process, using a mercury cathode in a solution of the crude hydroxide. The amalgam formed is decomposed by water.

A. J. W.

Theory of the Bell-Chamber Process. ANDRÉ BROCHET (*Bull. Soc. chim.*, 1909, [iv], 5, 202—207. Compare Abstr., 1908, ii, 1034).—A critical discussion of the causes of the divergence in the views of the author and of Chancel (this vol., ii, 235) as regards this process, is given.

T. A. H.

Potassium Perborates. CONWAY VON GİRSEWALD and A. WOŁOKITIN (*Ber.*, 1909, 42, 865—869).—The authors have prepared two *potassium perborates* having the formulæ $2\text{KBO}_3 \cdot \text{H}_2\text{O}$ and $2\text{KBO}_3 \cdot \text{H}_2\text{O}_2$.

The former is obtained by adding 100 c.c. of a cold 75% solution of potassium metaborate, KBO_2 , to 1020 c.c. of a cold 3% solution of hydrogen peroxide. After some hours the liquid is filtered and the perborate precipitated by adding 900 c.c. of methyl alcohol. The salt is collected after twelve hours and washed with ice-cold water. It is a microcrystalline powder, of which 1.25 parts are dissolved by 100 parts of water at 0° and 2.5 parts at 15° . The salt is stable when dry, but an aqueous solution loses its active oxygen at 50° in an hour and more slowly at lower temperatures.

The second salt, $2\text{KBO}_3 \cdot \text{H}_2\text{O}_2$, is obtained by the same process, but using 30% hydrogen peroxide. It is a fine, white powder, which is stable at the ordinary temperature. When rapidly heated it deflagrates at 150 — 160° , but when heated slowly, the active oxygen is quantitatively evolved. One hundred parts of water dissolve 0.70 part at 15° . Both salts have considerably stronger antiseptic properties than either boric acid or potassium chlorate.

J. C. C.

[**Preparation of Persulphates.**] VEREINIGTE CHEMISCHE WERKE (D.R.-P. 205067, 205068, and 205069).—It has been found that the yield of persulphate is considerably increased when simple or double cyanides are added to the sulphate solution in the electrolytic cell. A cold concentrated solution of sodium hydrogen sulphate containing a small proportion of potassium ferricyanide was electrolysed with a current of anode density of 0.167 ampere per sq. cm. The yield was maintained by the addition of further quantities of ferricyanide, and after thirty-six ampere hours a total yield of 84% of persulphate was obtained. Alkali cyanates, thiocyanates, and cyanamides produce a similar effect. The sodium persulphate obtained in this way separates from the concentrated solution as a sludge-like precipitate, which is purified only with difficulty. A granular form of sodium persulphate is, however, obtained when a small amount of a potassium salt, particularly a cyanide derivative, is introduced into the electrolytic solution.

G. T. M.

Chemical Composition of Colloidal Silver Produced Electrically. G. REBIÈRE (*Compt. rend.*, 1909, 148, 354—357).—Colloidal solutions of the noble metals have a conductivity much greater than that

of the water they are prepared from, but insufficient to be attributed to metallic conduction. The explanation suggested by Blake in the particular case of silver, that soluble silver oxide is the conducting agent, is now confirmed. On precipitating colloidal silver with an electrolyte (barium nitrate), a minute amount of silver remains in solution, which is roughly proportional to the original conductivity. If a small current is passed between silver poles under water, the colloidal solution obtained is brown, and has a low conductivity. As larger currents are employed, the colloid particles tend to increase in size, so that the solutions may be greenish or bright green. In these cases there is more electrolysis of the water, and hence more formation of silver oxide. In general, the conductivity of green colloidal silver is much greater than that of brown. The addition of an electrolyte to brown colloidal silver first produces a change of colour to green, and then a further agglutination of the granules into a flocculent precipitate.

Soluble silver oxide, often considerable in amount, may greatly influence the properties of colloidal silver, particularly its biological action.

R. J. C.

Lead Chromate. EDWARD E. FREE (*J. Physical Chem.*, 1909, 13, 114—137).—Solutions of lead nitrate of concentrations varying from molar to $1/16,384$ molar were mixed with solutions of potassium chromate of corresponding strength at intervals of temperature between 20 and 90°, and the colour of the precipitate and average size of the crystals examined. The mixing was effected by adding one solution slowly to the other with rapid stirring, but under corresponding conditions the same results were not always obtained. The largest crystals are obtained in dilute and hot solution, but the depth of colour is greatest for solutions of intermediate concentration ($1/8$ — $1/32$ molar). It follows that the depth of colour depends on factors other than the size of the crystals, probably on the basicity of the salt. As a chrome-yellow formed of small crystals possesses the clearer colour and greater covering power, the proper conditions for the manufacture of chrome-yellow are rapid mixing of cold and concentrated solutions under conditions which most successfully prevent the formation of basic salt. What the latter conditions are has not been determined. Glue retards precipitation and causes the formation of smaller crystals.

G. S.

Lead Chromate and its Change of Colour. CASIMIR JABŁCZYŃSKI (*Chem. Ind.*, 1908, 31, 731—733).—Freshly precipitated yellow lead chromate becomes orange after a short time and loses its lustre. This is prevented technically by the addition of lead sulphate. The nature of the change, and of the protective action, have been investigated.

Precipitation of potassium chromate with an excess of lead acetate gives a yellow product, which does not change colour in contact with the solution, even on boiling, but becomes orange if filtered. Acetic acid does not exert a protecting influence. When basic lead acetate

is used, the yellow precipitate always becomes red in time, losing water to form the basic salt, $O \begin{smallmatrix} \text{Pb} \\ \text{Pb} \end{smallmatrix} \text{CrO}_4$.

The presence of 10% of lead sulphate in the precipitate prevents the change, even if the two solids are only mechanically mixed after precipitation. It has no effect on basic lead chromate. Barium sulphate and lead phosphate are without influence. The conclusion is drawn that the presence of a soluble lead salt is necessary, and that the lead ions act by reducing the hydrolysis of the chromate, the change of colour of which is due to the formation of the basic salt.

Besides this irreversible change, a reversible change of colour is observed, the colour of the precipitate being deepened on boiling with water, but returning to its original shade on cooling. C. H. D.

Electrolysis of Copper Solutions. JEAN MEYER (*Zeitsch. Elektrochem.*, 1909, 15, 12—20, 65—73).—The addition of hydrogen peroxide to the acid copper sulphate solution of a copper voltameter diminishes the quantity of copper deposited. When a hot neutral solution of copper sulphate is electrolysed, in an atmosphere of hydrogen or carbon dioxide, with a small current density, cuprous oxide alone is deposited on the cathode; four farads yielding approximately one gram-molecule of it or about one-half the theoretically possible amount. The quantity of cuprous oxide formed is estimated by treating the cathode with a neutral solution of iron alum and titrating the ferrous sulphate produced by the reactions $\text{Cu} + \text{Fe}_2(\text{SO}_4)_3 = \text{CuSO}_4 + 2\text{FeSO}_4$ and $\text{Cu}_2\text{O} + \text{Fe}_2(\text{SO}_4)_3 = \text{CuSO}_4 + \text{CuO} + 2\text{FeSO}_4$. From the loss of weight of the cathode and the quantity of ferrous salt produced, the quantity of cuprous oxide is easily calculated.

When copper is warmed with neutral copper sulphate solution, cuprous oxide and a green basic cupric salt are formed, the quantity of the former is always less than equivalent to the quantity of copper dissolved. The reactions occurring are probably $\text{Cu} + \text{CuSO}_4 + \text{H}_2\text{O} = \text{Cu}_2\text{O} + \text{H}_2\text{SO}_4$ and $\text{Cu}_2\text{O} + \text{CuSO}_4 + \text{H}_2\text{O} = \text{Cu}_2\text{SO}_4 + \text{Cu}(\text{OH})_2$. The basic salt is formed even when air is excluded.

The greater part of the paper consists of criticisms of Foerster's views of the electrolytic reduction of cupric to cuprous ions and the formation of cuprous oxide by hydrolysis of cuprous sulphate (*Abstr.*, 1897, ii, 241; 1904, ii, 818). The author considers that copper is always deposited primarily, and that it then reacts with cupric sulphate, thus: $\text{Cu} + \text{CuSO}_4 + \text{H}_2\text{O} = \text{Cu}_2\text{O} + \text{H}_2\text{SO}_4$. T. E.

Electrolysis of Copper Sulphate. FRITZ FOERSTER (*Zeitsch. Elektrochem.*, 1909, 15, 73—76).—Meyer's explanation of the cathodic formation of cuprous oxide (preceding abstract) is equivalent to the two reactions: $\text{Cu} + \text{CuSO}_4 \rightleftharpoons \text{Cu}_2\text{SO}_4$ and $\text{Cu}_2\text{SO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{Cu}_2\text{O} + \text{H}_2\text{SO}_4$, that is, he supposes the cuprous salt to be a secondary product, whereas Foerster regards it as a primary product formed by the removal of one electron from a cupric ion.

The author has confirmed Luther's observation of the reduction of permanganate by a solution of cupric sulphate which has been boiled with copper (*Abstr.*, 1901, ii, 301), a reaction which Meyer failed to obtain. T. E.

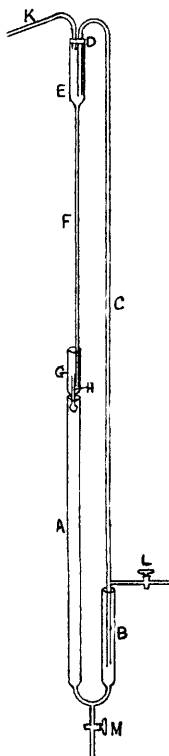
Equilibrium between Cuprous and Cupric Chlorides in Hydrochloric Acid Solution. G. POMA (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 133—138).—Cuprous chloride dissolves in a solution of cupric chloride in hydrochloric acid, forming a brown solution, from which water re-precipitates cuprous chloride. The solubility of cuprous chloride in solutions containing the same amount of hydrochloric acid is approximately proportional to the concentration of the cupric chloride, the proportionality being best seen in strongly acid (4*N*) solutions. The results indicate the formation of cuprous-cupric salts.

C. H. D.

Constitution of the Cuproso-cupric Chloro-salts. G. POMA (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 192—197. Compare preceding abstract).—The specific conductivity of a 3*N*-solution of hydrochloric acid is not notably altered by the addition of cupric or cuprous chloride, or both. By measuring the oxidation and reduction potentials at an electrode of platinised platinum in such a solution, it is found that as the concentration of cupric chloride is increased, that of cuprous copper increases enormously, whilst the number of cuprous ions in the solution shows only a very small increase, indicating that the cuprous copper is present in a complex ion, the cupric copper being free. Transport experiments show that the brown substance travels to the anode, the liquid round the cathode becoming green. The complex anion probably contains Cu^{II} as well as Cu^{I} . The investigation is being continued.

C. H. D.

An Apparatus for the Purification of Mercury. L. JUNIUS DESHA (*Amer. Chem. J.*, 1909, 41, 152—155).—The form of the apparatus, which, with the exception of the india-rubber stopper *D*, is entirely of glass, will be understood from the diagram. The tube *A* is 22 mm. in diameter and 90 cm. long; *B* is 35 cm. long and of the same diameter; *C* and *F* are of thick-walled capillary tubing 1.5 mm. in bore; *C* is 200 cm. long, and *F*, 76 cm. long; *E* is 20 mm. in diameter and 15 cm. long. Into the bottom of the mercury trap, *G*, a capillary tube, *H*, the lower end of which is blown into a small bulb pierced with several very small holes, is fused. The action of the apparatus is as follows. Mercury, sufficient (or excess) to cover the lower end of the tube *C*, is poured into *B*, and the remainder of *A* is filled with 1% nitric acid. After filling the mercury trap *G* with mercury, *K* is connected to a suction pump, and the stopcock, *L*, is adjusted so that alternate small portions of mercury and air are drawn up the tube *C* into *E*. Mercury is, of course, simultaneously drawn up into *F* to



balance that in *C*. The mercury so transferred to *E* gradually falls into the trap *G*, and thence through the fine holes in the lower end of the tube *H* into the column of dilute nitric acid in *A*.

The apparatus is obviously quite automatic, and the mercury can be passed through the cleansing solution any desired number of times by leaving the apparatus working a sufficient length of time.

E. H.

Copper Complexes in Ammoniacal Solution. HARRY M. DAWSON (*Ber.*, 1909, 42, 720—726. Compare *Trans.*, 1900, 77, 1239; Hantzsch and Robertson, this vol., ii, 44).—The copper tetrammine complex, $\text{Cu}(\text{NH}_3)_4$, is shown not to be so stable as Hantzsch and Robertson imagine, and the author, whilst admitting that the spectrophotometric method of these authors is satisfactory for the examination of ammoniacal copper solutions rich in ammonia, claims that his partition-coefficient method is simpler and gives more accurate results for solutions in which the concentration of the ammonia is relatively small.

C. S.

Double Salts of Mercuric Iodide. ANDRÉ DUBOIN (*Ann. Chim. Phys.*, 1909, [viii], 16, 258—288).—A résumé of work already published (compare *Abstr.*, 1905, ii, 637; 1906, ii, 85, 231, 286, 359, 544, 673; 1907, ii, 955; 1908, ii, 598). A second *thorium mercuric iodide*, $\text{ThI}_4 \cdot 2\text{HgI}_2 \cdot 12\text{H}_2\text{O}$, is described.

M. A. W.

Revision of the Atomic Weights of the Rare Earths. GEORGES URBAIN (*Bull. Soc. chim.*, 1909, [iv], 5, 133—172).—This paper forms Urbain's contribution to the work of the "International Committee on Atomic Weights," and gives a résumé of the data on which the 1909 "International Atomic Weights" for the following elements are based, namely, cerium, dysprosium, erbium, europium, gadolinium, lanthanum, lutecium, neodymium, ytterbium (neoytterbium), praseodymium, samarium, scandium, terbium, thulium, yttrium. It is also pointed out that holmium probably has an atomic weight between 162.5 and 167, but that the homogeneity of this substance is not yet satisfactorily established.

T. A. H.

Thermal Phenomena which Accompany the Action of Water on Aluminium Powder. ÉMILE KOHN-ABREST and J. CARVALLO (*Compt. rend.*, 1909, 148, 410—413).—The oxidation of aluminium powder by water is accompanied by an evolution of 45,000 cal. per gram-atom of aluminium, and subsequently by a slow absorption of heat as the oxide becomes hydrated. The grains in the resulting powder contain 23.1% of water and a core of unoxidised aluminium. The estimation of water is found to be complicated by the fact that oxidation takes place on heating, and a measurable amount of hydrogen is evolved.

The ratio of oxygen to combined aluminium is somewhat less than that required by the formula Al_2O_3 , whence the conclusion is drawn that a lower oxide is present. Confirmation is found in the fact that

the hydrogen evolved by the action of hydrochloric acid on the powder is more than equivalent to the ferric sulphate the powder can reduce.

R. J. C.

Examination of an Old Devitrified Glass which had become Violet in Colour under the Influence of Solar Radiation. DELACHANAL (*Compt. rend.*, 1909, 148, 639—640).—When heated to a temperature corresponding with complete fusion, 100 grams of the glass evolved about 70 c.c. of gas, most of which was absorbed by a solution of potash, the small remainder consisting of oxygen and nitrogen. A crystalline sublimate which was obtained consisted chiefly of sodium chloride with smaller quantities of potassium sulphate, arsenious oxide, and sodium sulphate.

H. M. D.

Solubility of Manganese Sulphate in Mixtures of Water and Alcohol. FRANS A. H. SCHREINEMAKERS (*Chem. Weekblad*, 1909, 6, 136—139. Compare Cuno, *Abstr.*, 1908, ii, 160).—The solubility of manganese sulphate in mixtures of water and alcohol in various proportions has been determined at 25° and 50°, and tables showing the percentages of water, alcohol, and manganese sulphate in the solutions are given.

A. J. W.

Double Salts of Ammonium Sulphate and Manganese Sulphate. FRANS A. H. SCHREINEMAKERS (*Chem. Weekblad*, 1909, 6, 131—136. Compare Cottrell, *Abstr.*, 1901, ii, 12).—At 25° the following double salts of ammonium and manganese have been isolated; $2\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 11\text{H}_2\text{O}$; $\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$; $\text{MnSO}_4 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. At 50°, the following have been isolated: $3\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}$; $2\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$; $\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$.

A. J. W.

The Hardening and Tempering of Iron and Steel. ED. MAURER (*Metallurgie*, 1909, 6, 33—52).—The hardness of steel quenched from 800° is only slightly altered by heating until nearly 400°, when a rapid fall takes place. Pure austenite (*Abstr.*, 1908, ii, 489) is little harder than annealed iron; its hardness is increased by heating to 400°, owing to its conversion into martensite. Above this temperature it behaves like other hardened steels. The curves of remanent magnetism show a marked maximum at 450°. Pure austenite shows a large increase of magnetism when heated to 450° or when cooled in liquid air.

The electrical resistance falls with increasing tempering temperature, becoming constant after 300°. The changes in resistance, unlike those in the other physical properties, are due to the hardening carbon, as is shown by experiments with pure iron.

The thermal and microscopic examination shows that γ -iron may occur in hypoeutectoid steels if the quenching temperature is not below 1000°. It is also produced by mechanical deformation in the cold.

The hardness is not due to carbon, but to the presence of allotropic forms of iron. A hypothetical explanation of all the facts

is proposed, based on the formation of solid solutions of the different modifications of iron, with and without carbon. C. H. D.

The Precipitation of Nickel Sulphide from Aqueous Solutions. ALFRED THIEL and H. OHL (*Zeitsch. anorg. Chem.*, 1909, 61, 396—412).—The addition of ammonium sulphide to dilute solutions of nickel salts only produces a brown coloration after an interval. The effect is not due to supersaturation. The velocity of precipitation increases with the concentration of the reacting substances and with the temperature. Both ammonia and acids delay the precipitation.

It is assumed that the first product of the reaction is the simple sulphide, NiS. A precipitate is only produced immediately when the solubility product for NiS is exceeded. In other cases the NiS remains in solution, slowly polymerising to $(\text{NiS})_x$, which is less soluble. The brown liquid is a colloidal solution. By precipitating a nickel solution with an excess of colourless ammonium sulphide and rapidly filtering, a clear solution may be obtained, which gradually becomes brown, confirming the above explanation.

The precipitation of nickel by dimethylglyoxime or potassium thiocarbonate is instantaneous. C. H. D.

Nature of the Metatungstates and the Existence of Rotatory Power in Crystals of Potassium Metatungstate. H. CORAUX (*Compt. rend.*, 1909, 148, 633—636).—A new formula is suggested for the metatungstates in order to express the isomorphous relationships which are exhibited by corresponding borotungstates and metatungstates. The barium salts are formulated as

$5\text{BaO}(\text{B}_2\text{O}_3, 24\text{WO}_3), 54\text{H}_2\text{O}$ and $6\text{BaO}(3\text{H}_2\text{O}, 24\text{WO}_3), 54\text{H}_2\text{O}$ respectively. According to these formulæ the molecular proportion of barium oxide is different in the two isomorphous salts. A similar difference is found when the potassium salts are compared. A new hydrated potassium metatungstate of the composition



has been isolated, which is not only isomorphous with the corresponding borotungstate and silicotungstate, but, as in these cases, the crystals exhibit dextrorotatory power. To bring out this above relationship the metatungstate is formulated as $6\text{K}_2\text{O}(3\text{H}_2\text{O}, 24\text{WO}_3), 36\text{H}_2\text{O}$, corresponding with the borotungstate, $5\text{K}_2\text{O}(\text{B}_2\text{O}_3, 24\text{WO}_3), 36\text{H}_2\text{O}$, and the silicotungstate, $4\text{K}_2\text{O}(2\text{SiO}_2, 24\text{WO}_3), 36\text{H}_2\text{O}$. The continuous series of compounds thus formulated is completed by the phosphotungstate, $3\text{K}_2\text{O}(\text{P}_2\text{O}_5, 24\text{WO}_3), 36\text{H}_2\text{O}$. H. M. D.

Analogies of Uranium with Other Elements. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1909, 175—176).—The parallelism existing between the uranates, $\text{R}'_2\text{UO}_4$, diuranates, $\text{R}'_2\text{U}_2\text{O}_7$, peruranates, $\text{R}'_2\text{UO}_5$, and the chromates, $\text{R}'_2\text{CrO}_4$, dichromates, $\text{R}'_2\text{CrO}_7$, and perchromates, $\text{R}'_2\text{CrO}_5$, is pointed out, and suggested as a confirmation of the formulæ of the peruranates. It also supports Moissan's view that perchromic acid is to be regarded as a true combination of chromic anhydride and hydrogen peroxide: $\text{CrO}_3 + \text{H}_2\text{O}_2 = \text{H}_2\text{CrO}_5$. Moreover, diuranic acid, $\text{H}_2\text{U}_2\text{O}_7$, is analogous to

dichromic and disulphuric ($\text{H}_2\text{S}_2\text{O}_7$) acids, and to a certain extent to pyrophosphoric, $\text{H}_4\text{P}_2\text{O}_7$, pyroantimonic, $\text{H}_4\text{As}_2\text{O}_7$, and pyrobismuthic, $\text{H}_4\text{Bi}_2\text{O}_7$, acids. E. H.

Uranates. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1909, 173—175. Compare Abstr., 1905, ii, 38).—Since the publication of previous work, the author has come to the conclusion that the formation of uranates by the action of alkalis on uranyl chloride is to be represented generally by the equation: $\text{UO}_2\text{Cl}_2 + 2\text{M}_2\text{O} = 2\text{MCl} + \text{M}_2\text{UO}_4$, M representing an atom of a univalent metal. If the reaction takes place in the presence of air, however, peruranates ($\text{UO}_5\text{M}'_2$ and $\text{UO}_5\text{M}''$) are formed, thus: $2\text{UO}_2\text{Cl}_2 + 4\text{K}_2\text{O} + \text{O}_2 = 4\text{KCl} + 2\text{K}_2\text{UO}_6$. The latter are various shades of red in colour, being thus distinguished from the uranates and diuranates, which are yellow or orange; they agree in properties and reactions with the salts described by Pissarjewsky and Melikoff (Abstr., 1898, ii, 165), and when heated for some time at the temperature of fused potassium hydroxide, lose oxygen, and are transformed into uranates. The peruranates of potassium, sodium, and barium have been obtained; that of calcium could not be obtained free from the uranate. E. H.

Explanation of a Contradiction connected with the Constitution of Alloys of Tin and Lead. W. GUERTLER (*Zeitsch. Elektrochem.*, 1909, 15, 125—129).—The electrical conductivity of alloys of tin and lead is a linear function of the composition, which is interpreted to mean that the metals form neither compounds nor mixed crystals. On the other hand, the study of the heat evolved on solidification (Stoffel, Abstr., 1907, ii, 357; Kurnakoff and Schemtschuschny, Abstr., 1908, ii, 932) indicates that mixed crystals are formed from 0 to about 10% of tin and from about 99.5 to 100%. The thermal data refer to the eutectic temperature (183°), whilst the conductivity data refer to temperatures below 150° . The author thinks it probable that the mixed crystals which exist at 180° decompose at lower temperatures into tin and lead; that some change occurs is proved by a small, but distinct, development of heat, which occurs about 150° . T. E.

Tin Phosphides. PIERRE JOLIBOIS (*Compt. rend.*, 1909, 148, 636—638).—The compounds formed by tin and phosphorus have been investigated by metallographic examination of the solid products obtained on cooling various fused mixtures of the two elements. Alloys, in which the percentage of phosphorus varies from one to thirteen, contain the phosphide Sn_4P_3 ; this was isolated by making the alloy the positive pole in a solution of sodium polysulphide. In these circumstances the uncombined tin dissolves in the solution, whereas the crystals of the phosphide are not acted on. The phosphide has a silver-white colour, and crystallises in small spangles; D^{20}_D 5.18, and it begins to dissociate at 480° . It is oxidised by warm nitric acid; hydrochloric acid decomposes it with the evolution of hydrogen and a mixture of the hydrides of phosphorus; it is also

acted on by a warm solution of potassium hydroxide with the formation of hydrogen phosphide.

Fused mixtures containing more than 13% of phosphorus can be obtained by heating under pressure. By acting on the products obtained from such mixtures with hydrochloric acid, warm sodium hydroxide solution, and finally with dilute nitric acid at 50°, the phosphide SnP was isolated. This is crystalline, has a metallic appearance, D_4^{20} 4.10, and it begins to dissociate into phosphorus and the phosphide Sn_4P_3 at 415°. It is acted on violently by fuming nitric acid.

H. M. D.

Thorium. RICHARD J. MEYER (*Zeitsch. Elektrochem.*, 1909, 15, 105—106. Compare this vol., ii, 53).—Replying to Karstens (this vol., ii, 243), the author still believes that von Bolton's thorium contained oxide.

T. E.

Electrolytic Production of Tin. A. J. M. THIROT (D.R.-P. 203519).—Tin is deposited electrolytically in a coherent deposit from a moderately concentrated solution of sodium stannate, providing that just sufficient sodium sulphide is added to precipitate other metals, such as lead and copper, and that the bath is maintained at 80° and the current density at 300 to 400 amperes per square metre.

G. T. M.

Hydrolysis of Bismuth Halides. WALTER HERZ and ALFRED BULLA (*Zeitsch. anorg. Chem.*, 1909, 61, 387—395).—Bismuth chloride was shaken with varying quantities of water for twenty-four hours at 25°, the bismuth and hydrogen chloride in the solution being then estimated. The relation $[\text{BiCl}_3]/[\text{HCl}]^2 = \text{const.}$ holds good over a considerable range of dilution. Alkali chlorides increase the solubility of bismuth chloride. Bromides have a greater influence than chlorides, and nitrates less, in reducing the hydrolysis; sodium sulphate is practically without influence.

Bismuth bromide behaves in the same manner as the chloride. The only basic compounds resulting from the hydrolysis are BiOCl and BiOBr .

Bismuth iodide reacts so slowly with water that equilibrium is hardly to be reached at 25°; experiments are therefore to be made at higher temperatures. Bismuth fluoride is not hydrolysed either by cold or by boiling water.

C. H. D.

Bismuth Hydroxide and Its Behaviour towards Alkalis. L. MOSER (*Zeitsch. anorg. Chem.*, 1909, 61, 379—386).—Bismuth hydroxide, free from basic salts, is best prepared by running a solution of a bismuth salt mixed with glycerol into sodium hydroxide and immediately neutralising almost the whole excess of alkali with dilute nitric or acetic acid. If sulphuric acid is used, as recommended by Thibault (*Abstr.*, 1901, ii, 106), the product contains some basic sulphate. The precipitate, after washing with a little alcohol and drying in air, has the composition $\text{Bi}(\text{OH})_3$, but readily absorbs carbon dioxide. Over sulphuric acid, water is given off continuously, an arrest at the composition $\text{BiO}\cdot\text{OH}$ not being observed.

In contact with alkaline solutions, the orthohydrate passes over into the more stable, yellowish-white metahydrate, $\text{BiO}\cdot\text{OH}$. On exposure to light the metahydrate obtained in the wet way, but not that prepared by heating the orthohydrate, is converted into a grey modification having the same composition. This grey substance is obtained as an intermediate stage in the conversion to oxide by gentle heat. Bismuth oxide also exists in several modifications (Guertler, *Abstr.*, 1904, ii, 130).

The solubility of bismuth hydroxide in alkalis has also been estimated, the bismuth content of the solutions being determined by Planes' colorimetric method (*Abstr.*, 1904, ii, 93). At 20° , freshly precipitated bismuth hydroxide is practically insoluble in sodium hydroxide up to $N/1$, slightly soluble in solutions up to $4N/1$, and markedly so in more concentrated solutions. At 100° the solubility is greater, although still small in dilute solutions.

C. H. D.

Compounds of Gold with Bromine. FERNAND MEYER (*Compt. rend.*, 1909, 148, 346—348. Compare Lengfeld, *Abstr.*, 1902, ii, 27).—The direct action of excess of bromine on precipitated gold gives rise to a film of auric bromide, AuBr_3 , which prevents further action of the bromine. If, however, precipitated gold is continuously shaken with bromine for twelve hours, or alternately heated with it to 100° and cooled, it is entirely converted into auric bromide, which is soluble in excess of bromine and can be obtained pure in black crystals attaining to 6 mm. in length.

The product obtained by subjecting gold to the prolonged action of bromine dissolved in carbon tetrachloride in such proportion as to give AuBr_2 is a black powder without definite properties, and is doubtless a mixture of gold with aurous and auric bromides. When auric bromide is heated to its dissociation temperature, bromine distils off and aurous bromide, AuBr , a green substance, remains. At a higher temperature this dissociates into its elements.

The dissociation curves of aurous bromide and auric bromide have been studied, but no evidence of the existence of the compound AuBr_2 could be obtained. Auric bromide is volatile in an atmosphere of bromine at 300° .

R. J. C.

Melting Point of Platinum. C. FÉRY and C. CHÉNEVEAU (*Compt. rend.*, 1909, 148, 401—404).—The melting point of platinum has been variously stated at temperatures varying from 1706° to 1855° , a recent research (Waidner and Burgess, *Abstr.*, 1907, ii, 882) indicating the value 1753° .

The authors have determined the melting point of platinum heated in a variety of ways. The optical pyrometer was employed, and as Wien's law only holds for radiation from black surfaces, it was necessary to determine the emissive power of platinum, which is a function of the temperature. A horizontal platinum wire, heated electrically, broke at 1690° , somewhat below its true melting point. A vertical wire fused into a drop at 1710° . A platinum wire held vertically in the flame of a Meker burner fused into a bead at 1740° . In

the coal-gas oxygen flame the temperature of fusion lay between 1700° and 1750°, according as an oxidising or reducing flame was employed.

The conclusion is drawn that the melting point of platinum, like that of silver, depends on the nature of the atmosphere in which fusion takes place. R. J. C.

Nature of the Platinum-Lead Alloys. NICOLAI A. PUSHIN and P. N. LASCHTSCHENKO (*Zeitsch. anorg. Chem.*, 1909, 62, 34—39; *J. Russ. Phys. Chem. Soc.*, 1909, 41, 23—28).—The electric potential of platinum-lead alloys was measured against lead in a *N/1* lead nitrate solution. Up to 33 atomic % Pt, the alloys have the same potential as pure lead. At that point a sudden fall occurs, indicating the existence of a compound Pb_2Pt . A second fall occurs at 50 atomic % Pt, corresponding with the compound $PbPt$. Both these compounds have been recognised by the freezing-point and microscopic methods (Doerinkel, *Abstr.*, 1907, ii, 785), although the composition of the former compound could not be determined with certainty. The third compound found by Doerinkel, richer in platinum than $PbPt$, is not recognisable by the electrolytic method, as the potential of $PbPt$ is already near that of pure platinum. C. H. D.

Solid Solutions in the Dissociation of the Oxides of Platinum. LOTHAR WÖHLER and W. FREY (*Zeitsch. Elektrochem.*, 1909, 15, 129—142).—When platinumous hydroxide was heated in a vacuous tube (containing phosphoric oxide) at 400°, oxygen was not evolved. After twelve hours the product contained metallic platinum, which was removed by means of *aqua regia*, leaving an oxide with 9.02% of oxygen; two and a-half days' heating gave a similar residue with 9.47% of oxygen. Platinumous oxide contains 7.6% of oxygen.

In other experiments at 450° to 470°, oxygen was evolved, and the residue, after extraction of platinum, contained from 9.5 to 10.3% of oxygen. It appears, therefore, that platinumous oxide decomposes into platinum and platinum dioxide, which dissolves in the monoxide, lowering its dissociation tension.

For example, a sample of the monoxide heated at 510° gave a pressure of 752 mm., which diminished in forty hours to 203 mm.

When platinum dioxide was heated at 510—515° in a vacuum until its oxygen content (14.1%) was diminished below that of the monoxide (7.6%), the residue contained much metallic platinum; after removing this with *aqua regia*, the residual oxide contained 13.0 to 13.2% of oxygen. When the quantity of oxygen removed was less, so as to leave a substance with approximately the composition of platinum sesquioxide, the result was the same; the oxide remaining after extraction of metallic platinum contained 13.33% of oxygen. It is shown that platinumous oxide (dried at 120—150°) is not oxidised by *aqua regia*. It appears, therefore, that platinum dioxide dissociates into the metal and a solid solution of either the monoxide or sesquioxide in the dioxide.

The equilibrium pressures could not be measured, owing to the extraordinary slowness of the reactions. The oxides may be heated for days at temperatures 150° to 200° above the temperature corre-

sponding with equilibrium without losing oxygen. The metal takes up oxygen equally slowly. The dissociation pressures of the monoxide and sesquioxide are, however, higher than that of the dioxide.

The rate of evolution of oxygen from the dioxide at constant temperature exhibits remarkable features. The evolution begins slowly, then becomes very rapid, and finally diminishes gradually. The rapid evolution begins (at 514—520°) when the oxygen content of the oxide has fallen to 11·6 to 12%. It is thought that a supersaturated solution of monoxide or sesquioxide in the dioxide is first formed, and when this has reached a certain concentration it decomposes suddenly. T. E.

Ruthenium and its Compounds. ALEXANDER GUTBIER (*Zeit. angew. Chem.*, 1909, 22, 487—493. Compare Abstr., 1905, ii, 463).—Previous to undertaking a determination of the atomic weight of ruthenium, a study has been made of the behaviour of some of its compounds, more especially the tetroxide and the chloride.

The tetroxide was first prepared by Claus (*Bull. Acad. Sci. St. Petersburg*, 1859, [ii], 1, 97), who fused the element with potassium nitrate and potassium hydroxide in a silver dish and treated the salt thus obtained with water and passed chlorine through the warmed solution, obtaining the volatile tetroxide in the distillate. This method of preparation, and, indeed, the apparatus described by Claus, has been found to be the best at present known. The quantities used and details of the operation are given in the present paper. Howe (Abstr., 1902, ii, 86) has described a method of preparation, making use of a nickel crucible and sodium peroxide, but it is found that an appreciable quantity of nickel becomes dissolved and is difficult to separate. The tetroxide was obtained by Claus' method as a yellow oil which solidified to a crystalline mass when cooled; the vapour vigorously attacks cork and rubber, and is very poisonous.

Ruthenium tetroxide was purified by repeatedly shaking with warm water to remove all traces of chlorine, separating as completely as possible from water, and finally subliming several times in a vacuum, when it was obtained in beautiful crystals.

Ruthenium chloride, RuCl_3 , has been prepared by treating the tetroxide with 20% hydrogen chloride solution, and placing it in a cooling mixture, under reduced pressure, for two hours. The solution thus obtained was freed from chlorine and unaltered oxide, and concentrated to a syrup by drawing a current of dry air over the warmed liquid. It was then left over concentrated sulphuric acid in an evacuated desiccator until it solidified to an almost black, crystalline mass.

This solid substance becomes liquid when in contact with the atmosphere, and dissolves in dilute aqueous or alcoholic hydrogen chloride, developing an intense purple-red colour. J. V. E.

Mineralogical Chemistry.

Iodyrite from Tonopah, Nevada. EDWARD H. KRAUS and C. W. COOK (*Amer. J. Sci.*, 1909, [iv], 27, 210—222).—A crystallographic description is given of material from this new locality for the mineral. The crystals occur on quartz and measure 1—5 mm. in length; they are pronouncedly hemimorphic in development, and show combinations of the basal plane, hexagonal prism, and several new hexagonal pyramids: $a:c=1:0.8204$. Etching figures, produced by a strong solution of sodium chloride, indicate that the symmetry is that of the dihexagonal-pyramidal class. Analysis gave: Ag, 45.95%; I, 54.01%; D 5.51. Crystals from Broken Hill, New South Wales, are also described. L. J. S.

Talc from Kossoi-Brod, Urals. L. L. IVANOFF (*Zeitsch. Kryst. Min.*, 1909, 46, 221; from *Bull. Soc. Nat. Moscou*, 1906, Nos. 1 and 2, 156—160).—Analysis gave:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ , FeO.	MgO.	H ₂ O.	Total.	Sp. gr.
60.37	1.79	3.13	28.71	5.18	99.18	2.805

Hydrochloric acid extracted SiO₂, 0.58; Fe₂O₃ + FeO, 0.88; MgO, 2.86%. L. J. S.

Physiological Chemistry.

Catalase of the Blood. GEORG LOCKEMANN, J. THIES, and HEINRICH WICHERN (*Zeitsch. physiol. Chem.*, 1909, 58, 390—431).—Sodium chloride inhibits the decomposition of hydrogen peroxide by light, especially by feeble light. The estimation of catalase in the blood by Jolles' method gives the same results if blood is diluted with physiological salt solution or laked with water. Sodium chloride inhibits the catalase action, especially if water has been added; sodium sulphate has scarcely any action. Ferrous ammonium sulphate, ferric ammonium sulphate, and ferric chloride inhibit the decomposition of hydrogen peroxide and the catalase action on blood in the order named, the least active being placed first. Many experiments on the influence of temperature on the reaction-velocity of catalase action are given. White light inhibits the action, then blue and red, red being the least active. Röntgen rays do not affect it. W. D. H.

Part played by the Dissociation of Carbophosphates in Nature. A. BARILLÉ (*Compt. rend.*, 1909, 148, 344—346. Compare Abstr., 1902, ii, 258; 1904, ii, 27).—Soluble carbophosphates, which are formed by the action of carbon dioxide under pressure on normal

phosphates, dissociate into hydrogen carbonates and monohydrogen phosphates (M_2HPO_4) in the air.

The production and decomposition of carbophosphates in the blood can give rise to phosphatic calculi, which always contain calcium carbonate as well as calcium phosphate. The carbon dioxide in venous blood is possibly held as sodium carbophosphate, which dissociates in the lungs. Acidic urine contains the carbophosphates of calcium and magnesium, which dissociate on heating, giving a turbidity. Thus the utility of carbonated mineral waters in phosphaturia depends on the formation of soluble carbophosphates. The occurrence of crystalline dimetallic phosphates in fossil bones and in a human skull which was found in a sealed lead coffin, as well as the formation of such natural phosphates as coprolite, are explained on a similar basis. It is supposed that soluble carbophosphates from atmospheric carbon dioxide and the insoluble phosphates of soil play an important part in plant nutrition.

R. J. C.

Parthenogenesis. ISIDOR TRAUBE (*Biochem. Zeitsch.*, 1909, 16, 182—186).—The theory of osmotic pressure described previously (Abstr., 1908, ii, 565) is applied more fully to the case of parthenogenesis. The relationship between the surface-tension of various acids and their parthenogenetic activity is clearly brought out, the values for the capillarity constants previously obtained (Abstr., 1891, 1408) being used for this purpose.

It is also pointed out that substances like chloroform, benzene, toluene, benzoic acid, saponine, solanine, and salts of gallic acid, which, according to Loeb, produce a membrane when added to seawater, also lower the surface-tension of water. The salts of fatty acids are less active than the fatty acids themselves, and it is shown that they produce a smaller lowering of surface-tension than the acids.

Loeb's views that the partition-coefficient, according to Overton, and the velocity of osmosis are primary factors, are not accepted. Neither is the view that the activity of strong mineral acids which are insoluble in lipoids is due to the liberation by these of free fatty acids from salts of these acids contained in the envelope of the egg.

According to the author, it is necessary that the acids in question diffuse or are adsorbed into the surface of the egg, but it is immaterial whether they are dissolved by the lipoids, as in the case of the higher fatty acids, or whether they are dissolved by the aqueous colloidal phase, as in the case of dibasic acids. A secondary factor is the rate of diffusion or adsorption.

The fundamental factor is the difference in capillary pressure between the surface of the egg and the surrounding aqueous medium produced by the diffusion or adsorption.

J. J. S.

Digestion of Mannans and Galactans. H. BERRY and J. GIAJA (*Compt. rend.*, 1909, 148, 507—510).—The mannans and galactans of various seeds (*Medicago*, *Trigonella*, *Phytelphas*, *Phoenix*) are not digested by the higher animals, but are converted into mannose and galactose by the digestive juice of species of snails (*Helix*) and of certain *Crustacea*.

G. B.

Gastric Digestion of Human and Asses' Milk. LOUIS GAUCHER (*Compt. rend.*, 1909, 148, 361—363).—By working with dogs provided with a duodenal fistula, it is found that both these kinds of milk pass through the stomach twice as fast as cow's milk. In the stomach the casein is not peptonised in any of the three cases. The greater digestibility of human milk is due to its clotting in small flakes; the milk of the ass forms a clot of slight consistency; in either case the evacuation of the stomach takes place with the minimum of mechanical work. G. B.

Comparative Digestibility of Proteins in Gastric Juice. WILLIAM N. BERG (*Amer. J. Physiol.*, 1909, 23, 420—459).—Under uniform conditions, proteins are digested with unequal speed. The order of digestibility in gastric juice is as follows, the most easily digestible being placed first: edestin, myosin, alkali-albumin, acid albumin, fibrin, coagulated egg-white, ossein, nucleo-protein, tendo-collagen, elastin, tendo-mucoid. W. D. H.

Normal Digestion of Proteins in the Dog's Alimentary Canal. V. EMIL ABDERHALDEN, E. S. LONDON, and E. B. REEMLIN. VI. EMIL ABDERHALDEN, FLORENTIN MEDIGRECEANU, and E. S. LONDON (*Zeitsch. physiol. Chem.*, 1909, 58, 432—434, 435—437. Compare Abstr., 1908, ii, 514).—Experiments *in vitro* have shown that certain amino-acids are more readily split off than others from the protein molecule by ferment action. The same occurs in the alimentary canal, and can be tested in dogs with fistulæ in appropriate positions; thus from gliadin, tyrosine cannot be detected in the ileum, whereas glutamic acid is still present. The early splitting off of tyrosine, and the later of glutamic acid, is also true for edestin.

The second paper deals with confirmatory results obtained by feeding on casein and egg-albumin. W. D. H.

Absorption Experiments on Dogs with Intestinal Fistulæ. KAORU OMI (*Pflüger's Archiv*, 1909, 126, 428—452).—The dogs employed had various forms of intestinal fistulæ, as in Pawloff's experiments. The quantity of sodium chloride, dextrose, sucrose, and peptone absorbed in the small intestine varies with the concentration of the solutions, whilst that of water varies inversely with the concentration. The secretion of alkali by the intestinal wall bears no relationship to absorption. The absorption of sodium chloride and peptone is less in the jejunum than in the ileum, whilst that of the sugars is better in the ileum than in the jejunum. The secretion of alkali is always smaller in the jejunum than in the ileum. Some preliminary experiments on the absorption of serum from the intestine are also described; a foreign serum (of ox or horse) is worse absorbed by the dog than is dog's serum. The foreign serum acts as a stimulus to intestinal secretion. This property disappears under the influence of the action of pancreatic extracts. W. D. H.

Action of Intestinal Lipase. ANT. HAMSIK (*Zeitsch. physiol. Chem.*, 1909, 59, 1—13).—The powdered intestinal mucous membrane

of the pig, sheep, and horse possesses the property of synthesising triolein from oleic acid and glycerol, whilst that of the dog and ox does not.

W. D. H.

Metabolism in Man with Greatly Diminished Lung Area. THORNE M. CARPENTER and FRANCIS G. BENEDICT (*Amer. J. Physiol.*, 1909, 23, 412—419).—A full account is given of an experiment on a man in the respiration calorimeter. The man had completely lost one lung, and yet his absorption of oxygen and elimination of carbon dioxide had not materially altered. Previous experiments on animals by Hedin have shown that a corresponding reduction of the lung area has no appreciable effect on gaseous exchanges. This is another instance of the liberal scale on which the animal body is constructed.

W. D. H.

Metabolism in Various Classes of Animals. I. EMIL ABDERHALDEN, CARL BRAHM, and ALFRED SCHITTENHELM (*Zeitsch. physiol. Chem.*, 1909, 59, 32—34).—A striking distinction of metabolic difference is seen in animals so closely related as the cat and dog; the latter animal secretes kynurenic acid, whereas the cat does not, tryptophan being differently catabolised in that animal.

It is found that after feeding a dog on pyridine, the urine contains methylpyridonium hydroxide. The present research confirms this statement, but in the rabbit the same change does not take place; pyridine passes unchanged into the urine.

W. D. H.

The Value of Protein Cleavage Products in Metabolism. IX. EMIL ABDERHALDEN, EMIL MESSNER, and HEINRICH WINDRATH (*Zeitsch. physiol. Chem.*, 1909, 59, 35—42. Compare Abstr., 1908, ii, 1051).—Details are given of metabolism experiments on dogs fed on the cleavage products of casein obtained by the successive action of gastric, pancreatic, and intestinal juices. Although vomiting, as in former cases, was produced after about a week's feeding in some dogs, they remained in equilibrium or even put on nitrogen. No carbohydrate, but only fat, was given in addition to the protein cleavage products.

W. D. H.

The Effect of Subcutaneously-administered Urea on Metabolism. ERNST HEILNER (*Zeitsch. Biol.*, 1909, 52, 216—235).—The administration of urea subcutaneously in rabbits increases nitrogenous metabolism, so that more nitrogen is discharged than can be accounted for in the urea given. This, however, only occurs if the urea is dissolved in physiological saline solution. Hypodermic injection of an aqueous solution of urea produces no effect. Injection of distilled water alone lessens nitrogenous metabolism considerably.

W. D. H.

Fat Synthesis in the Epithelium of the Frog's Intestine during Fat Resorption. ALFRED NOLL (*Arch. Anat. Physiol., Physiol. Abth.*, 1908, Suppl., 145—160, Reprint).—Various fats, fatty acids, and soaps were introduced into the intestines of frogs, and after

forty-eight hours the tissues were examined histologically; the solubility in various organic solvents of the fat drops found therein was determined, sometimes directly and sometimes after treatment of the tissues with 5% potassium hydroxide solution; the solubility of the drops after treatment with osmic acid was also investigated. From the differences of the behaviour of fatty acids and fats under these conditions, the conclusion was drawn that fatty acids do not exist in the free form in the cells, but that synthesis of fats takes place in the epithelium. The product obtained when olein is introduced is different from that obtained after introduction of oleic acid. In the former case the drops appeared to consist of pure olein, the cells using the glycerol of the olein for synthesis; in the latter case the oleic acid was in combination with some other component produced by the cells themselves.

S. B. S.

Carbohydrate Ferments in Lepidoptera and Diptera in Different Stages of Development. J. STRAUS (*Zeitsch. Biol.*, 1908, 52, 95—106).—A number of flies and butterflies were investigated; it will be sufficient to give the results in *Bombyx mori* as a sample of the sort of results obtained; this was worked out more thoroughly than the others. In the feeding larva, diastase, invertase, lactase, raffinase, and inulinase were present; in the non-feeding stage inulinase was present; diastase and invertase were present in small amount, and the remainder were absent; in the pupa ten days old there was no inulinase; otherwise the enzymes were the same as in the non-feeding larva; when fourteen days old they were the same, except that a little maltase was present; when eighteen days old there was no diastase and no maltase; otherwise they were the same as when ten days old. In the imago there was glycogen diastase, and a questionable amount of starch diastase; invertase was present, but no lactase or inulinase.

W. D. H.

The Rôle of the Small Intestine in Glycogen Formation. ALFRED C. CROFTAN (*Pflüger's Archiv*, 1909, 126, 407—415); EDUARD PFLUGER (*ibid.*, 416—427).—Croftan states that if dextrose is given by the alimentary canal, glycogen is increased in the liver. If administered by way of a mesenteric vein, there is no such increase. The view is advanced that during absorption dextrose undergoes polymerisation, and this renders it possible for the liver to form glycogen.

Pflüger denies the necessity of this preliminary action of the intestinal wall, and criticises Croftan's methods and conclusions.

W. D. H.

Mohr's Work on the Origin of Glycogen from Protein. EDUARD PFLUGER (*Pflüger's Archiv*, 1909, 126, 511—518).—A criticism of Mohr's work. His conclusions are considered to prove nothing.

W. D. H.

Formation of Glycogen from Formaldehyde in the Liver. KARL GRUBE (*Pflüger's Archiv*, 1909, 126, 585—589).—Previous work

has shown that the tortoise's liver is able to form glycogen when perfused by a dilute solution of formaldehyde. H. and A. Euler (*Abstr.*, 1905, i, 633; 1906, i, 140) have shown that in feebly alkaline solutions condensation of formaldehyde to sugar easily occurs, glycollaldehyde being an intermediate product. It has been suggested that the formaldehyde acts merely as a stimulus to the liver to form glycogen from other substances; this, however, cannot be the explanation (or the whole explanation), for other hepatic stimuli (phenol, mercuric chloride, acetic acid, etc.) do not act in the same way.

W. D. H.

The Diastatic Ferment of the Liver. PAUL ZEGLA (*Biochem. Zeitsch.*, 1909, 16, 111—145).—The splitting of glycogen in the liver is due to an intracellular enzyme, and not to one derived from blood or lymph. A study of its quantitative action is possible by several methods, for instance, estimation of the glycogen or of the sugar formed from it. The amount of the ferment decreases after death if the liver is kept in toluene; the loss in the human corpse may reach 60%. Phloridzin- and phloretin-diabetes lead to its increase; the same is true for adrenaline-glycosuria in rabbits, to puncture-diabetes, and after section of the vagi. In pancreatic-diabetes in dogs its amount lessens; with regard to human diabetes, further observations are considered necessary.

W. D. H.

Influence of Lead Salt on Autolysis. LUIGI PRETI (*Zeitsch. physiol. Chem.*, 1909, 58, 539—543).—Small quantities of normal lead acetate or nitrate favour, large quantities hinder, autolysis of the liver. The favouring action referred to increases the yield of monoamino-acids, but retards the formation of proteoses.

W. D. H.

Liver Extracts and Uric Acid. M. ASCOLI and G. IZAR (*Zeitsch. physiol. Chem.*, 1909, 58, 529—538).—If a known amount of uric acid is added to liver extract it disappears, but on passing oxygen through the mixture, it reappears again almost quantitatively. The absence of oxygen favours uric acid destruction.

W. D. H.

The Decomposition of Uric Acid in the Human Body. WILHELM WIECHOWSKI (*Arch. exp. Path. Pharm.*, 1909, 60, 185—207).—Allantoin is not present in the amniotic fluid or in infants' urine. The urine of adults contains mere traces; but if allantoin is given subcutaneously it is mainly excreted unchanged. It is therefore probable that in whatever way uric acid is decomposed in the body, allantoin is not an important intermediate product of catabolism. Experiments with surviving organs show that dog's liver and ox kidney decompose uric acid entirely, but that the human liver and kidney have practically no such power. If uric acid is given subcutaneously, it also appears to undergo no appreciable amount of destruction in the body.

W. D. H.

The Roe of the Perch. Percaglobulin. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1909, 58, 452—453).—Percaglobulin is a

name given to a characteristic protein obtainable from the roe of the *Perca fluviatilis*. So far, search for this protein in other fishes, even those closely related to the one named, has led to negative results.

W. D. H.

The Sodium of Frog's Skeletal Muscle. GEORGE FAHR (*Zeitsch. Biol.*, 1908, 52, 72—82).—The sartorius of the frog placed in sugar solution gains in weight, as it also does in Ringer's solution, whereas Urano (Abstr., 1907, ii, 978) states it loses weight in sugar solution. After a few hours in the latter, it is almost free from sodium, whilst the loss of potassium is trifling.

W. D. H.

The Influence of Chemical Agents on the Affinity of Nerve for Dyes ALFRED FISCHER (*Zentr. Physiol.*, 1908, 22, 591—597).—The observations were made on small water-living copepods and cladocera, and the dye employed was alizarin-blue. A number of reagents and drugs were employed, most of which were fatal. Physostigmine produced paralysis, but did not hinder the dyeing of the nerve. On the other hand, coloration of the nerve was seldom seen if magnesium chloride or caffeine hydrochloride was employed. In potassium nitrate, calcium chloride, chloral hydrate, guanidine carbonate, and quinine hydrochloride, the animals lived longer, but the nerves did not take the stain; the muscles, however, were coloured, which shows the dye had got into the circulation.

W. D. H.

Composition of the Membrane of the Fat Particles of Milk. EMIL ABDERHALDEN and W. VÖLTZ (*Zeitsch. physiol. Chem.*, 1909, 59, 13—18).—This membrane is generally supposed to consist of caseinogen, but an investigation of the cleavage products shows that it is not so. There are quantitative differences in the yield of tyrosine and glutamic acid, and glycine is present, whereas it is absent in caseinogen and lact-albumin. Possibly a mixture of proteins is present in the envelope of the oil globules.

W. D. H.

The Reducing Properties of Milk. Schardinger's Reaction. RICHARD TROMMSDORFF (*Centr. Bakt. Par.*, 1909, i, 49, 291—301).—It is known that milk which contains bacteria possesses strong reducing powers and also that fresh unheated milk gives a colour with Schardinger's reagent (5 c.c. formalin, 5 c.c. saturated alcoholic solution of methylene-blue, and 90 c.c. of water) under suitable experimental conditions. Many hypotheses have been put forward to account for these phenomena. The difficulty of deciding the exact part played by bacteria has hitherto been the impossibility of getting milk free from organisms without having recourse to heat or antiseptics. The author has got over the difficulty by drawing milk from the udder by means of a small catheter; in this way quantities of sterile milk can be obtained without having to treat the milk in any way whatsoever. Such milk shows no reducing action, and is therefore free from the so-called "reductase"; on the other hand, it does colour Schardinger's reagent, but the course of reaction could not be determined.

E. J. R.

Lævulose in Urine. HANS Malfatti (*Zeitsch. physiol. Chem.*, 1909, 58, 544—546).—A discussion of recent work and methods relating to the presence of lævulose in diabetic urine. With care, weakly positive reactions for lævulose are sometimes obtainable.

W. D. H.

Dicalcium Phosphate as a Urinary Sediment. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1909, 58, 440—451).—The occurrence of dicalcium phosphate, $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, in crystalline form as a urinary sediment is comparatively rare. The present paper relates to the form of the crystals and the circumstances which lead to their deposition. The reaction must be neutral, and the amount of calcium in the urine usually in excess; abundance of sodium chloride is also favourable. The deposit can be obtained from many urines by shaking with aniline or with alcohol, and in a larger number by the addition of both reagents (3 c.c. of aniline, and 20 c.c. of 90% alcohol per 100 c.c. of fresh non-alkaline urine).

W. D. H.

Oxygen and Creatinine Excretion. C. J. C. VAN HOOGENHUYZE and H. VERPLOEGH (*Zeitsch. physiol. Chem.*, 1909, 59, 101—111. Compare Abstr., 1908, ii, 971).—Creatine is regarded as a product of protein catabolism, and it is partly destroyed and oxidised and partly converted into creatinine and excreted. Some experiments on dogs are given which show that administration of creatine increases the creatinine output; but the bulk of the paper deals with the influence of oxygen. Inhalation of large quantities of oxygen causes no alteration in the excretion of creatinine. Residence at a great altitude produced very little change; thus in one of the authors (who were on a creatinine-free diet throughout) the daily excretion at Utrecht was 1.839 grams; on Monte Rosa it was 1.903 and 1.965. In the other author the rise was even less.

W. D. H.

Proteic Acids in Urine in Health and Disease. WITOLD GAWIŃSKI (*Zeitsch. physiol. Chem.*, 1909, 58, 454—468; *Bull. Acad. Sci. Cracow*, 1908, 851—853).—A method for the estimation of Bondzynski's proteic acids in urine is described in detail; it depends on the complete insolubility of the barium salts in absolute alcohol.

The effect of diet is negligible; in milk, meat, and mixed diet, the amount of proteic acid nitrogen varies from 4.5 to 6.8% of the total nitrogen. In typhoid fever, this figure rises to 9—14, falling off in the second week of the disease and still more so in the third week. It is also increased in cases of jaundice. Estimations are also given of the various forms in which sulphur is excreted under these conditions.

W. D. H.

The Relative Importance of Inorganic Cations, especially those of Sodium and Calcium in the Causation of Gout and the Production of Gouty Deposits. WILLIAM G. LITTLE (*Bio.-Chem. J.*, 1909, 4, 30—37).—It was found that the following is the order of the solubility of the acid urates of various metals: potassium, most soluble, then sodium, magnesium, and calcium urates. One part of acid calcium urate dissolves in 4760 parts of cold water, whereas

one part of the corresponding sodium salt dissolves in 1030. In the presence of sodium chloride, however, the conditions are quite different, and 3420 parts of 0.5% sodium chloride solution will dissolve one part of calcium urate, whereas sodium urate requires 44,400 parts of the same solution. The addition of small quantities of calcium salts to pure water also diminished the solvent capacity for sodium urate. The significance of these facts in reference to gouty attacks and the formation of gouty tophi is discussed. S. B. S.

Chloride Metabolism in Typhoid Fever. SCHWENKENBECHER and INAGAKI (*Arch. exp. Path. Pharm.*, 1909, 60, 166—184).—If 10 to 20 grams of sodium chloride are given to typhoid patients, a large fraction of the chlorine is retained. This is attributed to various circumstances, such as enfeebled circulation and kidney function, and degenerative processes in the tissues.

On the other hand, many healthy people, taking the same sort of diet as typhoid patients take, show also a slow excretion of chlorides, and certain typhoid patients do not exhibit it at all. W. D. H.

Antagonism between Trisodium Citrate and Calcium in their Action on the Heart and its Inhibitor Nerve Supply. H. BUSQUET and V. PACHON (*Compt. rend.*, 1909, 148, 575—578).—There is a chemical antagonism between trisodium citrate and calcium chloride in their action on the heart and on the vagus nerve. The beating of the frog's heart is stopped by perfusion *in situ* with 0.6% sodium chloride solution containing 0.12% sodium citrate and 0.005% calcium chloride, but is started again when the heart is supplied with a solution containing three times as much calcium chloride. Similarly, the inhibitor effect of vagus stimulation is abolished by perfusing the heart with saline solution containing 0.05% sodium citrate and 0.005% calcium chloride, but is re-established by a saline solution containing the same amount of citrate, but twice as much calcium. G. B.

The Behaviour of Salol and Distearyl Salicylyl Glyceride in the Organism. STANISLAUS BONDZYŃSKI and VINCENTY HUMNICKI (*Bull. Acad. Sci. Cracow*, 1908, 841—851).—The rate of elimination of salicylic acid and phenol in the urine was determined after the ingestion of salicylic acid, salol, and distearyl salicylyl glyceride, the last-named substance being prepared by the action of silver stearate on dichlorohydrin salicylate. It is a product of fat-like nature, m. p. 46—49°. Unlike trisalicylyl glyceride, it is completely resorbed after ingestion. It is found that salicylic acid is eliminated somewhat later after the ingestion of salol and the glyceride than it is after salicylic acid. The phenol is, however, eliminated much sooner (after salol ingestion) than the salicylic acid.

Salicylic acid is estimated in the urine by boiling first with hydrochloric acid, evaporating to dryness the solution after making alkaline with sodium hydroxide, and then extracting the residue with alcohol. After evaporation of the alcohol from this extract, the residue is dissolved in water, the solution thus obtained acidified, and the salicylic acid extracted therefrom by ether. This extract is

dissolved in alcohol, and barium hydroxide in concentrated aqueous solution added. The salicylic acid is thereby precipitated quantitatively as barium salt, from which it is recovered by dissolving the salt in acid and extracting the solution thus obtained with ether.

Phenol was estimated as the tribromo-compound. The author gives the details of the method for separating it from salicylic acid, which depends chiefly on the greater volatility of the former in steam.

S. B. S.

Physiological Action of the Alkaloids of the Papaveraceæ. WORTH HALE (*Amer. J. Physiol.*, 1909, 23, 389—405, 406—411).—Twelve alkaloids were investigated, and all in various strengths depress the frog's heart after previous stimulation. They are arranged in order of activity, and morphine is the least active in this direction.

The whole series act also as depressants of motor nerve endings; here narceine is the least active, morphine coming next. W. D. H.

Physiological Actions of *l*-, *d*-, and *dl*-Suprarenine (Adrenaline). II. EMIL ABDERHALDEN and FRIEDRICH THIES (*Zeitsch. physiol. Chem.*, 1909, 59, 22—28. Compare this vol., ii, 159).—*d*-Suprarenine causes little or no dilatation of the frog's pupil, or glycosuria, in doses in which *l*-suprarenine produces both these effects; *dl*-suprarenine produces these effects in degree corresponding to the amount of *l*-suprarenine it contains.

W. D. H.

Acid Poisoning. III. HANS EPPINGER and FRITZ TEDFSKO (*Biochem. Zeitsch.*, 1909, 16, 207—216. Compare Abstr., 1907, ii, 86).—The experiments recorded confirm previous results; the susceptibility to the toxic action of acids is not a fundamental distinction between carnivorous and herbivorous animals, for if a dog receives no protein food it is easily poisoned by acid, and the sheep becomes resistant to acid when it takes protein freely.

W. D. H.

The Injury to Health Caused by Long-continued Ingestion of Sodium Sulphite in Small Doses. KARL B. LEHMANN and ADOLF TREUTLEIN (*Arch. Hygiene*, 1909, 68, 303—318).—The authors failed to corroborate Kionka's statement that long-continued ingestion of sulphite of animals causes small hæmorrhages throughout the body, although in some cases the feeding with food containing the sulphite was continued for two hundred days. The doses chosen were of such magnitude as to be comparable with the quantity that could be ingested by the human subject living on foods preserved with the maximum quantity of sulphite.

S. B. S.

Hygienic Studies on Nickel. KARL B. LEHMANN (*Arch. Hygiene*, 1909, 68, 421—465).—The amounts of nickel which could be dissolved by cooking various classes of food-stuffs in nickel utensils were determined, and it was found that if the whole of the food were cooked in such vessels, the total amount of metal that a man could ingest amounted to 2 mg. per kilo. of body-weight. Cats or dogs which had

taken quantities of nickel amounting to from 6 to 10 mg. per kilo. for one hundred to two hundred days remained normal in life, and showed no abnormal post-mortem appearances, although in two cases large amounts of the metal were stored up in the tissues. The conclusion is drawn that there is no danger of toxic effects from the use of nickel utensils. S. B. S.

Chemical and Toxicological Studies on Tobacco, Tobacco-smoke, and Smoking. KARL B. LEHMANN [with JOSEPH BIEDERBECK, LUDWIG BITTER, ALBAN HEIMANNSEBERG, KREPELKA, JAKOB KUHLES, H. K. LANG, S. NODA, FRANZ SCHMIDT, T. TANI, HARRY WARBURG, and ADOLF WEGER] (*Arch. Hygiene*, 1909, 68, 319—420).—The investigations were directed towards the quantitative determination of the constituents of smoke, which were collected by means of specially devised apparatus. The smoke was divided into two portions, namely, a by-stream coming from the lighted end of the cigar or object smoked, and the main-stream, corresponding to the mouth end. The principal products quantitatively determined were nicotine, pyridine, and ammonia. Pyridine was separated from the other bases by steam-distilling in the presence of acetic acid, under which conditions it alone is volatile. Nicotine was estimated by the bismuth potassium iodide method of Keller. The amounts of the various products that are obtainable in the smoke from various kinds of tobacco smoked in varying ways were also determined; also the amounts of the bases that are absorbed in the mouth under varying conditions. The latter factors were determined either by estimating the bases obtained in the washings, when the smoker rinses the mouth after each whiff, or by estimating the bases in the smoke, when after each puff he exhales into a gas-holder, and comparing the amounts with the total obtainable from smoke of the same materials when smoked in the apparatus. Investigations were also made of the oily matters, carbon monoxide and hydrogen cyanide. The only product obtained which would account for toxic symptoms was nicotine. The difference between "strong" and "mild" tobacco was found to depend, not on the actual amount of nicotine contained therein, but rather on the quantity that was absorbed in the mouth during the process of smoking, which varies considerably with the different kinds of tobacco. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

The Part Played by Bacteria in the Formation of Fusel Oil. HANS PRINGSHEIM (*Biochem. Zeitsch.*, 1909, 16, 243—245. Compare Abstr., 1908, ii, 316). Rabuteau (*Compt. rend.*, 1878, 87, 500) has noticed previously the presence of *n*-butyl and isopropyl alcohols in a fusel oil obtained from potatoes. The author considers that these are formed from the fermenting material by means of bacteria.

J. J. S.

Sterilisation of Milk by Ultra-violet Rays. VICTOR HENRI and G. STODEL (*Compt. rend.*, 1909, 148, 582—583).—Milk infected with various bacterial cultures and the ordinary milk of commerce can be readily sterilised without appreciable rise of temperature by exposure to the ultra-violet rays of a quartz mercury lamp. G. B.

The Action of Bacteria on Azo-colouring Matters. KARL FRÉGONNEAU (*Centr. Bakt. Par.*, 1909, i, 49, 276).—Certain acid-producing organisms, including *Proteus vulgaris*, *P. mirabilis*, *Bacillus subtilis*, *B. coli communis*, etc., were grown in media coloured with methyl-orange, but no pink coloration appeared. It is therefore clear that the methyl-orange has been decomposed, and the author suggests that reduction to sulphanilic acid and *as*-dimethyl-*p*-phenylenediamine may have taken place, without, however adducing any experimental evidence of the reaction. The change is examined to a certain extent from the purely bacteriological side. E. J. R.

Azotobacter Chroococcum Beij. SEVERIN KRZEMIENIEWSKI (*Bull. Acad. Sci. Cracow*, 1908, 929—1051).—Pure cultures of *Azotobacter chroococcum* fix only very small amounts of nitrogen in ordinary non-nitrogenous nutritive media. A marked increase in nitrogen fixation is obtained by addition of free humic acid (from soil) or potassium, sodium, or calcium humate, the increase varying according to the soil from which the humus is obtained. Artificial non-nitrogenous humus from sugar and soil humus which has been boiled with hydrochloric acid have very little effect on nitrogen fixation by *Azotobacter*.

In presence of dextrose, *Azotobacter* can fix as much as 17 mg. of nitrogen per gram. The utilisation of carbonaceous nutrients varies with the amount present, and both an excess and a deficiency below the optimum amount result in a diminished fixation of nitrogen in relation to the amount of carbon consumed.

No acids, alcohol or hydrogen was found to be produced by *Azotobacter*. The relation of oxygen consumed to carbon dioxide produced is approximately 1, or a little higher when dextrose is employed, and a little lower with mannitol.

The optimum temperature for *Azotobacter* is about 28°. At 33° its development is greatly retarded, whilst at temperatures below 28° the utilisation of dextrose is less economical in relation to the amount of nitrogen fixed. At 9° development is stopped altogether.

Fixation of nitrogen by *Azotobacter* is not influenced by *Radiobacter* and other bacteria. N. H. J. M.

The Production of Indole by *Bacillus coli communis*. W. C. DE GRAAFF (*Centr. Bakt. Par.*, 1909, i, 49, 175).—Several varieties of *Bacillus coli* organisms were propagated on glycerol-agar and then inoculated into peptone water; they were kept under definite conditions, and the amount of indole they produced was determined by Herter and Foster's method. It was found that one and the same variety always gives rise to the same amount of indole under the same conditions. The formation of indole reaches a maximum in three

weeks; in doubtful cases the experiment should therefore be continued for this full period. Different varieties of the coli organism generally produce dissimilar amounts of indole. The quantity produced does not depend on the virulence of the organism; thus, of the organisms investigated, two were very virulent (*K* and *St*₁), yet the latter yielded only a small amount of indole. Alkalinity of the medium and absence of air diminish the production of indole, whilst dextrose stops it altogether. Peptone is necessary; from bouillon alone no indole is formed.

E. J. R.

The Coli-aerogenes Group of Organisms. ROBERT BURRI and M. DÜGGELE (*Centr. Bakt. Par.*, 1909, 1, 49, 145).—The authors have studied sixty-five organisms of the coli-aerogenes group with particular reference to methods of classification. They devised a simple method of estimating the volume of gas evolved during fermentation which can be applied to a large number of samples, and will, they consider, prove a useful addition to the technique of a bacteriological laboratory. Briefly, the method is to cultivate the organism on an agar medium in a thick-walled, inverted, and graduated test-tube, and arrange the conditions so that the gas evolved shall force the medium down the tube and thus allow a direct reading of its volume. A simple device for estimating the amount of carbon dioxide in the gas is also described.

Applying this method to a number of organisms, they find it enables them to discriminate fairly sharply between different types. The quantity of gas evolved under definite conditions, and the proportion of carbon dioxide present, form characteristic tests for the various organisms. By varying the carbohydrates, it is possible to observe other differences. In this way they succeeded in dividing up their organisms into a number of sub-groups containing similar members, but varying according to their origin. These sub-groups are discussed from the standpoint of mutation.

E. J. R.

Influence of Ethyl Alcohol on Yeast Fermentation. MARTIN KOCHMANN (*Biochem. Zeitsch.*, 1909, 16, 391—398).—The effect of alcohol on the fermentation of dextrose by brewery yeast has been studied with the help of the Schulz automatic recording apparatus. The addition of large quantities has an adverse effect; smaller quantities have an accelerating influence, the optimum being at concentrations of 1 in 300 to 500. Under these conditions, the initial fermentation is accelerated, and slightly more gas is produced in a given time. The accelerating influence of alcohol is regarded as quickening the production of ferment and not to any influence on the zymase.

E. F. A.

Calcium and Magnesium in Plant Seeds. RICHARD WILL-STÄTTER (*Zeitsch. physiol. Chem.*, 1909, 58, 438—439).—In the seeds of cereals (wheat, rye, maize, etc.), the amount of magnesium which the plant requires for the formation of chlorophyll is more abundant than that of calcium. The results are stated quantitatively in a table.

W. D. H.

Presence of Amylase in Old Seeds. BROCC-ROUSSEU and EDMOND GAIN (*Compt. rend.*, 1909, 148, 359—361).—Corn which had been preserved for fifty years in a glass bottle had lost its germinating power, but still contained a ferment capable of hydrolysing starch. G. B.

Plant Ferments. W. W. BIALOSUKNIA (*Zeitsch. physiol. Chem.*, 1909, 58, 487—499).—An investigation of many seeds shows that ferments capable of acting on animal protein are absent, although those acting on vegetable protein are present. The extract in most cases curdles milk. Oxydases are often present, but the results in different seeds present great variations. In relation to diastatic ferments, the rapidity of action and the kind of sugar formed vary.

W. D. H.

The Nature of Cyanogen Compounds in Kirschwasser. XAVIER ROCQUES and L. LÉVY (*Compt. rend.*, 1909, 148, 494—496 *).—When this spirit is two to three years old, it does not behave on distillation like a freshly-prepared or old solution of hydrogen cyanide in 50% alcohol; the hydrogen cyanide is only partly in the free state, and a portion of it has become combined with fatty substances of high molecular weight. G. B.

The Amount of Chlorine in Leaves. ALBERT J. J. VANDELVELDE (*Bull. Soc. chim. Belg.*, 1909, 23, 84—88).—A number of analyses are given, showing the percentage of chlorine in the dry matter of leaves gathered in May, July, and September. The percentage was found to increase regularly in *Tilia*, *Syringa*, *Ligustrum*, *Æsculus*, *Sorbus*, *Vitis*, *Ampelopsis*, from about 0.3 to about 1%. It fell to a minimum in July and rose to a maximum in September in *Sambucus*, *Corylus*, and *Salix* (about 0.3 to 0.6%). There was a minimum in May and maximum in July in *Fagus*, *Prunus*, *Ribes*, and *Rubus*, but irregularities showed themselves in this group. In *Carpinus*, and occasionally in *Ribes*, the chlorine rose to a maximum in July and a minimum in September. The percentage decreased regularly from May to September in *Quercus*, *Pyrus*, *Aucuba*, *Ilex*, *Rhododendron*, and *Hedera* (about 0.3 to 0.1%). It was a maximum in May and minimum in July in *Pavia*, *Castanea*, *Acer*, *Symphoricarpos*, *Betulus*, and *Deutzia*. In certain other cases the fluctuations were irregular, including *Populus*, *Ulmus*, *Fagus*, *Prunus*, *Ribes*, *Rubus*, but the causes of the fluctuations were not determined. E. J. R.

The First Stages in the Development of Perennial Plants Compared with those of Annuals. GUSTAVE ANDRÉ (*Compt. rend.*, 1909, 148, 515—517. Compare this vol., ii, 174).—The cotyledons yield to a perennial seedling about the same proportion of potassium and of nitrogen as is yielded by the cotyledons of an annual plant; in the latter case the transference of saline constituents from the cotyledons is more rapid, but not more complete. G. B.

* and *Ann. Chim. anal.*, 1909, 14, 138—140.

The Influence of Aluminium Salts on Protoplasm. M. FLURI (*Naturw. Rundsch.*, 1909, 23, 610—612).—*Spirogyra* cells in the light lose their starch under the influence of aluminium salts, very weak solutions of the latter sufficing to bring about this result. This effect may be due to an acceleration of the diastatic action induced by the aluminium salts, but is more probably due to an increase in the permeability of the protoplasmic membranes brought about by these salts. Precipitated albumin had a greater absorptive capacity than dissolved albumin, and as the soluble aluminium salts have a marked tendency to precipitate albumins, these substances are in this way rendered more permeable. G. T. M.

The Presence of Fluorine in Grapes. F. LEPPERRE (*Bull. Soc. chim. Belg.*, 1909, 23, 82—84).—These experiments were undertaken in connexion with the analysis of wines; if fluorine does not occur in grapes, it clearly should not occur in pure wines. Dried grapes from Malaga and from Asia Minor (sultanas) were incinerated, and 5 grams of the ash were tested for fluorine. In most cases the results were wholly negative; in the others there were possible indications of a slight trace of fluorine. When fluorides are found in wine, it is clear that they must have been added. E. J. R.

Occurrence of Stachyose and a Glucoside Hydrolysable by Emulsin in the Subterranean Parts of *Lamium album*. L. PIAULT (*J. Pharm. Chim.*, 1909, [vi], 29, 236—241).—An alcoholic extract of the subterranean portions of *Lamium album* can be separated by treatment with a mixture of alcohol and ethyl acetate into two parts. The insoluble portion contains stachyose (manneotetrose) (Tanret, Abstr., 1903, i, 606) and the soluble part a glucoside, which is decomposed by emulsin, yielding a dextrorotatory reducing sugar. T. A. H.

Vegetable Phosphatides. III. ERNST WINTERSTEIN. IV. ERNST WINTERSTEIN, and K. SMOLENSKI. V. K. SMOLENSKI. VI. ERNST WINTERSTEIN and L. STEGMAN (*Zeitsch. physiol. Chem.*, 1909, 58, 500—505, 506—521, 522—526, 527—528. Compare Abstr., 1908, ii, 218).—This series of papers relates to a number of vegetable phosphatides, but their final identification is not yet possible. The first paper relates to one prepared from the seeds of *Lupinus albus*. It contains phosphorus 3.6%, and nitrogen 0.9%, and yields 16% of sugar on cleavage. The second deals with phosphatides from wheat meal; one of these, soluble in alcohol, yields ammonia, choline, and other nitrogenous substances, some of which are basic; a carbohydrate-phosphatide is also present. The third paper deals with some points of detail in relation to wheat phosphatides, and the fourth with a phosphatide from green *Recinus* plants, which yields 5.3% of phosphorus, 6.7% of calcium oxide, and no sugar. W. D. H.

Maltases of Maize. R. HUERRE (*Compt. rend.*, 1909, 148, 505—507. Compare this vol., ii, 258).—Further examples of maltases acting at high and at low temperature are given. These differences

are due to differences in the medium ; each variety of maize appears to have its own special maltase. G. B.

The Fruit of *Medeola Virginica* and *Ampelopsis Quinquifolia*. LOIS E. POYNEER and H. LEROY DUFFIN (*Chem. News*, 1909, 99, 99—100).—The fruit of the Indian cucumber (*Medeola Virginica*) contains lævulose. The hard kernels enclosed in the fruits yield nearly 10% of oil, of which a portion is volatile and the remainder resembles porpoise oil and has a saponification equivalent 254·8.

The fruit of the Virginia creeper (*Ampelopsis quinquefolia*) contains lævulose, tannin, oxalic acid, and 11·27% of oil (D 0·9503), which on standing separates into two portions, of which the lower solidifies on cooling and then has m. p. 0·8°.

A complete analysis of the ash from each kind of fruit is given, showing that both are comparatively rich in potassium. T. A. H.

An Organic Vegetable Compound of Iron. P. JOSEPH TARBOURIECH and P. SAGET (*Compt. rend.*, 1909, 148, 517—519).—Of all the plants hitherto analysed, *Rumex obtusifolius* is richest in iron ; the dried root contains 0·447% Fe. The iron is in a state of organic combination in a substance containing C, H, N, P, and other inorganic constituents besides iron. This substance is soluble in alcoholic hydrochloric acid ; the iron is only partly split off by boiling with 1% hydrochloric acid. With acid of 10%, the substance is decomposed with formation of a reducing sugar. The substance appears to be related to the nucleones of Siegfried. G. B.

The Sugars of the Tobacco Plant. GASPARE AMPOLA and FRANCESCO SCURTI (*Ann. R. Staz. chim. agrar. sper. Roma*, 1907–8, [ii], 2, 312—316).—The suspected presence of sugars in normal tobacco leaves is important in connexion with the question of adulteration. The inflorescence and seeds are found to contain dextrose, identified by its reactions and its conversion into the phenylhydrazone. The sugar present in the leaves is gummy and uncrystallisable (compare Müller, Abstr., 1886, 904). The presence of allantoin in tobacco leaves (Scurti, Abstr., 1907, ii, 124), together with dextrose, makes it probable that the two compounds occur in the form of a readily hydrolysable allantoin glucoside. C. H. D.

Amount of Sugar in Beet Manured with Nitrogen. HERMANN BRIEM (*Zeitsch. Zuckerind. Böhm.*, 1909, 33, 391—394).—Experiments with beet grown in four different kinds of soils, without nitrogen and with 60 kilograms of nitrogen per hectare as sodium nitrate, ammonium salt, calcium cyanamide, and calcium nitrate. The average amounts of sugar for all the soils only varied from 17·1 (without nitrogen) to 17·3% (ammonium salt).

Further experiments with the different soils, in which the effects of sodium nitrate applied all at once or in two portions were compared, showed that a single application before June 20 does not lower the percentage of sugar. N. H. J. M.

Accumulation of Nitrogen in Relation to Soil Conditions.

THEODOR REMY (*Centr. Bakt. Par.*, 1909, ii, 22, 561—651).—Application of a suitable substance as source of energy is essential in the case of ordinary arable soil to obtain a marked accumulation of nitrogen. Small gains of nitrogen may occur in soils not too deficient in humus and calcium carbonate. The presence of free acids prevents any material fixation of nitrogen. Equivalent amounts of lime and magnesia have almost exactly the same effect on nitrogen fixation, whilst potassium and sodium carbonates are less favourable.

No definite relation between the percentage of nitrogen in soils and fixation of nitrogen could be established. No gain of nitrogen could ever be detected in peaty soils.

An experiment on nitrogen fixation in large quantities of soil is described. Three lots of soil, 300 kilograms, (1) without further treatment, (2) with addition of calcium carbonate, and (3) with calcium carbonate and 2% sucrose, were kept in layers 10 cm. high for a few weeks at a temperature of 22—25°. Addition of calcium carbonate alone had no effect, whilst addition of calcium carbonate and sucrose resulted in a gain of 141 mg. of nitrogen per kilogram. Pot experiments were next made with three similar lots of soil each with four different plants, all followed by mustard. The results showed that the nitrogen fixed under the influence of sucrose (the amount of sucrose was 1% in this experiment) was in a readily available form, and that the yields of mustard and maize grown in the soil were twice as great as in the other soils, whilst the difference in the case of beet was still greater. The average amounts of nitrogen in the first crops from the three soils and the amounts in the second crops (mustard) were :

Soil.	I.	II.	III.
Nitrogen in 1st crop	0·225	0·217	0·463
„ 2nd „	0·351	0·330	0·418

N. H. J. M.

Assimilation of Potassium from Soils. GUSTAV WIMMER, HERMANN WILFARTH, W. KRÜGER, HERMANN ROEMER, GERHART GEISTHOFF, O. RINGLEBEN, and J. STORCK (*Chem. Zentr.*, 1909, i, 395—396; from *Arb. deut. landw. Ges.*, 1908, No. 143)—Pot experiments with various plants to ascertain the laws by which potassium is taken up from the soil and also whether it is possible to ascertain by pot experiments whether and to what extent soils are deficient in potassium.

The influence of soil moisture and manuring and the return of potassium to the soil are discussed (in the original paper), and also the relation of lower organisms to potassium assimilation and the effect of nematodes.

N. H. J. M.

[Composition of Rain-water collected at Garforth.] R. S. SETON (*Rep. Univ. Leeds and Yorks. Counc. Agric. Education*, 1908, No. 74, 17).—Analyses of rain-water collected from October, 1906, to

September, 1907, and October, 1907, to September, 1908. The following results were obtained:

(1). In parts per million.

	Rainfall in inches.	Nitrogen				SO ₃ .	SO ₂ .	Acidity as H ₂ SO ₄ .
		As NH ₃ .	As N ₂ O ₅ .	Albuminoid.	Cl.			
1906—1907...	26·44	1·06	0·236	—	3·66	11·94	—	2·14
1907—1908...	29·16	0·773	0·481	0·163	3·36	10·85	2·71	4·34
Average ...	27·80	0·934	0·377	—	3·60	11·67	—	3·41

(2). In lbs. per acre.

1906—1907...	26·44	6·42	1·424	—	22·12	72·10	—	12·95
1907—1908...	29·16	5·327	3·316	1·128	23·17	74·81	18·65	29·93
Average ...	27·80	5·873	2·370	—	22·64	73·45	—	21·44

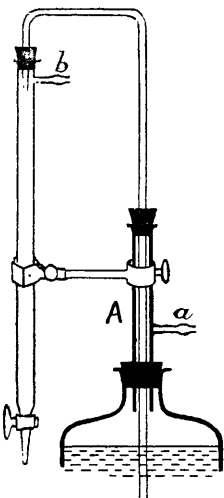
The nitrogen as ammonia amounted to 71·2%, and as nitrates, 28·8%, of the total (excluding albuminoid nitrogen). N. H. J. M.

Analytical Chemistry.

New Burette Attachment to Store Bottle. VON HEYGENDORFF (*Pharm. Zeit.*, 1909, 54, 159).—A description is given of a convenient arrangement for working with standard solutions, whereby the burette may be filled directly from the stock solution with a minimum chance of evaporation; the apparatus is, moreover, not easily broken. *A*, is a stout glass tube carrying the feed tube to the burette; the side tubes, *a* and *b*, may be closed by suitable caps when the apparatus is not in use.

From the accompanying sketch it should be evident that suction at *b* will cause filling of the burette; the air entering at *a* should be dried by attaching a drying tube to this inlet.

J. V. E.



Use of Pinchcock Burettes for Titrations with Iodine and Permanganate. LUCIEN L. DE KONINCK and LEJEUNE (*Bull. Soc. chim. Belg.*, 1909, 23, 79—82).—The authors confirm the experiments of Lunge showing the rapid action of iodine on rubber tubing; pinchcock burettes should, therefore, not be used when titrating with iodine. Stopcock burettes may be safely greased with vaselin.

Lunge's experiments agree with a statement made by de Koninck

and Dietz in 1869 that a pinchcock burette may be used for permanganate titrations if the rubber is not kept in contact with the permanganate for any length of time. L. DE K.

The Gasparini Electrolytic Process for the Removal of Organic Matter in the Detection of Poisons. MARIO MIORANDI (*Gazzetta*, 1909, 39, i, 175—179).—In Gasparini's method for decomposing organic matter (Abstr., 1904, ii, 785), the material is treated with nitric acid and subjected to electrolysis. The destruction is brought about by oxygen and by oxides of nitrogen. The process has some disadvantages, and it is found that by the use of carbon electrodes instead of platinum, and of ammonium persulphate in place of nitric acid, the destruction is made very rapid and complete. Hydrogen peroxide gives less satisfactory results. C. H. D.

Apparatus Used in Rapid Methods of Electroanalysis. Analysis of Brass. T. SLATER PRICE and T. C. HUMPHREYS (*J. Soc. Chem. Ind.*, 1909, 28, 117—123).—After describing the more important forms of apparatus with rotating anode, cathode, or electrolyte which have been employed in rapid electroanalysis, the authors give an account of experiments on the estimation of copper and zinc in brass by a constant current method. The apparatus and method of working have been described previously (compare Price and Judge, *Trans. Faraday Soc.*, 1906, 2, 85).

From the results of a series of experiments at 3 volts and 3 amperes with rotating cathode, it is shown that copper is seldom deposited quantitatively when nitric acid is the only acid present, but precipitation is complete when sulphuric acid or zinc sulphate is added.

In estimating the copper and zinc in brass, about 0.7 gram of the latter is dissolved in 4 c.c. of concentrated nitric acid and a little water; the solution is diluted to 75—100 c.c. One c.c. of strong sulphuric acid is added, and the copper deposited at 3 volts and 3 amperes, which takes about twenty to thirty minutes. The solution is evaporated nearly to dryness to drive off the nitric acid, diluted, a concentrated solution of sodium hydroxide added until the zinc begins to precipitate, ammonia is added to redissolve the precipitate, the solution is warmed, any ferric hydroxide is filtered off, glacial acetic acid is added until the solution is just acid, and the latter electrolysed at 4—4.5 volts and 2 amperes. The zinc is completely deposited in about twenty minutes. A modification of this method, which avoids the lengthy evaporation to get rid of the nitric acid, is also described.

In order to obtain satisfactory results, it is necessary to remove the lead, tin, and iron, if they would otherwise be present as precipitates suspended in the electrolyte. G. S.

Preparation of Standard Hydrochloric Acid. GEORGE A. HULETT and W. D. BONNER (*J. Amer. Chem. Soc.*, 1909, 31, 390—393).—Hydrochloric acid, D 1.10, is distilled until three-quarters has passed over. The residue then shows a constant boiling point (108.54° at 763 mm. pressure) and contains exactly 22.242% of hydrogen chloride

(D 1-0962). By suitable dilution, the requisite standard solutions may then be made.

L. DE K.

Estimation of Dissolved Oxygen in Water. WILLEM P. JORISSEN (*Chem. Weekbl d.*, 1909, 6, 123—125. Compare Winkler, Abstr., 1889, 79; Romyn, Abstr., 1894, ii, 28, and 1896, ii, 579; Jorissen and Ringer, Abstr., 1906, ii, 490).—Experimental data are given in support of the view advanced by Jorissen and Ringer that with sea-water Romyn's method for the estimation of dissolved oxygen yields results which are much too low.

A. J. W.

Estimation of Sulphur in Coals and Cokes. M. HOLLIGER (*Zeitsch. angew. Chem.*, 1909, 22, 436—439, 493—497).—A criticism of the various methods proposed from time to time. For the estimation of the total sulphur, a modification of Brunck's method (combustion with cobalt oxide and sodium carbonate in a current of oxygen, Abstr., 1905, ii, 95) is recommended as being the only trustworthy method. The mass instead of being extracted with water is dissolved in hydrochloric acid and evaporated to render the silica insoluble. To the dry mass is added the contents of the Peligot tube, in which any volatilised sulphur has been absorbed, this previously having been neutralised and boiled to expel the excess of hydrogen peroxide. A little hydrochloric acid is now added, and the filtrate is precipitated with barium chloride as usual.

For the estimation of the volatile sulphur, Sauer's method is recommended as the most trustworthy. The process consists in burning the substance in a current of oxygen and absorbing the products of combustion in a suitable oxidising medium. The author has improved the process by filling the front part of the combustion tube with platinum wire cuttings, which are then heated to redness.

L. DE K.

Estimation of Sulphur in Urine. EMIL ABDERHALDEN and CASIMIR FUNK (*Zeitsch. physiol. Chem.*, 1909, 59, 121. Compare this vol., ii, 263).—Reference is made to a paper by Modrakowski (*Zeitsch. physiol. Chem.*, 1903, 38, 362) in which the authors' work has been largely anticipated.

W. D. H.

Volumetric Estimation of Sulphurous Acid in Wines [and Food Products]. CHARLES BLAREZ and L. CHELLE (*Ann. Fabrif.*, 1909, 2, 76—79; *Bull. Assoc. Chim. suc. dist.*, 1909, 26, 690—693).—Two hundred and fifty c.c. of the wine and 2 c.c. of syrupy phosphoric acid are heated in a water-bath under greatly reduced pressure, and the distillate, which contains all the sulphur dioxide, is collected in a receiver containing 20 c.c. of *N*-sodium hydroxide. A slight excess of dilute hydrochloric acid is added, and the liquid is at once titrated with *N*/0 iodine, using starch as indicator. If desired, the sulphuric acid formed in the reaction may be estimated gravimetrically.

L. DE K.

Estimation of Sulphuric Acid as Barium Sulphate. JULIUS F. SACHER (*Chem. Zeit.*, 1909, 33, 218—219).—A criticism of Ruppin's

paper (this vol., ii, 180). Pure barium sulphate precipitates are obtained by working with highly diluted solutions, about 0.1 gram of the sulphate in 100 c.c. of liquid; 1% of hydrochloric acid is added, and the solution is heated to boiling. A 3% solution of barium chloride is then added in slight excess with constant stirring. After twenty-four hours, the precipitate is collected and treated as usual.

L. DE K.

Estimation of Sulphuric Acid in the Air of Accumulator Rooms. KARL BECK (*Arb. Kais. Gesund. Amt.*, 1909, 30, 77—80).—

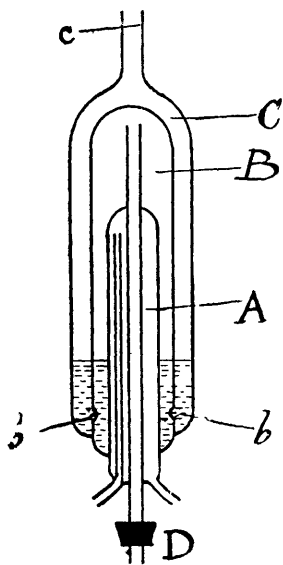
The amount of acid was estimated by passing about 100 litres of air in the course of ten to fifteen minutes through a definite quantity of $N/100$ potassium hydroxide solution contained in a specially constructed absorption apparatus, which is figured in the paper, and titrating back the unneutralised alkali with $N/100$ hydrochloric acid, using iodoeosin as indicator, the titration liquid being covered with ether. The quantities of acid found in the accumulator rooms varied between 9.3 and 45.3 mg. of 33% acid per cubic metre of air.

S. B. S.

Influence of Chlorides on the Estimation of Nitrates in Water. GUSTAVE PERRIER and L. Farcy (*Bull. Soc. chim.*, 1909, [iv], 5, 178—180).—It is pointed out that in the colorimetric process for the estimation of nitrates in water, devised by Grandval and Lajoux, the addition of the sulphuric acid solution of phenol to the dry

residue from the water leads to the evolution of hydrogen chloride when the water under examination contains chlorides. Comparative trials showed that this acid decolorises to a greater or less extent the colouring matter formed and so leads to low results. To avoid this difficulty it is suggested that the standard solution used for the comparison should be prepared, by the addition of sodium chloride, so as to contain the same quantity of chloride as the water under examination.

T. A. H.



Apparatus for Gutzeit's Test. P. B. DALLIMORE (*Pharm. J.*, 1909, [iv], 28, 324).—The apparatus depicted consists of a water condenser, *A*, on which is fused the double jacket, *B* and *C*, communicating with each other by the holes, *b*. Lead acetate solution is poured through *c* and partly fills *B* as well as *C*.

When a flask containing the substance to be tested is attached to *D*, water is circulated through the condenser, *A*, and the gas evolved, passing up *D*, bubbles through the lead acetate solution in *B* and *C*, and finally comes in contact with the mercuric chloride paper fastened on to the outlet, *c*.

J. V. E.

Detection of Phosphoric and Phosphorous Acids in Organs.

RICHARD EHRENFELD and W. KULKA (*Zeitsch. physiol. Chem.*, 1909, 59, 43—53).—An aqueous extract of the organ is evaporated to dryness on a water-bath in an atmosphere of carbon dioxide. The residue containing the hypophosphite is moistened with a few drops of hydrochloric acid, again dried, placed in a porcelain boat, and ignited in a stream of hydrogen. Phosphorus trihydride is given off and imparts the characteristic green colour to the flame of the hydrogen.

W. D. H.

Detection and Estimation of Arsenic in Cemetery Soil.

CARL MAI (*Pharm. Zentr.-h.*, 1909, 50, 169—170).—About 200—250 grams of the soil are mixed with sufficient hydrochloric acid, D 1.125, to form a thin paste. One to two grams of potassium chlorate, and, if necessary, a few drops of ferric chloride, are added, and after twenty-four hours the whole is heated for another hour on the water-bath. The solution is filtered, and the residue is washed with water. The filtrate and washings are then precipitated with ammonia, when the iron precipitate will carry down any arsenic present, and it may, for qualitative purposes, be introduced at once into the Marsh apparatus.

For quantitative purposes, the precipitate is dissolved in dilute sulphuric acid and made up to a definite volume. An aliquot part is then treated by the authors' electrolytic process (*Abstr.*, 1905, ii, 284).

When testing disinterred corpses in an advanced state of decomposition for arsenic, the bones should be examined, as these rapidly absorb arsenic. Attention is also called to the occurrence of arsenic in coffin nails, screws, etc.

L. DE K.

Precipitation of Arsenic by Hydrogen Sulphide.

LUCIEN L. DE KONINCK (*Bull. Soc. chim. Belg.*, 1909, 23, 88—93).—In order to precipitate arsenic rapidly and completely as sulphide, it is necessary to reduce the arsenate to arsenite, and this is most effectually done by warming the solution with hydrochloric and hydriodic acids. Instead of hydriodic acid, a solution of potassium or, preferably, ammonium iodide may be used. The hot solution is then treated with hydrogen sulphide.

Sulphur dioxide cannot be recommended as a suitable reducing agent.

L. DE K.

Estimation of Boron.

HIPPOLYTE COPAUX and G. BOITEAU (*Bull. Soc. chim.*, 1909, [iv], 5, 217—225).—Comparison of the three methods in general use for the estimation of boric acid, namely, (1) extraction with ether, (2) isolation as methyl borate, and (3) titration in presence of glycerol, shows that a modified form of the last-mentioned gives the best results. The first method gives approximate results, but is tedious, since at least three extractions with ether have to be made. The second process is simple and trustworthy in cases where it is applicable, but it cannot be used in presence of tungstates. Where it is used, it is recommended that the methyl borate should be collected in a known volume of standard

alkali and the boric acid determined by titration in presence of glycerol. The third process, as modified by the authors, is essentially that described previously (Abstr., 1899, ii, 181), but it is now pointed out that the presence of methyl alcohol does not, as then stated, interfere with the end reaction. The process is applicable to borides and borotungstates, and exact details of manipulation required in these and other cases are given in the original. T. A. H.

Use of Quartz Combustion Tubes, especially for the Direct Estimation of Carbon in Steel. BERTRAM BLOUNT and ARTHUR GARFIELD LEVY (*Analyst*, 1909, 34, 88—95).—Tubes of clear silica were found to be well suited for the purpose of organic combustions; they withstand the action of copper oxide, lead chromate, etc., very well, but at temperatures above 900° copper oxide rapidly attacks and destroys quartz tubes. The authors have also used quartz tubes in the estimation of oxygen in copper by fusion in hydrogen. The tube was heated by a furnace similar to that described by Tucker (Abstr., 1907, ii, 842); iridium-platinum foil was wrapped round the tube, and a current of 200 volts was employed, the initial resistance being not less than 25 ohms, which was lowered gradually to about 7 ohms so as to keep the current constant at 6 amperes. For the estimation of carbon in steel, a silica tube can be employed; it is heated by an electric furnace, and special means are provided for supplying the large volume of oxygen which is absorbed as soon as the steel begins to burn. The current of oxygen is drawn through the combustion tube and potash bulbs, and its rate through the latter regulated by means of an exhaust pump; the oxygen is supplied to the other end of the tube through a Y-tube, one arm of which connects through a trap with the open air. At the commencement of the operation, more oxygen is supplied than can be drawn off by the pump, and a portion consequently escapes into the air, but when the steel commences to burn, this escape ceases, and air itself is drawn into the tube along with the oxygen. To ensure complete combustion of the carbon monoxide evolved, the exit end of the combustion tube is packed with platinised quartz, and a supplementary current of oxygen is passed into the tube through a narrow tube which enters at the exit end of the combustion tube and reaches through the platinised quartz. The steel to be burnt is placed in a boat containing a layer of ignited alumina, and injury to the combustion tube by sparks of molten oxide is prevented by enclosing the boat in a piece of iridium-platinum foil rolled into the form of a tube. A piece of silver foil, placed immediately before the boat, protects the rubber stopper from the intense radiation characteristic of quartz tubes. The results obtained by the method differ by less than 0.02% from those given by the solution method, and agree well with each other. W. P. S.

Gravimetric Estimation of Silver as Chromate. FRANK A. GOOCH and ROWLAND S. BOSWORTH (*Amer. J. Sci.*, 1909, 27, 241—244; *Zeitsch. anorg. Chem.*, 1909, 62, 69—73).—A method based on a reversal of the process for the estimation of chromic acid (Abstr., 1908, ii, 737).

Silver may be precipitated quantitatively as chromate by adding a

solution of potassium chromate. The silver chromate is collected on a Gooch asbestos filter, and washed first with a weak solution of potassium chromate and then with water. The precipitate is then dried and weighed.

A precipitate more readily collected and washed may be obtained by redissolving the silver chromate in dilute ammonia and reprecipitating by prolonged boiling. Should the silver solution contain free nitric acid, an excess of potassium chromate should be added, more than sufficient to react on the acid.

L. DE K.

Separation of the Alkali Earths. ERICH EBELER (*Zeitsch. anal. Chem.*, 1909, 48, 175—179).—The filtrate from the ammonium sulphide group is evaporated to dryness and the residue is heated to expel ammonium salts. The residue is then dissolved in water and a little hydrochloric acid, and precipitated with ammonia and ammonium carbonate; care must be taken to have just sufficient ammonium chloride present to prevent precipitation of magnesium.

The precipitate is dissolved in as little as possible dilute hydrochloric acid, and the barium is then precipitated as chloride by adding 10 vols. of strong hydrochloric acid. The precipitate is collected on a hardened filter and washed with hydrochloric acid. The filtrate is evaporated to dryness and the residue dissolved in water. The strontium is then precipitated with very dilute (0.15%) sulphuric acid, and the calcium is separated as usual with ammonia and a large excess of ammonium oxalate.

The filtrate containing the magnesium may be tested for that metal by placing a drop on an object glass and adding a minute particle of microcosmic salt; the triple phosphate which soon forms may then be recognised under the microscope. If desired, the whole of the magnesium may then be precipitated as usual.

L. DE K.

Precipitation of Magnesium as Ammonium Magnesium Arsenate. ERCOLE RAFFA (*Gazzetta*, 1909, 39, i, 154—162. Compare this vol., ii, 183).—The precipitation of magnesium as arsenate has been studied by a similar series of experiments to those made with the phosphate. When the method employed is similar to that of Neubauer for the phosphate (*Abstr.*, 1896, ii, 674), the results are too high, owing to the formation of the salt, $\text{Mg}(\text{NH}_4)_4(\text{AsO}_3)_2$, which yields the meta-arsenate, $\text{Mg}(\text{AsO}_3)_2$, on ignition.

It is impossible to avoid some reduction of the precipitate during ignition, even when this is carried out in a current of oxygen. The solubility of ammonium magnesium arsenate is also considerable (compare Fages Virgili, *Abstr.*, 1905, ii, 652, 858), even when dilute ammonia is used for washing. Precipitation as arsenate is therefore less accurate as a means of estimating magnesium than precipitation as phosphate.

C. H. D.

Rapid Electro-analysis with Stationary Electrodes. JOHN T. STODDARD (*J. Amer. Chem. Soc.*, 1909, 31, 385—390).—*The Gauze Cathode.*—The cathodes are cylinders of platinum gauze (52 mesh to the inch) 3 cm. in diameter and 3 cm. long, and weigh about

12 grams each, and the anodes are cylinders of platinum foil about 0.8 cm. in diameter and 2.5 cm. long, and are placed concentrically within the cathodes. The precipitations are carried out in 80 c.c. beakers with about 50 c.c. of solution. The wires of both electrodes are bent at an angle of a little over 90° so as to rest on the spout of the beaker and allow a watch-glass cover to be used. When precipitation is complete, the solution, without interrupting the current, is drawn off and the cathode is washed with water by the aid of a siphon, the end of which is slipped between the electrodes.

By the use of a powerful current satisfactory results were obtained with (a) cadmium nitrate dissolved in solution of potassium cyanide, (b) copper sulphate with 7 to 8 drops of nitric acid at 60° , (c) nickel sulphate with 1.5 grams of ammonium sulphate and 12—15 c.c. of ammonia, (d) silver nitrate with the least excess of potassium cyanide at nearly boiling heat, and (e) zinc sulphate with excess of sodium hydroxide, or an insufficiency of the same and addition of potassium cyanide; the solution is heated. The precipitations are complete in fifteen to thirty minutes.

The Mercury Cathode.—A 40—50 c.c. beaker is used with about 40 grams of mercury, and an anode consisting of a flat spiral of platinum wire placed 0.5—1 cm. from the surface of the mercury. The electrode wires are bent as in the case of the precipitation on gauze. A powerful current is employed, and when precipitation is complete, the mercury is washed by the aid of a siphon without interrupting the current. It is then finally washed with alcohol and ether, and dried at a gentle heat.

Satisfactory results were obtained with solutions of cadmium and silver nitrates and copper, nickel, and zinc sulphates; to each were added 5—6 drops of dilute sulphuric acid (1:4), except in the case of silver, where nitric acid was used. The precipitations were complete in ten to fifteen minutes.

The strength of the current does not affect the character of the deposited metal, except in the case of silver, where it should not exceed 1.5 ampere when a gauze cathode is employed. L. DE K.

Volumetric Estimation of Thallium. WOLF J. MÜLLER (*Chem. Zeit.*, 1909, 33, 297—298).—The oxidised solution in which the excess of permanganate has been destroyed by boiling is diluted to 500 c.c. and mixed with a definite volume (3—6 c.c. in excess) of standard thiosulphate, 25 c.c. of 1% solution of potassium iodide are added, and the liquid is titrated with standard iodine, with starch as indicator. The end point is shown by a decoloration of the previously bright yellow- or orange-coloured liquid; one drop of thiosulphate should cause the original colour to reappear.

One c.c. of thiosulphate = 0.09727 gram of thallium, but in practice it should be taken as 0.09800 so as to obtain accurate results.

L. DE K.

Volumetric Estimation of Copper by means of Potassium Iodide. FRANZ M. LITTERSCHEID (*Chem. Zeit.*, 1908, 33, 263—264).—The solution, which should contain about 0.1 gram of copper in

50 c.c., is made alkaline with ammonia. Should free nitric acid be present, the neutralised liquid is boiled for a minute and then allowed to cool. Eighteen or 20 c.c. of *N*/10 arsenious acid (prepared as usual) are added, and then acetic acid to acid reaction. Crystals of potassium iodide are now added one by one until the characteristic cuprous iodide has formed. After an hour, the whole is made up to 200 c.c., and when settled, the solution is filtered. One hundred c.c. of the filtrate are then mixed with an excess of sodium hydrogen carbonate, and the excess of arsenious acid is titrated with *N*/10 iodine, using starch as indicator. One c.c. of *N*/10 arsenious acid = 0.00636 gram of copper.

L. DE K.

Titration of Copper and Chromium and of Copper, Chromium, and Iron in Admixture. EVA HIBBERT (*J. Soc. Chem. Ind.*, 1909, 28, 190—192).—*Copper and Chromium.*—The copper should be present as a cupric salt and the chromium as a chromate. The joint amount is found by titration with titanous chloride, the excess of which is in turn titrated with standard solution of iron-alum. The copper only may then be estimated by a second titration, after reducing the chromate by means of sulphur dioxide. Or the copper may be removed with hydrogen sulphide and the chromium re-oxidised with hydrogen peroxide and then titrated as described.

Copper, Chromium, and Iron.—The iron should be present as a ferric salt and the chromium as a chromate. A portion of the solution is titrated for the joint metals with titanous chloride until it turns green, potassium thiocyanate is then added, and the titration continued until the red colour has disappeared. A second portion is freed from copper by means of hydrogen sulphide, and the filtrate after being re-oxidised with potassium chlorate and hydrochloric acid is titrated for iron only, using potassium thiocyanate as indicator. A third portion is then treated with sulphur dioxide to reduce the chromate, and the solution after having been re-oxidised with potassium chlorate and hydrochloric acid is titrated for joint copper and iron.

L. DE K.

New Method of Estimating Cuprous Oxide in Copper. GIULIO COFFETTI (*Gazzetta*, 1909, i, 137—143).—The method is based on the solubility of cuprous oxide in ammonia in absence of oxygen, metallic copper being insoluble under these conditions. The weighed sample is introduced into an apparatus of special construction, and a current of hydrogen is passed over it, ammonia gas being admitted after all the air has been expelled. Ammonium hydroxide is then run into the apparatus through a tap funnel, the gas inlet tube being so arranged that the gas bubbles continuously pass through the liquid. When the solution no longer increases in depth of colour, it is siphoned off through a plug of glass wool, the residue washed with a solution of ammonia in recently boiled water, and the operation repeated. The united filtrates are acidified, and the copper estimated electrolytically. A comparison with Hampe's silver nitrate method shows that the new method is equally accurate and much more rapid.

C. H. D.

Method for the Estimation of Mercury in Solutions containing Iodides. HENRIK WEGELIUS and SULO KILPI (*Zeitsch. anorg. Chem.*, 1909, 61, 413—416).—In the estimation of mercury in potassium mercuric iodide, the iodine is first removed from the solution by addition of an excess of moist silver chloride. After heating until clear, the solution is filtered and acidified with hydrochloric acid, and the mercury precipitated with hydrogen sulphide.

A reversible colour change of the compound Ag_2HgI_4 at 50° has been observed and is under investigation. C. H. D.

Separation of Iron from the Elements of Groups IV and V and Detection of the Rare Earths in Arable Soils. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. suc. dist.*, 1909, 26, 694).—The hydrochloric acid solution of the substance is rendered alkaline with aqueous sodium hydroxide or ammonia and an excess of sodium sulphide or ammonium sulphide is added. Acetic acid in fair excess is then added, and the precipitate is collected on a filter and washed with a 2% solution of sodium sulphide in 5% acetic acid. It contains any iron and zinc, whilst the filtrate contains any aluminium, manganese, uranium, glucinum, the rare earths, and the earthy phosphates. L. DE K.

New Colour Reaction of Ferrous Salts and Some of its Applications. A. RICHAUD and BIDOT (*J. Pharm. Chim.*, 1909, [vi], 29, 230—234).—When a solution of sodium phosphotungstate, acidified by hydrochloric acid, is added to a solution of a ferrous salt and the liquid is then made alkaline with sodium hydroxide, a sky-blue coloration is produced. The reaction is more delicate than that with potassium ferricyanide, and may be employed for the detection of ferrous iron in urine, milk, gastric juice, mineral waters, etc. All the samples of urine examined gave the colour reaction, but it could not be obtained with blood-serum, so that the test may possibly prove useful in legal cases. No coloration is produced with ferric salts.

T. A. H.

Estimation of Ferrous Oxide in Magnetite. R. B. GAGE (*J. Amer. Chem. Soc.*, 1909, 31, 381—385).—0.5 Gram of the sample, which need not be reduced to an impalpable powder, is heated in a platinum crucible with 10 c.c. of hydrofluoric acid and 15 c.c. of dilute sulphuric acid (1:3) in a current of carbon dioxide. To prevent bumping, a few coils of platinum wire are introduced. After some five minutes, the decomposition is complete and the crucible and contents are placed in a beaker containing about 400—500 c.c. of recently boiled water. In order to render the hydrofluoric acid harmless, a solution is added, made by dissolving 5 grams of calcium carbonate in 50 c.c. of water and 10 c.c. of 85% ortho-phosphoric acid, and the liquid is then at once titrated for ferrous iron with permanganate. The first permanent colour is taken for the end-point. L. DE K.

Examination of Mint-Nickel. WILLEM J. VAN HETEREN and H. VAN DER WAERDEN (*Chem. Weekblad*, 1909, 6, 157—165).—A rapid

electrolytic method for the estimation of nickel in the Dutch standard coinage is described. The alloy contains 75% of copper and 25% of nickel. It was found that the presence of 0.5 gram of ammonium nitrate did not interfere with the deposition of the nickel, but that the presence of larger quantities is to be avoided. Ten grams of the alloy, cut up as finely as possible, are dissolved in a mixture of 15 c.c. of nitric acid (D 1.3), 25 c.c. of sulphuric acid (D 1.8), and 40 c.c. of water. The solution is cooled, diluted with water to 1 litre, and two portions of 100 c.c. each electrolysed for copper at 80° with Winkler's wire gauze cathode. The completion of the precipitation of the copper is determined by introducing into the liquid two platinum wire electrodes connected to an accumulator, the absence of a copper deposit on the cathode indicating the end-point. Without interrupting the current, the copper-covered cathode is then removed, and washed with a minimum quantity of water during the process. To the acid nickel solution are added 50—60 c.c. of ammonium hydroxide (D 0.95) and 5 grams of ammonium sulphate. The volume of the resulting solution should be about 200 c.c. The nickel is deposited at a temperature near the b. p. of the solution, the end-point being determined by Tschugaeff's reagent (*Abstr.*, 1905, ii, 613). The deposition of the copper requires twenty to thirty minutes, and that of the nickel twenty-five to forty minutes. The whole operation can be completed in an hour and a-half, and the results are almost quantitative.

A. J. W.

Separation of Tin and Antimony. LE ROY W. MCCAY (*J. Amer. Chem. Soc.*, 1909, 31, 373—381).—The process is briefly as follows: the mixed higher sulphides of tin and antimony are redissolved in 5 c.c. of hydrochloric acid, and when the hydrogen sulphide has been expelled, a solution of tartaric acid is added and the filtrate is neutralised with sodium hydroxide. Five c.c. of 48% hydrofluoric acid are added, and then an excess of sodium acetate. The whole is diluted to about 300 c.c., and the antimony precipitated with hydrogen sulphide; the fluoride present prevents the precipitation of the stannic tin. The antimony precipitate is converted as usual into the black anhydrous sulphide.

The filtrate is evaporated in a platinum dish on the water-bath with addition of 20 c.c. of sulphuric acid to expel the fluorine, and, after dissolving the residue in water, the tin is precipitated with hydrogen sulphide and treated in the usual manner.

L. DE K.

Volumetric Estimation of Titanium, and of Titanium in the Presence of Iron. EVA HIBBERT (*J. Soc. Chem. Ind.*, 1909, 28, 189—190).—The titanic salt dissolved in dilute hydrochloric acid is introduced into a flask fitted with a trebly-perforated rubber cork; one of the holes is fitted with a Bunsen valve, through which a platinum wire, having a piece of zinc attached to it, is passed, and the other two holes, *A* and *B*, are temporarily closed with glass rods. In this way the zinc is suspended in the liquid, and when the reduction has lasted for about twenty minutes and the solution has been boiled, the rod is removed from *A* and a current of carbon dioxide is passed;

the rod is then removed also from *B*. After withdrawing the zinc out of the liquid by means of the wire and washing it, the solution is titrated for titanous chloride with standardised solution of methylene-blue, the point of the burette being introduced into the opening *B*.

As ferrous chloride does not react with that reagent, the method is also applicable in presence of iron. An aliquot part of the original solution is then titrated for ferric iron with standard titanous chloride.

L. DE K.

Estimation of Thorium in Monazite Sand. OTTO HAUSER and FRITZ WIRTH (*Zeitsch. angew. Chem.*, 1909, 22, 484—487).—A modification of Borelli's method (*ibid.*, 21, 2275). Fifteen to twenty grams of the finely-powdered sample are boiled with strong sulphuric acid for several hours, and the bulk of the acid is then expelled by heating. When cold, the residue is treated with a litre of 4—5% hydrochloric acid. After removing any lead, the filtrate is mixed in the cold with an excess of oxalic acid, and after the precipitate has settled, it is collected on a filter. The oxalates are heated with nitric acid and a few drops of weak permanganate, or else ignited and dissolved in hydrochloric acid, and the thorium is then precipitated by boiling with sodium thiosulphate, which operation is repeated in order to get a perfectly pure precipitate.

L. DE K.

The Opening-up of Minerals Containing Tantalum, Niobium, and Titanium. WILLIAM B. GILES (*Chem. News*, 1909, 99, 1—4, 25—27).—The powdered mineral is mixed with two and a-quarter parts of potassium carbonate and introduced into a steel crucible fitted with a lid, which is in turn placed in a plumbago crucible also fitted with a cover, which is then filled up partly with powdered and partly with lumps of wood charcoal. After placing the whole in a furnace and exposing it for an hour to a most intense heat, the mass, owing to the action of the reducing gases, will contain the heavier metals, either as such (tin, copper) or else as lower oxides (iron, manganese), whilst the tantalum and niobium may be extracted as soluble potassium compounds with water. The solution is then treated as usual for their separation.

The insoluble matter contains the titanium and any zirconium present in the mineral, but in accurate analysis it should also be tested again for tantalum and niobium.

L. DE K.

A Reaction of Gold Chloride. DAUVÉ (*J. Pharm. Chim.*, 1909, [vi], 29, 241).—When a piece of aluminium foil is placed in a solution of auric chloride in water, colloidal gold is formed after some hours, and the liquid presents an appearance similar to that obtained by immersing zinc foil in a solution containing auric chloride, ferric chloride, and arsenic acid (Carnot, *Abstr.*, 1884, 115). The gold is simply replaced by the aluminium, no colloidal gold being formed if aluminium chloride is first added to the auric chloride solution.

T. A. H.

Messina Oils. Analysis of the Oils of Lemon, Orange, and Bergamot. ENRICO BERTÉ and ROMEO (*Chemist and Druggist*, 1909, 74, 81).—The analyses of the oils of lemon, orange, and bergamot

tabulated in this paper were carried out under the auspices of the Messina Chamber of Commerce. The citral in lemon oil was estimated by Romeo's method, which consists in titrating the alkali liberated in contact with sodium sulphite in presence of potassium hydrogen sulphite. The sp. gr., optical rotation, and initial boiling point of the oils were ascertained, and the properties of some of the possible adulterants are also given. Of these, the most difficult to detect is Grecian turpentine from *Pinus halepensis*; the physical constants of this oil were determined in detail: D^{15}_D 0.8620—0.8718; $[\alpha]_D$ 37.6' to 39.45'; b. p. 155°; fixed residue, 2.75%; acid value, 0.17%; solubility in 80% alcohol, 1 vol. in 13.7. G. T. M.

Sensitive New Reactions for Detection and Identification of Glycerol. GEORGES DENIGES (*Compt. rend.*, 1909, 148, 570—572. Compare this vol., ii, 272, 273).—The colour reactions previously studied in connexion with dihydroxyacetone furnish a convenient and delicate test for glycerol. To oxidise glycerol to dihydroxyacetone, the following procedure is adopted. 0.08—0.1 Gram of glycerol is placed in a test-tube with 10 c.c. of bromine water freshly prepared by dissolving 0.3 c.c. of bromine (exactly measured) in 100 c.c. of distilled water. The mixture is heated on the water-bath for twenty minutes and then boiled to expel bromine. The tests already described are now applied to portions (0.4 c.c.) of this solution.

Other reactions suitable for the detection of glycerol, depending on the formation of glycerosazone and the osazone of methylglyoxal, are described. W. O. W.

Estimation of Phenol. LUIGI MASCARELLI (*Gazzetta*, 1909, 39, i, 180—189).—The various methods proposed for the estimation of phenol are reviewed. In the precipitation by means of bromine, the precipitate is tribromophenol, even when an excess of bromine (dissolved in sodium bromide and bromate) is added. The precipitation is practically complete (error, 0.77—0.89%) and is unaffected by the presence of other compounds which react with bromine. C. H. D.

Detection of Methylpentoses in Presence of Pentoses. LEOPOLD ROSENTHALER (*Zeitsch. anal. Chem.*, 1909, 48, 165—172).—The tests for methylpentoses now used are applied to the hydrochloric acid distillates. By simply heating the methylpentoses with hydrochloric acid, D 1.19, for a few minutes in the boiling water-bath, a liquid is obtained showing a characteristic spectrum even in presence of pentoses. The following method, however, is preferable. A little of the substance is heated in the boiling water-bath for ten minutes with 10 c.c. of fuming hydrochloric acid and 1—2 c.c. of pure acetone. The red solution when examined spectroscopically exhibits a sharp absorption band in the yellow which covers the D -line, and slightly extends to the right and the left. The red colouring is insoluble in most of the immiscible solvents, but dissolves readily in creosote and guaiacol.

In order to detect pentoses in presence of methylpentoses the hydrochloric acid distillate should be tested for furfuraldehyde as

follows. An equal volume of fuming hydrochloric acid and a few crystals of resorcinol are added, and the liquid is examined in the spectroscope. Large portions of the right side of the spectrum are obscured, but soon an absorption line in the red appears, which, increasing in width, soon occupies half of the still clear space. In presence of but little furfuraldehyde, the line situated between *C* and *D* is very conspicuous. If the solution darkens and a precipitate forms, this is filtered off, washed with water, and redissolved in glacial acetic acid, which, after being diluted with water, again shows the absorption band between *C* and *D*.

A large number of gums, gum-resins, and glucosides have been tested, and the results are given in a table. L. DE K.

Estimation of the Various Sugars Occurring Together in Diabetic Urines. H. CHRISTIAN GEELMUYDEN (*Zeitsch. anal. Chem.*, 1909, 48, 137—163).—A lengthy paper containing a large number of mathematical formulæ and three tables.

The process, which aims at the estimation of dextrose, maltose, lævulose, etc., is carried out by means of titration (by Knapp's mercury solution) before and after inversion and by polarisation. Advantage is also taken of the fact that certain yeast cultures act only on mono-, but not on di-saccharides. L. DE K.

Estimation of Sugar in Meat. EMIL BAUR (*Arch. Kais. Gesund. Amt.*, 1909, 30, 63—73).—The method is an adaptation of the Moisch-Udransky test for sugars for purposes of quantitative analysis. One c.c. of the liquid to be tested is allowed to drop into the bottom of a test-tube with a ground stopper. To this are added 9 c.c. of pure sulphuric acid, and then 8—10 drops of alcoholic thymol solution containing 15 grams of thymol in 100 c.c. The contents of the test-tube are then mixed, and left for half an hour. By measuring the breadth of the absorption band due to the coloured product of the reaction, the amount of sugar present can be ascertained after having determined once the breadth of the band corresponding with the various concentrations of sugar. The solution used for the test must be diluted sufficiently to give a measurable band. The method of applying the reaction to estimation of sugar in meat and urine is described. The total carbohydrates, and not the dextrose alone, were determined by this method.

S. B. S.

Estimation of Glycogen. BERNHARD SCHÖNDORFF, PETER JUNKERSDORF, and VICTOR HESSEN (*Pflüger's Archiv*, 1909, 126, 578—581); B. SCHÖNDORFF, P. JUNKERSDORF, and PAUL HEYDEN (*ibid.*, 582—584).—In the estimation of glycogen in liver and muscle by the potash method, the yield is the same whether the boiling with potassium hydroxide (30%) is continued for thirty minutes, one, two, or three hours.

If the potassium hydroxide is of less concentration, the full yield is not obtained. W. D. H.

Micro-chemical Detection of Glycogen. MAX BLEIBTREU (*Pflüger's Archiv*, 1909, 127, 118—124); KAN KATO (*ibid.*, 125—142).—The micro-chemical test for glycogen in tissues if negative does not prove absence of glycogen without a chemical analysis. The frog's ovary, for instance, contains glycogen, but does not respond to the microscopic test with iodine, probably because the glycogen enters into combination with some tissue constituent. The following test is proposed as more trustworthy as a micro-chemical reaction. The section is placed on a slide in a drop of water and alcohol, and a crystal of potassium ferricyanide added until the liquid is yellowish-green, and then a crystal of potassium iodide; the fluid is then allowed to pass over the section, and the excess taken up with blotting-paper; it is then mounted in a drop of syrup of either lævulose or achroodextrin, and the glycogen reaction can then be seen. W. D. H.

Estimation of Formic Acid in Fruit Juices. F. SCHWARZ and O. WEBER (*Zeitsch. Nahr. Genussm.*, 1909, 17, 194—197).—As preparations containing formic acid are now sold and used for the preservation of fruit juices, the authors describe the following method for the estimation of this acid. Shortly, the process consists in separating the formic and other volatile acids by distillation, titrating the distillate, and re-distilling after removing the formic acid by oxidation. The difference in the amount of acidity of the two distillates gives the amount of the formic acid. Fifty grams of the sample of fruit juice are steam-distilled until 400 c.c. of distillate have been collected; if superheated steam is used, it is only necessary to collect 250 c.c. of distillate. The distillate is then titrated with $N/10$ alkali solution, using phenolphthalein as indicator, and the neutral solution is evaporated to dryness in order to remove the alcohol which is present in small quantity in most fruit-juices; the addition of the indicator also introduces a little alcohol. The residue is dissolved in 20 c.c. of water and 30 c.c. of a solution, containing 12 grams of potassium dichromate, 30 c.c. of concentrated sulphuric acid, and 100 c.c. of water, are added. The mixture is boiled for ten minutes in a reflux apparatus and then steam distilled, the same volume of distillate being collected as in the first distillation. The distillate is titrated as before, and the difference in the two titrations is a measure of the formic acid which has been removed by the oxidation. Experimental evidence is given showing that the process is trustworthy. W. P. S.

Volumetric Estimation of Formic Acid and its Salts. FRIEDRICH AUERBACH and WERNER PLÜDDEMANN (*Arch. Kais. Gesund. Amt.*, 1909, 30, 178—194).—The method is based on the reduction of mercuric chloride by formic acid or formates according to the equation $2\text{HgCl}_2 + \text{H}\cdot\text{CO}_2\text{H} = \text{Hg}_2\text{Cl}_2 + \text{CO}_2 + 2\text{HCl}$. This reaction proceeds to completion if the concentration of hydrogen ions is not too great, and this is prevented by carrying out the reaction in presence of a sufficient quantity of sodium acetate. Mercuric chloride solution of known concentration is used, and the amount of formic acid present can be determined by estimating the quantity of mercuric salt still present

after filtration from the precipitated mercurous salt. This can be effected by titration with potassium iodide: $\text{HgCl}_2 + 4\text{KI} = \text{HgI}_2 + 2\text{KI}$. The double iodide remains in solution until mercuric chloride is in excess, when the red mercuric iodide commences to separate. This happens, however, before the quantity of mercuric salt corresponding with the above equation has been added, owing to a secondary reaction: $\text{HgI}_2 + 2\text{KI} + \text{HgCl}_2 \rightarrow 2\text{HgI}_2 + 2\text{KCl}$, which depends on the relative concentrations of the salts in solution. The error due to this factor can be eliminated by titrating the mercuric salt into a definite quantity of potassium iodide solution of a certain standard strength. The deviations from the true stoichiometric relations having been once experimentally determined for this particular quantity of solution of given strength and tabulated, it is easy to estimate the amount of mercuric chloride in any solution. S. B. S.

The Chemistry of Vinegar and the Methods of Investigation. JOHANNES BRODE and WILHELM LANGE (*Arch. Kais. Gesund. Amt.*, 1909, 30, 1—54).—The concentration of the hydrogen ions at the points of change of colour of the various indicators, both at the ordinary temperature and on warming, were determined, using normal solutions with known concentration of hydrogen ions, such as hydrochloric acid solutions of given strengths, acetic acid, mixtures of acetic acid and sodium acetate, of disodium and monosodium phosphates, of ammonia and ammonium chloride, and of sodium hydroxide. The results were compared with numbers obtained by Salm, Friedenthal, Salessky, and Felo. The results were applied to the titration of vinegars. It was found that the free mineral acids could be estimated accurately by diluting with an equal volume of alcohol and titrating in the presence of methyl-orange according to Schidrowitz's method. In this solution the concentration of hydrogen ions due to the acetic acid dissociation is negligible. The estimation of acid by the sugar inversion method was also tried, but was not so satisfactory as the indicator method, owing to the fact that tartaric acid acts as a weaker acid in this respect than acetic acid.

The methods used for estimation of other substances in vinegar were also subjected to examination by the authors. A modification of the Zeisel-Fanto method (conversion into isopropyl iodide) is recommended for the estimation of glycerol. Details are also given in the paper for estimation in the extractives of oxalic acid, boric acid, heavy metals, and salicylic and benzoic acids. The processes are all based on known methods. S. B. S.

Action of Light on Milk Preserved with Potassium Dichromate. ALBERT GASCARD (*Compt. rend.*, 1909, 148, 580—582).—The compulsory addition of potassium dichromate to milk intended for analysis is objectionable for various reasons, but the objections may be minimised by keeping the sample in the dark. G. B.

General and Physical Chemistry.

Solubility Determinations with the Refractometer.

FREDERICK H. GETMAN and F. B. WILSON (*Amer. Chem. J.*, 1909, 41, 344—348).—Osaka has shown that the relation between the angles of refraction of a mixture and its components may be expressed by the equation $ax + bx^2 = \delta - \delta^1$, in which δ and δ^1 represent the angles directly observed on the divided circle of the refractometer for the solvent and the solution, x the quantity of solute in grams per 100 c.c., and a and b are constants. This equation has been tested by the data obtained for aqueous solutions of potassium chloride, bromide, iodide, nitrate, and chromate, and also of sucrose. The calculated values of x are only in approximate agreement with the experimental values. The simpler equation $ax = N_s - N_w$, in which a is a constant and N_s and N_w are the refractive indices of the solution and the solvent respectively, expresses the experimental data equally well.

H. M. D.

Anomalous Dispersion of Light in Metallic Vapours.

HERMANN GEISLER (*Zeitsch. wiss. Photograph. Photophysik Photochem.*, 1909, 7, 89—112).—The experiments were undertaken in order to find whether Kirchhoff's law regarding emission and absorption holds for the spectra of metallic vapours. The method depends on observing whether the emission lines show anomalous dispersion. Absorption and anomalous dispersion are intimately connected, and if anomalous dispersion is observed, it follows that the lines also suffer absorption.

The apparatus consisted of a combination of a Jamin's interference refractor and a grating. The material (metal or salt) used to produce the vapour was inserted in the positive carbon of the arc, and from the effect of the vapours on the fringes, registered photographically, the occurrence of anomalous dispersion could be decided. Practically all the common metals, and some rare metals, were investigated in this way, and the bands and lines for which anomalous dispersion was observed are given in tabular form as well as the approximate intensity of the dispersion. Anomalous dispersion was observed in a very large number of cases, and it is considered probable that under suitable conditions all the lines would show this phenomenon, proving the qualitative validity of Kirchhoff's law in this case. The lines also show great differences in the degree of anomalous dispersion, the strongest lines generally showing the greatest anomaly, but the results are not sufficient to show whether Kirchhoff's law holds quantitatively for the spectra of metallic vapours.

A bibliography of the subject is given.

G. S.

The Spectra of Spark Discharges in Liquids. HEINRICH KONEN and HERMANN FINGER (*Zeitsch. Elektrochem.*, 1909, 15, 165—169).—The spectra of spark discharges between metals under water are studied; twenty-one different metals are used. Compared

with the spectra in air, the air lines are entirely absent; a strong, continuous spectrum is often, but not always, superposed on the spectrum of the metal. The lines of hydrogen and oxygen are not present, or those of salts dissolved in the water. The lines observed in air are sometimes absent, sometimes enhanced, broadened or reversed, but details are not given. As a general rule, lines belonging to a series behave in the same way. T. E.

Two New Arrangements for producing Emission Spectra. RUDOLF KRULLA (*Zeitsch. physikal. Chem.*, 1909, 66, 78—80.)—Two pieces of apparatus for the production of emission spectra, in which both electrodes consist of a solution of the metallic salt, are described and figured. The first arrangement consists of a dropping-funnel and doubly-bent U-tube, each of which contains the salt solution and a platinum wire (for conveying the current) sealed through the glass and in contact with the solution. The spark passes between a falling drop and the top of the salt solution in the U-tube. The second apparatus consists of two funnels with sealed-in platinum wires; the capillary ends of the funnels are so bent that the out-flowing salt solution forms two thin streams which cross each other, and the spark passes at the point where the streams are most nearly in contact. G. S.

Influence of Temperature on the Emissive Power of Metals. E. HAGEN and HEINRICH RUBENS (*Sitzungsber. K. Akad. Wiss. Berlin*, 1909, 478—492).—Whilst the optical constants of metals in the visible spectrum are little affected by temperature, in the infra-red region, as demanded by the electro-magnetic theory, the variation with temperature is large.

The metals used in these experiments were silver, platinum, and nickel, and the alloys brass, platinum-silver, constantan, and nickel steel. Instead of comparing the emissive power of the polished surface in each case with that of a black body for the same temperature and wave-length, it was found better to examine the variation with temperature of the metal and of the black body (a hollow copper vessel blackened with cobalt oxide) separately, comparing the curves thus obtained. The metals were heated in dry nitrogen by an electric furnace. The rays examined were the residual rays after four reflexions from fluorite ($26\cdot0\ \mu$), and after three reflexions from quartz ($8\cdot85\ \mu$, the rays of $20\cdot75\ \mu$, also present, being absorbed by a plate of fluorite).

The relation $\nu = 36\cdot5 \sqrt{(\sigma/\lambda)}$, where ν is the emissive power, σ the electrical resistance, and λ the wave-length, is found to hold good very accurately for all the metals and alloys examined, and for both sets of rays. The emissive power of platinum increases with the temperature at a slightly faster than the calculated rate. Nickel shows an inflexion of the curve at 320° , the magnetic critical point. Alloys with a small temperature-coefficient of resistance, such as constantan, approach the black body in their optical behaviour.

The region in which the optical temperature-coefficients of the metals first coincide with the electrical must lie between $\lambda = 0\cdot7\ \mu$ and $8\cdot85\ \mu$. C. H. D.

Secondary Spectrum of Hydrogen. C. F. HOGLEY (*Phil. Mag.*, 1909, [vi], 17, 581—583).—A vacuum tube containing hydrogen was connected with a bulb containing charcoal. On cooling this in liquid air, the intensity of the lines was seen to decrease, but the relative intensities of the two spectra remained unchanged until the entire spectrum had disappeared, and discharge would no longer take place on account of the high degree of exhaustion. The observations indicate that hydrogen is really the source of the secondary spectrum.

H. M. D.

Red Region of the Arc Spectra of Nickel, Cobalt, and Chromium. LEANDER STÜTING (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1909, 7, 73—88).—The arc was passed between rods of the metals themselves; the spectra were obtained by means of a concave grating, and photographed on the special colour-sensitive plates of Wratten and Wainwright. The wave-lengths of the lines, their relative intensity, and the probable error of the measurements are given in tabular form for the three metals in question, and the lines measured by previous observers are also given. In the case of chromium there are a number of bands as well as lines, and the positions of the heads of five groups of bands are given. Whether the bands belong to the metal or to its oxide has not been definitely determined.

G. S.

Demonstration of the Absorption of Colourless Solutions in the Ultra-violet. CARL SCHALL (*Zeitsch. physikal. chem. Unterr.*, 1908, 21, 389—390).—In a previous paper (compare Abstr., 1908, ii, 139) the preparation of a test-paper has been described which turns blue in ultra-violet light, but does not alter in diffused daylight. This paper may be used to show differences of absorption in the ultra-violet as follows. A trough, the front and back of which are made of transparent quartz, is partly filled with alcohol, and along with a second (empty) trough of glass is set up in front of a sheet of the test-paper in question; the troughs and paper are then exposed, at a distance of 4 cm., to the light from a Heraeus lamp. After a few minutes, white silhouettes of the troughs on a blue background are observed on the paper; only where the rays of short wave-length meet air, alcohol, or quartz have they penetrated sufficiently to produce colour. If instead of alcohol, a concentrated solution of naphthalene in the latter solvent is used in the quartz trough, a completely white image of the trough is obtained, as naphthalene absorbs the ultra-violet rays.

G. S.

Absorption Spectra of Solutions of a Number of Salts in Water, in Certain Non-aqueous Solvents, and in Mixtures of these Solvents with Water. XXIV. HARRY C. JONES and JOHN A. ANDERSON (*Amer. Chem. J.*, 1909, 41, 163—208, 276—326. Compare Abstr., 1907, ii, 147, 211, and 212).—The authors have obtained photographic records of the absorption spectra of solutions of cobalt chloride, bromide, nitrate, sulphate, thiocyanate, and acetate, and of nickel, cupric, ferric, and chromic chlorides. In

certain cases, solutions in methyl alcohol, ethyl alcohol, and acetone, as well as in water, were examined, and the effect of the addition of dehydrating agents, like calcium and aluminium chlorides, was studied.

With the object of ascertaining what components of the solutions give rise to the various absorption bands, comparative measurements were made in such a way (1) that the product of depth of layer and concentration remained constant; (2) that the total number of undissociated molecules in the path of the beam of light was constant; (3) that the total number of ions was constant.

The ultra-violet absorption exhibited by aqueous solutions of cobalt salts diminishes with dilution, and increases with rise of temperature; this is consistent with the view that this band with its middle at about $\lambda = 3300$ is due to a relatively simple hydrate. The absorption band in the green, which is exhibited by all solutions, is probably due to the cobalt atom, the absorbing power of which is modified to some extent by the atoms or groups with which it is in combination. The absorption in the red, which is much more intense in the non-aqueous solutions, and increases when we pass from methyl alcohol to ethyl alcohol, and from this to acetone, is supposed to be due to relatively simple combinations of the cobalt salt with water or other solvent molecules.

The absorption bands of nickel chloride appear to be very similar in their behaviour to the green band of cobalt, and are therefore probably due to the nickel atom.

In the case of cupric chloride, the photographic records indicate that the absorption band in the red is due to the copper atom, and that in the ultra-violet to simple combination of the salt with the solvent.

The variations in the three absorption bands of solutions of chromic chloride indicate that these are due to chromium atoms, whether these are present in the solution as ions, or are combined with other atoms in the form of molecules.

Photographic records of the absorption spectra of solutions of salts of neodymium, praseodymium, and erbium have been obtained. The influence of concentration and of the nature of the solvent on the absorption spectrum was investigated in a manner similar to that previously described for salts of cobalt. The results obtained are considered to furnish strong evidence in favour of the view that compounds are formed between the solute and solvent molecules.

In particular, it may be noted that the absorption spectra of aqueous solutions of the chloride and bromide of neodymium change very little with the concentration. Concentrated solutions of the nitrate show a somewhat different spectrum, but with diminishing concentration the spectrum changes so as to become more nearly identical with the spectra of the chloride and bromide. The addition of large quantities of calcium or aluminium chloride to a solution of neodymium chloride has but little effect on the spectrum. In non-aqueous solvents the spectra of the different salts are different, and the spectrum of

any one salt varies with the nature of the solvent. When neodymium chloride is dissolved in mixtures of water and methyl or ethyl alcohol, and the relative proportion of the two solvents is varied, there is no marked change in the spectrum until the percentage of water falls to 15 or 20. On further reduction of the proportion of water, the solution gives a spectrum which consists of the spectra for the aqueous and non-aqueous solutions superposed; the former decreases and the latter increases in intensity as the proportion of water in the mixture is diminished. Praseodymium chloride behaves similarly to the neodymium salt, except that the alcoholic solutions show a band in the ultra-violet which has no analogue in the aqueous solution.

The observations lead to the view that both molecules and ions of the dissolved salts form compounds with molecules of the solvent.

H. M. D.

Fluorescent Substances Contained in Water. F. DIENERT (*Bull. Soc. chim.*, 1909, [iv], 5, 326—329).—Water in white glass phials of 45 c.c. capacity is strongly illuminated by the concentrated beam from an arc, and is viewed from the side through a crystal of doubly refracting material. Since light reflected from suspended particles is polarised, the principal image consists of reflected as well as fluorescent light, whereas the extraordinary image is entirely of fluorescent light.

By employing light of various colours, the test for fluorescence is often rendered more delicate, and it is possible to distinguish between one fluorescent substance and another. The presence of one part of *æsculin* in 200,000,000 parts of water could only be detected in violet light, whilst *fluorescein* is more readily detected in white light.

The author has found at least three distinct fluorescent substances in natural waters. Deep well-water contains a greenish, fluorescing substance, destroyed by light or by acid, like *fluorescein*, but not by boiling. Surface-waters, particularly of peaty or sewage-contaminated origin, contain a greenish-blue, fluorescent substance, more resistant to light and acid than the preceding. This substance is greenish in blue light, in which spring-waters give a fluorescence equivalent to a 1 in 20,000,000 solution of *æsculin*. A third fluorescent substance, which is found in town fogs, rain, and snow-waters, is somewhat more bluish.

R. J. C.

Processes Used to Measure the Fluorescence of Waters. F. DIENERT (*Bull. Soc. chim.*, 1909, [iv], 5, 330—332).—The water under examination is illuminated and matched with a standard solution of *æsculin* or a standard fluorescent spring-water, the solutions being simultaneously observed through the same birefringent crystal. If the fluorescence is strong, the beam of light may be roughly split into two, and a more accurate method followed of substituting a standard solution for the unknown solution, matching each with a second standard.

R. J. C.

The So-called Asymmetry Product. II. EMIL BOSE and FR. A. WILLERS (*Zeitsch. physikal. Chem.*, 1909, 65, 702—726. Compare this vol., ii, 2).—Instead of Guye's form of the asymmetry

product, a simpler form without denominator, of the type $R = (C_1 - C_2)(C_1 - C_3)(C_1 - C_4)(C_2 - C_3)(C_2 - C_4)(C_3 - C_4)$, appears to possess certain advantages as a representation of optical rotatory power. The formula is tested by the available data as to the rotatory power of forty-two pure non-associated substances (esters), the molecular rotatory power being represented both by the usual formula, $M[\alpha] = Ma/l$, and by the alternative formula, $\alpha/l \cdot \sqrt{M/d}$, where the symbols have the usual significance. The results of the calculations are given in tabular form, and completely disprove the theory that the rotatory power is determined by the masses of the substituting groups. From the available data other constants are calculated for the substituting groups (seventeen in all) by an approximate method, both expressions for the molecular rotatory power being taken into account, and it is shown that these constants represent the experimental results much more accurately than the mass constants in the asymmetry formula.

G. S.

Electrical Method for Measuring the Changes Produced in Chromate-Gelatin Films by Light. HANS MAYER (*Zeitsch. physikal. Chem.*, 1909, 66, 33—70).—The chromate mixture with which the plates were covered was prepared by warming together 96 grams of distilled water, 4 grams of soft "emulsion" gelatin, and 0.5 gram of potassium dichromate. The dried plates were provided at the ends with electrodes of tin foil, and the resistance of the film under varying conditions as to illumination and temperature determined with a condenser and ballistic galvanometer. The resistance is greatly influenced by moisture, and the film was therefore provided with a varnished glass cover in order to obtain comparable results. The arrangements used in keeping the temperature constant and in measuring the light intensity are fully described.

In measuring the effect of illumination, the plate was exposed to diffused daylight. The conductivity diminishes considerably on exposure to light, the change being progressive with time of exposure. Even when again placed in the dark, the change proceeds for some time as when exposed. The conductivity, both for the illuminated and unilluminated plates, increases rapidly with the temperature, but the temperature-coefficients in the two cases are not the same. When a fresh plate is exposed to light and again placed in the dark, the resistance does not return to its original value. The percentage alteration of the conductivity brought about by illumination is independent of the original value of the conductivity (before illumination), and is therefore a characteristic property of the system. The sensitiveness of the gelatin to light diminishes with age, rapidly at first, and then more slowly.

The nature of the chemical changes taking place on the plate are discussed on the basis of Hardy's theory of colloid coagulation, but no final conclusions have been drawn. The investigation is being continued.

G. S.

Electro-chemistry of Light. V. WILDER D. BANCROFT. (*J. Physical Chem.*, 1909, 13, 181—250. Compare this vol., ii, 200).—A

further compilation of extracts from papers on the problem of solarisation.
R. J. C.

Radioactivity of the Thermal Springs of Bagnères-de-Luchon. CHARLES MOUREU and ADOLPHE LÉPAPE (*Compt. rend.*, 1909, 148, 834—837).—Of twenty different springs at Bagnères-de-Luchon, only five exhibit spontaneous evolution of gas, the radioactivity of 10 litres of the latter, expressed in milligram-minutes of radium emanation, varying from 4.19 to 18.36. The waters vary in radioactivity from zero to 2.20, ten of them giving values above 0.50. T. H. P.

Radioactivity of the Mineral Springs of Switzerland. Emanation Content of the Water. I. ALFRED SCHWEITZER (*Arch. sci. phys. nat.*, 1909, [iv], 27, 256—274).—Measurements have been made of the amount of emanation which is present in the water of a large number of springs. In order to avoid the loss of radioactivity which is involved in transport of the water, the measurements were all made at the source. For each water examined, the chemical nature, the geological formation in which it originates, the temperature, and the activity in Mache units are recorded. Three only contain a large proportion of emanation, these being the mineral waters of Disentis, Lavey, and Solis.
H. M. D.

Radioactivity of the Atmosphere. ALBERT GÖCKEL (*Arch. sci. phys. nat.*, 1909, 27, 248—255. Compare Gockel and Wulf, this vol., ii, 109).—The relative proportion of thorium and radium emanation in the atmosphere at different places has been examined. Observations were made at Fribourg, at the summit of the Rothorn (2300 metres above sea-level), in the neighbourhood of Zermatt (2600 metres) and of the Matterhorn (3000—3300 metres). At Fribourg, the ratio of the quantity of thorium emanation to that of radium emanation in the atmosphere varies from 0.4 to 0.7; the ratio is a little smaller on the Rothorn. On the other hand, the ratio at Zermatt and on the Matterhorn varies from 0.03 to 0.1. The latter result is due to the fact that the neighbouring glaciers do not give off an emanation. Observations relating to the activity of the air extracted from the soil at Fribourg and to that of rain-water and the water obtained from hail, snow, and ice are also recorded.
H. M. D.

Action of Radium and Ultra-violet Rays on the Colours of Minerals. CORNELIO DOELTER (*Monatsh.*, 1909, 30, 179—229. Compare this vol., ii, 109; Simon, *Abstr.*, 1908, ii, 954).—A record of a large number of observations relating to the changes in colour of various minerals and coloured glasses on exposure to the action of radium rays and ultra-violet light.

It follows from the results obtained that, generally speaking, the colouring materials of minerals are not of an organic nature; the colours are due principally to the presence of oxides of iron, chromium, and manganese.

The change in colour under the influence of radium rays is in many cases the outcome of a reducing action. The ultra-violet rays, on the

contrary, have an oxidising action ; consequently, ultra-violet light and radium rays frequently induce opposite changes.

The bearing of the results on the origin of the colour of many minerals and precious stones is discussed. W. H. G.

Decomposition of Water by Radium Salts. ANDRÉ DEBIERNE (*Compt. rend.*, 1909, 148, 703—705).—The author has made frequent measurements of the rate of decomposition of water by radium salts ranging over considerable periods of time, and finds that the rate remains constant. In the course of an enquiry as to whether the decomposition of water is due to radium, the emanation, or later disintegration products, or to the radiations emitted, it has been found that the action is brought about by radium chloride contained in a sealed glass tube.

The β - and γ -rays are therefore capable of decomposing water, and it is calculated that about 1% of the absorbed radiant energy appears in the form of chemical energy. H. M. D.

Chemical Action of the Penetrating Radium Rays on Water. MIROSLAW KERNEBAUM (*Compt. rend.*, 1909, 148, 705—706. Compare preceding abstract).—The gaseous product obtained by the action of the β - and γ -rays from radium on water has been examined. About 200 cubic millimetres of gas were collected and found to consist almost entirely of hydrogen. On addition of potassium iodide to the water, from which the gas had been liberated, iodine was set free, and the author considers that hydrogen peroxide had been formed. H. M. D.

Ionisation Phenomena due to Snow. K. BERGWITZ (*Jahrb. Radioaktiv. Electronik.*, 1909, 6, 11—12).—Experiments are described which indicate that the ionisation produced in air which has been passed through a layer of snow is due to the active products radium-A, -B, and -C, which have been formed from radium emanation in the atmosphere and removed by the falling snow. The observations are opposed to the view of Costanzo and Negro (*Abstr.*, 1908, ii, 551), according to which the current of air liberates the ions which acted as condensation nuclei in the formation of the snow flakes.

H. M. D.

Velocity of the Cathode Rays Ejected by Substances Exposed to the γ -Rays of Radium. R. D. KLEEMAN (*Proc. Roy. Soc.*, 1909, A, 82, 128—145. Compare *Abstr.*, 1907, ii, 923).—In one series of experiments the scattering of the cathode particles produced by different thicknesses of metal-foil placed in the path of the rays was measured ; in another series, in which the velocity of the rays was investigated, the cathode rays were deflected into an ionisation chamber by an electro-magnet, and the ionisation in the chamber measured for magnetic fields of different strengths. The results show that part of the cathode radiation from a plate exposed to the γ -rays consists of very soft rays, which are absorbed in 1—2 cm. of air ; the

softness is practically independent of the thickness of the radiator. The radiation is softer on the side of the plate where the γ -rays emerge than on the side where they enter, and in the latter case the softness of the radiation is independent of the nature of the radiator, as shown by experiments with lead, tin, zinc, copper, iron, and other elements. The soft radiation produced by the β - and γ -rays of radium together is more penetrating than that produced by the γ -rays alone.

The penetrating cathode rays produced directly by the γ -rays are of different velocities. Their velocity, as determined by comparison under the same conditions, is approximately equal to that of the β -rays of radium. G. S.

Secondary γ -Radiation. JOHN P. V. MADSEN (*Phil. Mag.*, 1909, [vi], 17, 423—447).—The γ -rays of radium, carefully purified from β -radiation, were allowed to impinge on plates of various metals, and the quantity and absorption coefficient of the secondary γ -radiation emitted on both sides of the plates were determined. There is a marked lack of symmetry in the amounts of secondary γ -radiation emitted from the two sides, and in some cases a difference in the quality of the radiation.

The nature of the incidence (reflected) and emergence secondary γ -radiation depends on (1) the hardness of the primary γ -rays, (2) the metal employed as radiator, (3) the thickness of the radiator. With the most favourable thickness of metal, the secondary emergence radiation from zinc and aluminium is much more than from lead, but of a softer average character. Incidence (reflected) secondary γ -rays are less in amount and softer than emergence rays, and are also much less from lead than from zinc, aluminium, or carbon. It is supposed that much of the reflected γ -radiation from lead is of so soft a character that it is unable to penetrate into the electroscope.

The theory is put forward that the γ -rays of radium and, possibly, of thorium, consist of two distinct homogeneous bundles, the absorption value (λ/Δ) of the softer rays being approximately four times that of the harder rays whatever the absorbing material may be. Secondary radiation is derived from primary by a process of scattering, which also involves a reduction in the penetrating power (hardness) of the rays. Soft γ -rays from radium are turned back to a somewhat greater extent than hard γ -rays, and metals of high atomic weight have more scattering power than those of low atomic weight. The experiments are held to give little or no support to Kleeman's theory of selective absorption (*Abstr.*, 1908, ii, 553). R. J. C.

Passage of Röntgen Rays through Gases and Vapours. J. ARNOLD CROWTHER (*Proc. Roy. Soc.*, 1909, A, 82, 103—127).—A number of experiments on the absorption of primary Röntgen rays and the degree of ionisation produced in different gases by the passage of the rays are described; part of the results have already been published (this vol., ii, 287). The amount of ionisation produced by the direct action of the rays on a gas is directly proportional to the pressure of the latter. The relative ionisation (compared with air as standard) is an approximately additive property, as shown by experi-

ments with air, hydrogen, methyl and ethyl chlorides and iodides, and this is the more nearly true the harder the rays.

In continuation of earlier experiments on secondary Röntgen radiation (compare Abstr., 1907, ii, 922), it is now shown that the amount of secondary radiation emitted by different gases relatively to air is approximately independent of the hardness of the primary rays. Further, comparison experiments with primary and secondary rays indicate that the absorbing power of a gas for the secondary rays emitted by itself is normal. The total ionisation produced by the complete absorption of Röntgen rays in different gases is not the same, and the relative values depend on the hardness of the rays. The amount of energy required to produce an ion in different gases is somewhat different, and also depends on the hardness of the rays.

G. S.

Diffusion of Actinium and Thorium Emanations. SIDNEY RUSS (*Phil. Mag.*, 1909, [vi], 17, 412—422).—Rutherford's method of measuring the velocity of diffusion of active gases, namely, by comparing the amount of active deposit formed at varying distances from the source of activity, has been applied to the emanations of actinium and thorium. The rates of diffusion of actinium emanation in air, hydrogen, carbon dioxide, sulphur dioxide, and argon are, in accordance with Graham's laws, within the limits of error. The velocities of diffusion of actinium emanation in air at pressures varying from 764 mm. to 14 mm. are also in agreement with the ordinary laws of diffusion. Thorium emanation diffuses in a normal manner in argon and in air at various pressures. Since actinium emanation diffuses 1.19 times as quickly as thorium emanation, the molecular weights of the two emanations are as 1 to 1.42. Radium and thorium emanations have practically the same molecular weight, but actinium emanation has a much smaller molecule. Hence it is urged that actinium is not one of the products in the direct line of descent from uranium to radium.

R. J. C.

Presence of Thorium in Rocks. GIAN A. BLANC (*Atti R. Accad. Lincei.*, 1909, [v], 18, i, 241—246).—From measurements of the quantity of emanation liberated from a definite area of the soil of the garden surrounding the Physical Institute of Rome, the conclusion is drawn that one gram of this soil contains at least 1.45×10^{-5} gram of thorium (compare Abstr., 1908, ii, 248).

The author has examined a number of samples of rock in order to ascertain whether they contain amounts of thorium sufficient to account for an appreciable proportion of the radioactivity of the earth's crust, the procedure being as follows. A weighed portion taken from the interior of the specimen was powdered and fused with sodium and potassium carbonates, the part of the fusion insoluble in water being treated with hydrochloric acid, and the solution freed from silica by filtration. After adding sulphuric acid and separating the insoluble sulphates, including that of radium, ammonia was added and the precipitated hydroxides dried, powdered, and tested for radioactivity. These hydroxides exhibit activity which gradually increases

for about a week, and which is not due, in appreciable proportion, to radium. The presence of uranium in the hydroxides is excluded, since uranium carbonate is soluble in dilute solutions of the alkali carbonates; further, by adding known quantities of uranium to the hydroxides, it is found that the quantities of this metal necessary to produce the observed effects are considerably greater than would be expected from the values of the ratio uranium: radium calculated theoretically by Rutherford and confirmed experimentally by Boltwood.

The proportions of thorium found in one gram of various rocks are as follows: Syenite, 8.28×10^{-5} and 6.30×10^{-5} gram; granite, 3.14×10^{-5} and 2.07×10^{-5} . It will be seen that these amounts are of the same order as the amount found in the soil of Rome (*vide supra*).

T. H. P.

Behaviour of Bound and "Free" Electrons towards Electromagnetic Radiation. JOHANN KOENIGSBERGER and K. KILCHLING (*Ann. Physik*, 1909, [iv], 28, 889—924).—A critical comparison is made of the various electron theories as applied to the phenomena of absorption and dispersion. In reference to these, measurements have been made of the absorption of various organic colouring matters, coloured minerals, and coloured glasses, and of the variation of the absorption with the temperature. The data obtained are used to calculate the number of vibrating particles (p) which are associated with one molecule of the organic colouring matter. The value of p is one, and from the value of $p.e/m$ the authors conclude that this vibrating particle is a negative electron. Since the value of p is practically independent of the temperature, it follows that the total number of vibrating electrons remains unchanged when the temperature is varied. In the last section of the paper, the selective absorption of the elements and its relationship to Abegg's theory of valency is discussed.

H. M. D.

Existence of Positive Electrons in Vacuum Tubes. A. DUFOUR (*Compt. rend.*, 1909, 148, 481—484).—J. Becquerel (*ibid.*, 1908, 146, 1308; Abstr., 1908, ii, 751) has described certain experiments which have led him to assume the existence of free positive electrons. The author has repeated and confirmed Becquerel's observations, but shows that the deviation of the beam on which the theory of the latter is based is not due directly to the field, but is only the consequence of the displacement of the patch where the rays strike the glass when a magnetic field acts on the cathode rays. The beam in question is therefore a beam of canal rays, produced under somewhat unusual conditions.

G. S.

Hypothesis of Positive Electrons. JEAN BECQUEREL (*Compt. rend.*, 1909, 148, 546—548. Compare Abstr., 1908, ii, 751).—A reply to Dufour (compare preceding abstract), in which the author maintains the correctness of the observations which led him to formulate the hypothesis of positive electrons. It is also claimed that the conditions obtaining in the experiments of Dufour were not identical with those in the experiments of the author.

H. M. D.

The Kinetic Energy of the Positive Ions Emitted by Hot Platinum. F. C. BROWN (*Phil. Mag.*, 1909, [vi], 17, 355—361).—The kinetic energy of the positive ions emitted by hot platinum has been determined by measuring the rate of charging up of a metal plate by the ions from a hot strip of platinum contained in a parallel plate. Provided the distribution of energy follows Maxwell's laws, the gas constant should be calculable from the relation of current to voltage under these conditions. The temperature of the platinum was not allowed to exceed 1020° , since at higher temperatures negative ions are also evolved. In all cases the gas constant could be satisfactorily calculated, showing that Maxwell's laws hold good. The ions do not arise from chemical action, nor are they electrons, but are more probably evaporated atoms of some foreign substance. New platinum gives an abnormal number of ions when first heated.

R. J. C.

Absolute Zero of Potential. HERBERT FREUNDLICH and E. MÄKELT (*Zeitsch. Elektrochem.*, 1909, 15, 161—165).—Billitzer (*Ann. Physik*, 1903, [iv], 11, 923) found that silver powder falling through a solution of silver nitrate produces a current the direction of which changes when the concentration of the silver ions is diminished by adding a halogen salt and ammonia or potassium cyanide. In the solution in which the reversal occurs, the difference of potential between silver and solution is zero, and a measurement of the *E.M.F.* of a combination of a calomel electrode with silver in this solution gives the absolute *E.M.F.* of the calomel electrode. Billitzer found +0.13 volt in this way, the usually accepted value obtained by means of a mercury-dropping electrode being -0.57 volt. The authors have repeated Billitzer's experiment and confirmed it. They find, however, that the sign of the charge on the silver is but little affected by the silver ions. Hydrogen ions give a positive, hydroxyl ions a negative, charge to the silver, but in a solution of barium hydroxide it is positive, owing to the stronger action of the barium ions. The charge varies with the nature of the ions in the solution in exactly the same way as the charges on colloidal particles or on particles of non-metallic substances, and are probably due to friction and have nothing to do with the equilibrium between silver and silver ions, and therefore can give no information about the zero point of the potential series.

T. E.

Potential Energy of the Elements. DANIEL J. RANKIN (*Chem. News*, 1909, 99, 195. Compare Abstr., 1908, ii, 680).—In view of the fact that the values for the potential energy of the elements are functions of the atomic weights, and a change in the second decimal place of the latter effects, in some instances, two integers in the value of the potentials, it is necessary that the potentials should be subject to revision concomitantly with the atomic weight. The potential energy of the elements have been corrected by the atomic weights for 1909 and are tabulated. Graphically representing the volumes of static energy and potential energy of the elements by concentric circles, the effect of external energy on the sphere of potential is

regarded as determining whether or not combination occurs; in this view, the hypothesis of an interatomic fluid (ether) appears unnecessary.

J. V. E.

Potential of the Ferro-Ferricyanide Electrode. GILBERT N. LEWIS and LEDYARD W. SARGENT (*J. Amer. Chem. Soc.*, 1909, 31, 355—363).—The potential of a gold electrode dipping in a solution of potassium chloride containing potassium ferrocyanide and ferricyanide has been measured against a calomel electrode in the usual way. The three salts were used in varying concentrations, and the results are reproducible to 0.0001 volt. The temperature-coefficient of the *E.M.F.* was measured at two different concentrations, and from the results it has been calculated by the Helmholtz formula that the heat of the reaction represented by the equation $\text{Hg} + \text{Cl}^- + \text{Fe}(\text{CN})_6^{4-} = \text{HgCl} + \text{Fe}(\text{CN})_6^{3-}$ is 18,500 cal., in moderate agreement with the value determined directly.

The data obtained form the most accurate test so far made of the validity of the rule that in a mixture of salts having a common ion, the degree of dissociation depends solely on the concentration of that ion. The exact influence of the K^+ ion on the potential cannot be calculated, but increasing the concentration of that ion diminishes the ionisation of the ferrocyanide more than that of the ferricyanide, as theory indicates. In the presence of 0.8*N*-potassium chloride the ionisation of potassium ferrocyanide into the $\text{Fe}(\text{CN})_6^{4-}$ ion does not exceed 2—3%, a result which can only be reconciled with electrical conductivity measurements on the assumption that intermediate ions play an important part in the process of conduction. The potentials are independent of the nature of the anion.

G. S.

Potentials between Liquids. GILBERT N. LEWIS and LEDYARD W. SARGENT (*J. Amer. Chem. Soc.*, 1909, 31, 363—367).—The potential of a gold electrode in a solution of a potassium salt containing small quantities of potassium ferro- and ferri-cyanide depends only on the concentration of the potassium ion and the ratio of ferro- to ferri-cyanide (preceding abstract). If two such electrodes in solutions of two different potassium salts of the same K^+ ion concentration, and containing the same quantities of ferro- and ferri-cyanide, are combined, the electrode potentials balance, and the observed potential is that between the two liquids. The method, which has already been employed by Sauer (*Abstr.*, 1904, ii, 307), has been used to determine the contact differences of potential between dilute solutions of certain alkali salts with univalent anions, and the results are in excellent agreement with those calculated by a slightly modified form of the well-known Planck formula. Even when the alkali ion concentration is not quite the same for the two solutions, a correction can be applied and the method is applicable.

G. S.

[Electromotive Force of the Hydrogen-Oxygen Cell.] Correction. J. N. BRÖNSTED (*Zeitsch. physikal. Chem.*, 1909, 65, 744. Compare this vol., ii, 10).—When a slight error in calculating the value for the *E.M.F.* of the hydrogen-oxygen cell is corrected, the

value $E=1.234$ volts is obtained, in still better agreement with Nernst's value, 1.232 volts. G. S.

Electromotive Form of Nickel and the Effect of Occluded Hydrogen. EUGENE P. SCHOCH (*Amer. Chem. J.*, 1909, 41, 208—232).—Experiments have been made to determine the true reversible potential difference between nickel and *N*-nickel sulphate solution. This potential difference depends very considerably on the mode of preparation and previous treatment of the nickel electrode; it is diminished by air or oxygen, increased by hydrogen, and lowered by slight acidity of the nickel sulphate solution. The true equilibrium potential, which was reached from both sides, is given as 0.48 ± 0.005 volt. This value is reached in about twelve hours if an electrode of commercial nickel is immersed in the sulphate solution, which is boiled for some minutes and allowed to cool out of contact with the air. The solution should be perfectly neutral to litmus. The effect of occluded hydrogen on the potential difference was examined in detail. For both sheet nickel and finely divided nickel, prepared by reduction of the oxide in a current of hydrogen, the potential difference is increased. In consequence of this it is found that the electrolytic deposition of nickel does not take place until the potential is from 0.2 to 0.3 volt higher than the equilibrium potential, hydrogen being simultaneously deposited.

The equilibrium potential for finely divided nickel in contact with *N*-nickel sulphate solution is about 0.52 volt. A similar increase in the potential of finely divided iron as compared with solid iron was found by Richards and Behr. H. M. D.

Behaviour of the Nickel Anode and the Phenomena of Passivity. EUGENE P. SCHOCH (*Amer. Chem. J.*, 1909, 41, 232—256. Compare preceding abstract).—The dependence of the anode potential of nickel on the current density has been examined for normal solutions of nickel sulphate, nickel chloride, and potassium sulphate. The effect of the addition of the corresponding acids to the nickel salts and of potassium hydroxide to the potassium sulphate was also investigated. The nature of the observed phenomena may be described with reference to the nickel sulphate solution.

For current densities less than 4 milli-amperes per square decimetre, the nickel shows normal anodic behaviour, and the potentials are readily reproducible. This is not the case if higher current densities are used, and with excessive densities the potential falls continuously until the evolution of oxygen sets in. The chemical action which takes place as long as the potential for the evolution of oxygen has not been reached, is a quantitative solution of nickel. There is neither a critical voltage nor a critical current density which marks the termination of the normal anodic behaviour and the transition to the passive condition. The potential and density values corresponding with this transition depend on the previous electrolytic treatment. When the current is discontinued, the potential at the anode begins to rise immediately, the rate of rise diminishing with

increase in the extent of the preceding electrolysis and with diminution in the accompanying potential.

The observations lead the author to conclude that nickel has a very small ionisation velocity ; in consequence of this, comparatively small current densities result in the liberation of oxygen. Whether the nickel in the passive condition is protected by a layer of oxygen or covered by an oxide film cannot be decided on the basis of the observed facts.

H. M. D.

Maximum Voltage of Electrolytic Valve Cells. GÜNTHER SCHULZE (*Ann. Physik*, 1909, [iv], 28, 787—807. Compare Abstr., 1907, ii, 842 ; 1908, ii, 350, 560, and 658).—Experiments are described in which the author has examined the dependence of the maximum potential of the aluminium valve on the period of formation of the electrode, the nature of the dissolved electrolyte, and the thickness of the gas layer. The observations are in agreement with the view that the valve action is not due to the layer of oxide on the electrode, but to a much thinner layer of gas which is confined within the pores of the solid covering and separates the electrolyte from the metal. The phenomena observed in the process of formation of the valve are readily explained if it is assumed that the anions give rise to electrons when they reach the gas layer. The cause of the maximum voltage is attributed to the fact that the layer of gas cannot increase in thickness in consequence of spark discharge taking place when a certain potential is reached. The spark potential increases with the dilution of the electrolyte, and for different electrolytes at the same concentration it appears to increase as the degree of dissociation decreases ; it is independent of the current density used in the formation of the valve electrode and also of temperature. The paper contains a series of plates showing oscillographic records of the current through valve cells under conditions corresponding with continuous flow and spark discharge.

H. M. D.

Oxide Theory of the Oxygen Electrode. II. RICHARD LORENZ and E. LAUBER (*Zeitsch. Elektrochem.*, 1909, 15, 157—161. Compare this vol., ii, 15).—A cell consisting of two lead plates immersed in sulphuric acid is used. Hydrogen is passed through the acid surrounding the cathode plate. The cell is polarised under varied conditions, and the discharge curves then observed in the way previously described (this vol., ii, 15). Arrests were observed in the discharge curve at 2·05, 1·62, 1·43, 1·09, 0·79, 0·63, 0·53, 0·43, 0·12, 0·05, -0·14, -0·24, -0·29, and -0·45 volts. Streintz has measured the *E.M.F.* of combinations of different lead oxides and zinc in sulphuric acid ; these are 0·34 volt greater than the *E.M.F.*'s of corresponding cells with a hydrogen-lead cathode. Streintz's measurements give for the combination $\text{Pb} \mid \text{PbO}_2 \mid \text{H}_2\text{SO}_4 \mid \text{H}_2 \mid \text{Pb}$, 12·07 volt, and when the lead peroxide is replaced by other compounds, the following results : H_2PbO_3 , 0·62 volt ; Pb_3O_4 , 0·41 volt ; PbO , 0·12 volt ; Pb_2O , 0·08 volt ; massive lead, -0·14 volt ; lead sponge, -0·23 volt ; PbSO_4 , -0·28 volt. These results agree well with eight of the fourteen arrests observed, the substances corresponding with the remainder are not identified.

T. E.

Actinic Influence on Electrochemical Action. L. RAY FERGUSON (*J. Physical Chem.*, 1909, 13, 262—265).—It was stated by Robert Hunt (this Journ. 1845, 2, 311) that on exposing the element $\text{Pt} | \text{KI} | \text{AgNO}_3 | \text{Pt}$ to sunlight, although iodine was liberated at the anode, no silver was precipitated at the cathode, whereas in the dark crystals of silver were produced. The author finds that the *E.M.F.* of this element is 0.3 volt whether in dark or light, and under all conditions silver is liberated on completing the circuit. Hunt's experiments could not be repeated. R. J. C.

Electrical Conductivity of Solutions of Electrolytes in Water, Methyl or Ethyl Alcohol, Acetone, or in Binary Mixtures of these Solvents. S. W. SERKOFF [*J. Russ. Phys. Chem. Soc.*, 1908, 40, 399—427; 1909, 41, 1—43 (Physical Part)].—The author has measured the conductivities of solutions of various concentrations of lithium chloride, bromide, iodide, and nitrate, ammonium thiocyanate, and sodium iodide and salicylate in the above-mentioned solvents.

The solutions in a mixture of water and methyl alcohol all exhibit a minimum in the conductivity curve, this minimum corresponding closely with the maximum viscosity of the mixed solvent. The conductivities in mixtures of water and ethyl alcohol are for all the electrolytes much smaller than those calculated from the law of mixtures, owing to the greatly increased viscosity of the mixed solvent. With mixtures of methyl and ethyl alcohols, the conductivity curves are approximately rectilinear for all the electrolytes examined.

For mixed solvents of which one constituent is acetone, no parallelism exists between the conductivity and viscosity curves; when the mixture contains 75% of acetone, all the electrolytes exhibit a more or less well-marked maximum of conductivity. Sodium and lithium iodides, dissolved in a mixture of acetone and one of the three other solvents, give conductivity curves very similar to the corresponding fluidity curves; with lithium chloride and nitrate and sodium salicylate, however, the conductivity and fluidity curves are totally dissimilar, whilst with lithium bromide and ammonium thiocyanate, intermediate behaviour is observed. This maximum conductivity is not due to increase of the degree of dissociation, but is explained by the resolution of the compounds of the ions with the solvent. The lower the conductivity of an electrolyte in acetone at infinite dilution, the more marked is its maximum conductivity. In a mixture of 75% acetone with 25% of one of the alcohols, the conductivities at infinite dilution of all the lithium salts are approximately equal. T. H. P.

Action of Electrolytes on Copper Colloidal Solutions. E. F. BURTON (*Phil. Mag.*, 1909, [vi], 17, 583—597. Compare Abstr., 1906, ii, 275, 841).—The influence of electrolytes on the velocity with which the positively charged colloidal particles of copper move in an electric field has been investigated. The colloidal solutions were prepared by Bredig's method, and the electrolytes used were potassium chloride,

sulphate, phosphate and ferricyanide, and aluminium sulphate. Corresponding with the positive charge of the colloidal particles, it is found that the negative ion is the active agent in diminishing the velocity. The specific activity of the anion depends on its valency, and the relative activities of anions of different valency are approximately the same as the relative activities of these ions in respect of coagulative power. Observations on the coagulation of the copper solutions indicate that this takes place when the charge on the particles is neutralised, and these are no longer capable of moving in an electric field.
H. M. D.

Electrolytic Precipitation of Cuprous Oxide. D. MILLER (*J. Physical Chem.*, 1909, 13, 256—261).—The author has endeavoured to find the conditions for the electrolytic production of cuprous oxide in the finest state of subdivision. Sodium chloride solutions at 60° to 100° were electrolysed between copper poles. The higher the temperature and smaller the current density, the larger the particles and darker the colour of the precipitate. Increased concentration of the salt solution appeared slightly to decrease the size of the particles obtained. A very small proportion of gelatin had a very marked effect in reducing the size of the particles and lightening the colour. It was found that in the lighter (yellow) precipitates the cuprous oxide was largely hydrated.
R. J. C.

Formation of Autocomplexes in Solutions of Cupric Bromide, Cupric Chloride, and Cobalt Bromide. HENRY G. DENHAM (*Zeitsch. physikal. Chem.*, 1909, 65, 641—666).—Kohlschütter (Abstr., 1904, ii, 338) has shown that the transport number for the Cu^{++} ion in aqueous solutions of cupric chloride diminishes with increasing concentration of the solution, and finally becomes strongly negative; this result is accounted for on the assumption that complex anions of the type CuCl_4^{--} and $\text{Cu}(\text{H}_2\text{O})\text{Cl}_3^-$ are formed in increasing amount as the concentration of the solution is increased. In the present paper, it is shown that the transport number for the Cu^{++} ion in aqueous solutions of cupric bromide and cupric chloride and in alcoholic solutions of the former salt diminishes, and finally becomes negative, with increasing concentration, and the increased complex formation goes parallel with the change of colour in aqueous solution from bluish-green to brown. The transport number is more negative in alcoholic than in aqueous solutions of corresponding concentration, indicating greater tendency to complex formation in the former solvent. In the transport measurements the copper is precipitated at the cathode, mainly in the form of cuprous salt, but the amount of the latter is not proportional to the amount of silver liberated in the silver voltmeter, and a correction has to be applied for the cuprous salt remaining in solution. The neglect of this precaution probably accounts for the fact that Kohlschütter's results, although in qualitative, are not in quantitative agreement with those described in the present paper.

Further, the transport numbers for the Co^{++} ion in aqueous and alcoholic solutions of cobalt bromide diminish with increasing concentration of the solutions, and finally become negative.

The results of all these transport measurements are satisfactorily accounted for on the assumption that complex anions of the type CuX_3' and CuX_4'' , respectively CoX_3' and CoX_4'' (X = halogen ion), are formed in increasing amount as the concentration increases (compare Donnan and Bassett, *Trans.*, 1902, 81, 939). The question as to how far the accompanying changes of colour are also connected with differences of hydration is left undecided. G. S.

Dissociation Constants of the Dihydroxybenzenes. HANS EULER and IVAN BOLIN (*Zeitsch. physikal. Chem.*, 1909, 66, 71—77).—The acid dissociation constants of catechol, resorcinol, and quinol have been obtained by measuring the electrical conductivity of the ammonium salts in aqueous solution at 18° with the following results: catechol, $K_a = 3.3 \times 10^{-10}$; resorcinol, $K_a = 3.6 \times 10^{-10}$; quinol, $K_a = 1.1 \times 10^{-10}$ at 18° , 0.57×10^{-10} at 0° . When quinol forms salts in very dilute solution, an intense yellow colour is observed; this is not due to oxidation, but probably indicates that the salt exists in a quinonoid form. Quinone also forms a salt with an equivalent amount of alkali in dilute solution (K_a in this case exceeds 10^{-13}), but the conductivity of the mixture rapidly diminishes; this is connected with a chemical change (in absence of oxygen) in which quinol and a higher acid oxidation product are formed.

It is a general rule that in the carboxylic acids negative substituents increase the strength to a greater extent in the ortho than in the meta or para position (Ostwald), but resorcinol is rather stronger than catechol, and the authors confirm the statement of Hantzsch that *p*-nitrophenol is rather stronger than *o*-nitrophenol, so that the above rule does not hold for the acidic properties of hydroxy-compounds. G. S.

The Electron Theory of the Carbon Arc. JAMES A. POLLOCK (*Phil. Mag.*, 1909, [vi], 17, 361—366).—The author discusses the distribution of potential in a direct current arc on the basis of the theory that negative electrons are projected from hot carbon whether it be positive or negative pole. This projection gives rise to a forward or backward *E.M.F.*, according as it is from the negative or positive carbon. The electrons are arrested by collision with molecules, giving rise to a comparatively immobile layer of negative ions. This layer is the cause of the well known anode fall of potential, which is equal to the back *E.M.F.* at the anode, both depending on the temperature of the crater. The cathode fall of potential attains a characteristic value in all carbon arcs. The theory is shown to be in quantitative agreement with Duddell's results. R. J. C.

Magnetic Properties of Certain Compounds of Iron. S. WOŁOGDINE (*Compt. rend.*, 1909, 148, 776—777).—The temperatures have been determined at which various compounds of iron are demagnetised. The powdered substances were immersed in a suitable liquid, which was placed in a magnetic field. The temperatures at which the particles ceased to form chains between the poles were observed. The following values are recorded: magnetic iron oxide, 525° ; iron

sulphide (pyrrhotine), 300° ; iron carbide, 180° ; iron phosphide, 445° ; franklinite, 61° ; iron tungsten carbide ($2\text{Fe}_3\text{C}, 3\text{W}_2\text{C}$), 80° .

H. M. D.

Dependence of the Ratio of the Specific Heats of Gases on the Temperature. ROBERT FÜRSTENAU (*Ber. deut. physikal. Ges.*, 1909, 11, 137—138).—In reference to the author's measurements of the specific heat ratio (this vol., ii, 17), it is pointed out that two small corrections were omitted, these being necessary because the entire apparatus was not at one and the same temperature, and because of the influence of the diameter of the tube on the velocity of sound. In the case of air and carbon dioxide at 500° , the specific heat ratio is probably about 1·7% greater than the value previously given.

H. M. D.

Specific Heats of Solutions. I. HERMANN SCHLESINGER (*Physikal. Zeitsch.*, 1909, 10, 210—215).—A method is described for measuring the true specific heats of liquids and solutions at definite temperatures. The apparatus consists of a cylindrical glass vessel of 400—600 c.c. capacity, at the centre of which a spiral wire of platinum is supported; the ends of this are connected with thicker wires, which are sealed through the walls of the vessel. On passing a current through the wire a definite quantity of heat is generated in the interior of the liquid contained in the glass vessel, and the rise of temperature is determined by the expansion which takes place. For the purpose of measuring the increase in volume, the vessel is provided with a capillary tube, which is sealed into the upper part of the apparatus and dips into a small mercury cup. The displacement of the mercury in the graduated capillary tube measures the rise of temperature. The heat developed by the current is obtained by measuring the quantity of electricity by means of a gas voltmeter, and the potential difference at the ends of the platinum spiral by means of a voltmeter. In carrying out an experiment, the apparatus, which is provided with two carefully ground taps for the purpose of filling, is placed in a bath, the temperature of which must be kept quite constant during the time required by the experiment. This is absolutely essential, for the method depends on the assumption that the rise of temperature is entirely confined to the inner portions of the liquid, and that the outer portions are subjected to no heat exchange.

Measurements of the specific heat of 5, 65, and 85% sulphuric acid at temperatures ranging from 0° to 70° , and of that of pentane at 0° and -78° , are recorded. The specific heat of normal sulphuric acid solution falls from 1·000 at 0° to 0·845 at 35° , and then increases to 0·954 at 60° .

H. M. D.

Calculation of Specific Heats of Solutions. ARTHUR BAKOWSKI (*Zeitsch. physikal. Chem.*, 1909, 65, 727—736).—Taking into account the ionisation, as deduced from electrical conductivity measurements, and on the assumption that the specific heats of the different constituents of a solution are independent of their respective

concentrations, a formula, one form of which is $c = [C(\lambda - \lambda') + \delta + nMC_w]/(N + nM)$, is obtained as representing the specific heat, c , of salt solutions. In this expression, λ represents the equivalent conductivity, δ the difference between the water value of the specific heat of the solution and that of the water in the solution, n the number of molecules of water present for each molecule of salt, N and M the molecular weights of salt and water respectively, and C is a constant for any one solution. The formula admits of the calculation of the specific heat of a solution of any concentration when the specific heat at one concentration and the constant C (which depends on the conductivity of the solution) are known, and it is shown from Thomsen's data that it gives satisfactory results. Certain deviations are satisfactorily accounted for on the assumption that in some cases association between solvent and solute occurs. When this is taken into account, the same formula holds, the only effect being that the original significance of the constant C is altered. G. S.

Melting-point or Freezing-point Curves of Binary Systems when the Solid Phase is a Mixture of the Two Components and a Compound is Formed. JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1909, 66, 197—237. Compare Abstr., 1908, ii, 808).—A mathematical paper. A general expression is deduced for the thermodynamic potential of the systems in question when a compound is present, and then a somewhat complicated but quite accurate expression for the dissociation constant K is obtained. It is shown that the above expression yields the well-known formula $\delta \log K / \delta T = q / RT^2$, where q is the total heat of dissociation, and a definite expression is given for q in terms of the internal heat of dissociation and other factors. Nernst's method of setting up a purely empirical expression for q is adversely criticised, as is his theoretical treatment of equilibria in several other respects.

The possible forms of curves in the systems in question are discussed in detail. G. S.

New Form of Platinum Resistance Thermometer, and Molecular-weight Determinations in Fused Potassium Nitrate. JOH. GEORG LEONH. STERN (*Zeitsch. physikal. Chem.*, 1909, 65, 667—694).—The construction of a new form of platinum resistance thermometer, and its application to measure small differences of temperature in the neighbourhood of 300°, are described in detail. The chief sources of error are thermo-*E.M.F.*'s, induction phenomena, and the effect on the melting point of variations in the external temperature, but they have been so far overcome that values constant to within 0.04% were obtained for the freezing point of potassium nitrate. The values of the molecular lowering obtained with different salts are as follows: KNO_3 , 7.5; KCl , 14; NaNO_3 , 15; AgNO_3 , 18.5; $\text{Sr}(\text{NO}_3)_2$, 20; $\text{Ba}(\text{NO}_3)_2$, 20; SrCl_2 , 43; BaCl_2 , 43; K_2SO_4 , 52; Na_2SO_4 , 56. As the depression constant, calculated from the heat of fusion of potassium nitrate by van't Hoff's formula, is about 16, the above results indicate that potassium nitrite is bimolecular, potassium chloride unimolecular, the nitrates of sodium, silver, barium, and

strontium slightly ionised, whilst sodium chloride is split up into two parts, barium and strontium chlorides into three parts, and the sulphates of sodium and potassium into more than three parts (ions).
G. S.

Condition of Substances in Absolute Sulphuric Acid. GIUSEPPE ODDO and E. SCANDOLA (*Zeitsch. physikal. Chem.*, 1909, 66, 138—152. Compare Abstr., 1908, ii, 353).—A reply to Hantzsch (Abstr., 1908, ii, 14, 462; this vol., ii, 18). The authors have previously found that organic bases and certain other substances in sulphuric acid give values for the molecular weight about half the theoretical value, whilst according to Hantzsch the true values are about two-thirds of the theoretical. Hantzsch has expressed the view that the difference is due to the employment by the authors of insufficiently-dried preparations, but this is now shown to be erroneous. Experiments have been made with a large number of carefully dried organic bases, including pyridine, α -picoline, aniline, tribromoaniline, and acridine, and in all cases the molecular weights are about 50% of the theoretical value when calculated on the acid sulphates. Similarly, ammonium, sodium and potassium hydrogen sulphates have about half the theoretical molecular weights in this solvent. For water, up to a concentration of 4%, values about 7/12 of the theoretical molecular weight are obtained, rather less than the value found by Hantzsch.

The cause of the difference is not clear, but it is pointed out that if the first observation in each series of Hantzsch's experiments is neglected, and the authors' value for the freezing-point constant used in the calculation, the values then approximate to half the theoretical value. Traces of sulphur trioxide raise the apparent molecular weight.
G. S.

Cryoscopy of Colloids. JACQUES DUCLAUX (*Compt. rend.*, 1909, 148, 714—716).—The author considers that the proportionality which exists between the osmotic pressure and the lowering of the freezing point of a solution should also be found in the case of colloidal solutions. Measurements of the osmotic pressures and freezing points of solutions of ferric and thorium hydroxides have been made, and the experimental results support this view.
H. M. D.

Calculation of the Critical Temperature of an Associated Liquid from Surface-tension Results. J. LIVINGSTON R. MORGAN (*J. Amer. Chem. Soc.*, 1909, 31, 309—322).—The molecular surface tension of an associated liquid can be represented over a wide range of temperature by means of the interpolation formula $\gamma(M/d)_t^{\frac{2}{3}} = A + Bt + Ct^2$, where A , B , and C are constants. The formula may also be written in the form $\gamma(M/d)_t^{\frac{2}{3}} = \gamma(M/d)_0^{\frac{2}{3}} - k_0t - \frac{1}{2}dk/dt.t^2$, where k is the ordinary "constant" of the Eötvös-Ramsay-Shields formula (which for associated liquids varies with the temperature), k_0 is its value at 0° , and the other symbols have the usual significance. The constants are calculated from the data of Ramsay and Shields for a number of associated liquids by the method of least squares, and it is shown that

for a wide range of temperature two sets of coefficients are necessary to represent the experimental results at low and at high temperatures respectively. When the agreement is good at high temperatures, the critical temperature of the liquid is found by equating $\gamma(M/d)^{\frac{1}{3}}$ to zero and solving for the corresponding temperature, which is 6° less than the critical temperature. If, however, there is good agreement at low temperatures, the critical temperature can be calculated from the first differential coefficient of the above equation, $k_t = k_0 + t.dk/dt$, by solving it for the critical temperature. As k for associated liquids proves to be a linear function of the temperature, and attains its maximum value at 6° below the critical temperature, it would become zero at 6° above the negative critical temperature if the latter were attainable. Hence, from the last equation, the critical temperature $t_c = \frac{k_0}{dk/dt} + 6$.

The critical temperatures for water, acetic acid, methyl and ethyl alcohols, calculated by the above methods, are in excellent agreement with the observed values. G. S.

Laboratory Separation of Liquids with Slightly Different Boiling Points by a Process of Distillation. D. D. GADASKIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 66—80).—The author finds that beads of aluminium and, to a slightly less extent, of lead make a far more efficient fractionating column than those of glass, the liquid experimented with being a mixture of benzene, b. p. $80-82^{\circ}$, and toluene, b. p. $109-112^{\circ}$. In order to avoid washing of the liquid by the vapour, a cone of aluminium wire, 3 mm. in thickness, is placed with its base resting on the bottom of the dephlegmator and its point uppermost; this arrangement greatly increases the effectiveness of the separation. T. H. P.

New Dephlegmators: Fractional Distillation of Substances of High Boiling Points. MICHAEL M. TICHWINSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 81—89).—Details are given of a number of new forms of dephlegmator. T. H. P.

Vapour Pressure of Saturated Solutions. ALEXANDER W. SPERANSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 90—105).—By means of the tensimeter, using α -bromonaphthalene as manometric liquid, the author has determined the differences in vapour pressure between water and saturated solutions of sodium chloride and nitrate, potassium chloride, tartaric acid, and resorcinol at temperatures 23° to 51° .

The relation between the vapour pressure p of the saturated solution and the temperature T is expressed by Bertrand's formula: $p = K[(T - \lambda)/T]^{50}$, where K and λ are constants. Such a formula is also applicable to saturated solutions of magnesium chloride at $0-25^{\circ}$.

The relation between the vapour pressures of saturated solutions and the percentage concentration, C , is given by the formula: $\log p = a \log C + b$, where a and b are constants. This formula is applicable with moderate accuracy to solutions of sodium chloride and nitrate,

potassium chloride, tartaric acid, and magnesium chloride. For resorcinol the deviations are greater, but this may be due to inaccuracy in the determinations of the vapour pressure and solubility, the latter only varying very slightly. This relation $\log p = a \log C + b$ may be expressed in the form $p_1/p_2 = C_1^a/C_2^a$, that is, the vapour pressures of the saturated aqueous solutions of one and the same substance at two temperatures are related to one another as the corresponding concentrations raised to the power a .

The two expressions $p = K[(T - \lambda)/T]^{50}$ and $\log p = a \log C + b$ are applicable to saturated solutions of potassium sulphate at temperatures from the boiling to the cryohydric point.

Combination of these two formulæ gives $C = A[(T - \lambda)/T]^n$, which expresses Bertrand's formula in its general form. T. H. P.

New Method of Measuring the Partial Vapour Pressures of Binary Mixtures. MARTIN A. ROSANOFF, A. B. LAMB, and F. E. BREITHUT (*J. Amer. Chem. Soc.*, 1909, 31, 448—456 *).—The method described is based on the fact that if a mixed vapour of constant composition is passed through a liquid mixture of the same substances, the composition and temperature of the liquid will steadily change until complete equilibrium, as regards both temperature and pressure, has been established. A stationary temperature indicates that equilibrium has been attained, and the vapour bubbling through the liquid may then be condensed in any quantity and analysed. The liquid can be also withdrawn and analysed. Assuming that the ratio of the partial pressures in the vapour is equal to the molar ratio of the components, and knowing the total pressure from direct observation, the partial pressures can be readily calculated. In cases in which the above assumption is inadmissible, the exact relation between molar ratios and partial pressures can be determined by separate experiments.

The older methods are criticised, and the new method is described in detail. The apparatus consists essentially of an inner tube, in which the saturated mixed vapour of constant composition is passed through the liquid mixture, and an outer vessel surrounding it, in which the vapour is produced by boiling a liquid mixture, the composition of which is kept constant by the introduction of the more volatile component in such quantities as to keep the boiling liquid at a constant temperature. The results of some experiments are quoted which prove that the method is trustworthy. E. G.

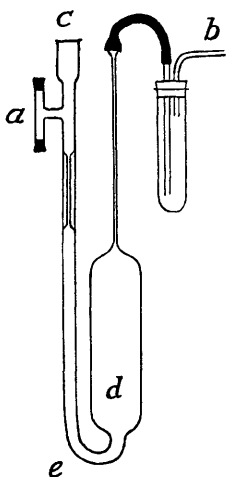
Electric Thermoregulator. REGAUD and FOUILLAND (*Ann. Chim. anal.*, 1909, 14, 141—146).—The apparatus consists essentially of a mercurial siphon barometer, the short limb of which is sealed into a larger tube containing dry hydrogen.

The lower part of the mercurial column is traversed by a portion of the heating current, the conducting wires being so placed that the expansion of the hydrogen will cause the contact to be broken if the temperature of the bath exceeds that desired. This temperature can be altered if needful by inclining the barometer from the vertical.

L. DE K.

* and *Zeitsch. physikal. Chem.*, 1909, 66, 349—358.

Simple Method for Filling Toluene Thermoregulators. J. P. MCGOWAN (*Chem. News*, 1909, 99, 181).—The author has devised the following method for filling toluene thermoregulators,



considered to be especially advantageous where a salt solution is used between the toluene and mercury. If the side tube *a* is closed, suction at *b* and the introduction of toluene in *c* will cause the filling of the regulator with toluene. The salt solution is then poured into *c* until sufficient has been introduced into the bulb *d*. Finally, mercury is introduced into *c*, and is likewise sucked into the bend *e*; the capillary tube is fused in a blowpipe flame, and the tube *c* is filled with mercury in the usual manner.

J. V. E.

The Metalloids Arsenic and Antimony. Thermochemical Point of View.

JOHN C. THOMLINSON (*Chem. News*, 1909, 99, 133. Compare Abstr., 1908, ii, 1016).—It is found that the heats of formation of NH_3 , PH_3 , AsH_3 , and SbH_3 continually decrease as the atomic weight of the elements N, P, As, and Sb increase, and, consequently, are not

in accord with the expected values. This apparent discrepancy is considered to be due to the fact that these compounds are gases, whilst the elements above referred to are solid at the temperature for which the data are reckoned. Hence allowance must be made for the latent heats of fusion and volatilisation of these elements, and, in general, for the difference of heat content between the solid and gaseous state at that temperature. When this is done, the amounts of heat absorbed by phosphorus, arsenic, and antimony in assuming the gaseous state in their hydrides are found to be roughly proportional to their atomic weights. Calculations are made showing an approximate agreement between the calculated and experimentally observed heats of formation of phosphorous acid, arsenic trioxide, and arsenic pentoxide.

J. V. E.

Heat of Oxidation of Tin. Heat of Combination of Acidic Oxides with Sodium Oxides.

WILLIAM G. MIXTER (*Amer. J. Sci.*, 1909, [iv], 27, 229—234. Compare Abstr., 1908, ii, 929).—The heat of oxidation of tin has been determined by burning the metal in oxygen in a calorimetric bomb, and also by oxidising it by means of sodium peroxide; the methods of procedure were analogous to those described in a previous paper (*loc. cit.*). In the experiments, tin-foil, tin-turnings, and a specimen of tin prepared by decomposing an alloy of tin and sodium by means of alcohol and water were used. The mean results are represented by the equation $\text{Sn} + \text{O}_2 = \text{SnO}_2$ (cryst.) + 137,200 cal. and $\text{Sn} + 2\text{Na}_2\text{O}_2 = \text{Na}_2\text{SnO}_3 + \text{Na}_2\text{O} + 133,800$ cal. When tin prepared from the alloy was burned in oxygen, a heat development higher than the average was obtained, although combustion was not quite

complete; it is considered probable that the mono- and di-oxides combine with formation of a little sesquioxide, Sn_2O_3 , heat being developed in the latter change.

The heat of combustion of stannous oxide was determined with material prepared by two methods: $\text{SnO}(\text{cryst.}) + \frac{1}{2}\text{O}_2 = \text{SnO}_2(\text{cryst.}) + 71,000$ cal. Finally, the heat of combination of amorphous stannic oxide, prepared by heating metastannic acid and sodium oxide, has been determined: $\text{Na}_2\text{O} + \text{SnO}_2(\text{amorphous}) = \text{Na}_2\text{SnO}_3 + 37,100$ cal. The thermal relationship between crystalline and amorphous stannic oxide is represented by the equation $\text{SnO}_2(\text{amorphous}) = \text{SnO}_2(\text{cryst.}) + 1700$ cal. G. S.

General Formula for Saturated Vapours. O. PILLING (*Physikal. Zeitsch.*, 1909, 10, 162—168).—On the assumption that there is a gradual change in density in passing through the surface which separates a liquid from its saturated vapour, and that the behaviour of the substance in the transition layer is regulated by van der Waals' equation, the author deduces the relationship $\log P/p = 2r/3ART$, in which P is the molecular pressure ($= a/v^2$), p the vapour pressure of the liquid at temperature T , r the latent heat of vaporisation, and A and R are constants. P is shown to be equal to $S(1/v + 1/V)/2A$, S being the internal heat of vaporisation, v and V the specific volumes of the saturated vapour and of the liquid respectively. It is further shown that the vapour pressure p (in atmospheres) at the temperature T is given by the equation $T_s/T = (1 - m \log p)^{\frac{1}{2}}$, T_s being the boiling temperature at atmospheric pressure, and $m = 3T_s/\log e \cdot r_s/M$, in which r_s is the latent heat of vaporisation at the temperature T_s , and M is the molecular weight of the substance. A further relationship is given by the equation $r/r_s = (T_s/T)^{\frac{1}{2}}$. The experimental data for water, mercury, ethyl ether, ethyl alcohol, acetone, chloroform, carbon tetrachloride, and carbon disulphide are shown to be in agreement with these two equations. H. M. D.

Modifications in Victor Meyer's Vapour Density Apparatus. EUGENIO MORALES CHOFRE (*Anal. Fis. Quim.*, 1909, 7, 10—12).—Slight alterations are suggested in the ordinary apparatus to facilitate the automatic introduction of the substance to be vaporised, and the direct measurement at a constant temperature of the displaced air.

W. A. D.

Molecular Volumes, Densities, and Atomic Weights. ANATOLE LEDUC (*Compt. rend.*, 1909, 148, 548—550).—The values of the relative molecular volume ϕ , as given by the equation $Mpv = RT\phi$, are recorded for twenty different gases. The densities calculated from the molecular weights by the equation $D_0 = 31.225 M/\phi$ are compared with the experimental values of the density. Molecular-weight values, calculated from this equation by inserting the experimental density values, are also recorded. The atomic-weight values of nitrogen deduced from the densities of nitrogen, nitric oxide, nitrous oxide, and ammonia are respectively 14.006, 14.004, 14.0045, and 14.0042. The values for carbon deduced from the densities of carbon monoxide, carbon dioxide, methane, and acetylene are respectively 12.004, 12.003,

12·0056, and 12·005. The value for chlorine, 35·463, is identical with that obtained by Dixon and Edgar, and that for sulphur, 32·072, agrees with that obtained from chemical data. The author draws the conclusion that the method of molecular volumes yields very accurate values for the atomic weights, and that the method is trustworthy both in the case of gases liquefied with difficulty and those which are readily condensed.

H. M. D.

Calculation of Molecular Weights by means of Vapour Densities: Toluene. ANATOLE LEDUC (*Compt. rend.*, 1909, 148, 832—834).—The inaccurate value obtained by Ramsay and Steele (Abstr., 1903, ii, 635) for the molecular weight of toluene is a result of the method followed by these authors to arrive at the limiting value of pv/T , when $p = 0$.

From Ramsay and Steele's numbers, the author finds that the mean coefficient of deviation of toluene vapour from Boyle's law between 60 and 27 cm. pressure agrees closely with the calculated value, so that this vapour exhibits normal behaviour. Calculation of the molecular weight, according to the equation given previously by the author (preceding abstract), leads to numbers varying from 92·074 to 92·094, the mean being 92·083, which is in very close agreement with the real molecular weight, 92·088. This result is so satisfactory that the vapour density of toluene may be employed to calculate the atomic weight of carbon, for which the value 12·003 is obtained.

T. H. P.

Viscosity and Fluidity. EUGENE C. BINGHAM and MISS J. PEACHY HARRISON (*Zeitsch. physikal. Chem.*, 1909, 66, 1—32. Compare Abstr., 1906, ii, 218; 1908, ii, 1017).—The fluidities of a large number of liquids, obtained from the viscosity data of Thorpe and Rodger (Abstr., 1897, ii, 374), are plotted against the corresponding temperatures. For a number of non-associated liquids (hydrocarbons, ethers, halogen derivatives) the curves are nearly straight lines, showing that the fluidity is approximately a linear function of the temperature, and the same rule holds approximately for certain associated liquids (organic acids) and also for alcohols at high, but not at low, temperatures. The fluidity of mercury is also approximately a linear function of the temperature. The fluidities of non-associated compounds at their boiling points lie on a straight line, an indication that for these compounds the fluidities are additive properties.

In dealing with different liquids, it is found most satisfactory to compare the slopes of the curves, or the temperatures corresponding with a definite fluidity. On this basis, constants for different atoms (carbon, hydrogen, oxygen, the halogens, etc.) and also for the double linking and the benzene ring are calculated; the constants calculated from different classes of compounds are in good agreement. It is shown that for non-associated liquids the absolute temperatures at which the respective liquids have the fluidity in question can be calculated from the constants with an accuracy of 1%.

The temperatures at which associated liquids have a given fluidity are much higher than those calculated from the constants applicable

to associated liquids. On the assumption that viscosities are additive, the degrees of association for a number of associated liquids are obtained by dividing the observed by the calculated temperatures; the results are in general agreement with those obtained by other methods.

For convenience of reference, the fluidities at intervals of 10° for a large number of liquids are given in tabular form. G. S.

Theory of Anisotropic Liquids. II. EMIL BOSE (*Physikal. Zeitsch.*, 1909, 10, 230—244. Compare this vol., ii, 215).—A detailed account is given of the author's theory that anisotropic liquids consist of molecules which have the form of ellipsoids of rotation and tend to move by preference in the direction of the long axes of the molecules. A division of anisotropic liquids into two classes is suggested, according to whether the transition from the isotropic to the anisotropic form is accompanied by a decrease or an increase in the viscosity. In general, liquids belonging to the second class have a greater molecular weight than those which belong to the first. For liquids belonging to the first group it is shown that the ratio of the maximum viscosity of the isotropic form to the minimum viscosity of the anisotropic form can be accounted for in nearly all investigated cases by the assumption of molecules having the form of ellipsoids of rotation. To account for the existence of two anisotropic forms, the conception of the ellipsoid of rotation is replaced by that of a triaxial ellipsoid. The transition temperatures which limit the stable existence of the anisotropic forms and of the isotropic variety are determined by the relationships which exist between the energy corresponding with the irregular molecular motions and that of the special orientated motions in the direction of the axes of the ellipsoids. The heats of fusion, of transition, and of clearing are discussed, and it is shown that the optical properties of an isotropic liquid are considerably influenced by a magnetic field. H. M. D.

Experimental Investigation of Gibbs's Theory of Surface Concentration regarded as the Basis of Adsorption. II. WM. C. MCC. LEWIS (*Phil. Mag.*, 1909, [vi], 17, 466—494. Compare Abstr., 1908, ii, 357).—Further measurements have been made of the surface condensation at the boundary between aqueous solutions and a hydrocarbon oil. The interfacial tension was measured for aqueous solutions of about twenty electrolytes, and in all cases the effect of the electrolyte was to lower the tension. It was found previously that the adsorption effect in the case of aqueous solutions of sodium glycocholate, Congo-red, and methyl-orange is very much greater than that indicated by Gibbs's theory. A similar discrepancy is now found in the case of sodium oleate and sodium hydroxide. On the other hand, the results obtained for aqueous solutions of caffeine are in agreement with Gibbs's equation, and in the case of potassium chloride, silver nitrate, barium chloride, and cupric chloride the adsorbed quantities are of the same order as those indicated by theory, although the experimental values are in every case greater than the calculated values.

Evidence has been obtained that the adsorption of electrolytes is to some extent selective, the cation being more readily adsorbed than the anion; this is probably due to an electrical effect, for the hydrocarbon oil is negatively charged with reference to the aqueous solution, the difference of potential between the oil and water being approximately 0.15 volt. This electrical effect may account for the discrepancies between experiment and theory in the case of the inorganic salts examined, but it is not sufficient to account for the much larger difference found in the case of sodium glycocholate and the other substances in the same group. It is suggested that the greater discrepancies may be due to the change in density of water on passing from the bulk to the surface film, or that an irreversible phenomenon of the nature of gelatinisation upon the oil surface plays a part in the process of surface condensation.

H. M. D.

Adsorption of Sugar. PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1909, 16, 489—498).—The composition of a dextrose solution shaken with animal charcoal is the same after three minutes' treatment as after twenty-four hours, indicating that the retention of sugar is due to true absorption and not to decomposition. Increasing quantities of acetone or acetic acid reduce the adsorption, and in presence of 10% of either it is possible to clarify sugar solutions with charcoal without loss. The presence of protein does not influence the adsorption of dextrose. The above statements apply equally to sucrose.

Normally, a substance is only adsorbed in aqueous solution when it reduces the surface tension of the water. Traube has shown the surface tension of sucrose solutions to be greater than that of water, and similar measurements are now given for dextrose. It is pointed out that a substance may also be absorbed when it increases the compressibility of the solvent, or when under increased pressure it becomes more soluble.

E. F. A.

Dissociation of Carbon Dioxide in the Carbon Monoxide-Oxygen Flame. FRITZ HABER and ROBERT LE ROSSIGNOL (*Zeitsch. physikal. Chem.*, 1909, 66, 181—196).—Le Chatelier (1888), on the basis of experiments by Deville, which appeared to indicate that carbon dioxide in the flame of carbon monoxide burning in oxygen was dissociated to the extent of 40% at 3000°, calculated the dissociation of carbon dioxide at different temperatures by a thermo-dynamical method, and obtained values in good agreement with the recent observations of Nernst and Wartenberg. The authors point out, however, that the calculation is unsatisfactory in more than one respect, and have been led to repeat Deville's experiments by a modified method. A silver capillary tube, surrounded by a condenser of the same metal, through which cold water circulated, was placed in the flame so that the end of the capillary was 1—2 mm. over the inner cone of the flame, and gases were withdrawn from the latter and analysed. The results indicate that the equilibrium constant

$$K = [\text{CO}_2]/[\text{CO}] \times [\text{O}_2]^{\frac{1}{2}}$$

(where the brackets denote partial pressures) is about 4, corresponding

with a dissociation of about 37%. The temperature of the flame is calculated from thermal and other data as lying between 2600° and 2670° , but radiation and other causes render the value somewhat uncertain. This estimate is confirmed by the observation that a very thin piece of iridium foil begins to melt when held just over the inner cone.

Nitric oxide cannot be detected in the flame just above the inner cone, but can just be detected at a point 15 mm. higher. The proportion of nitrogen in the first position is 1.7%, in the second position 4.3%. The proportion of oxygen in both the positions mentioned is about 13%. The original oxygen from the bomb contained 4.5% of nitrogen. G. S.

Molecular Diffusion of Gases through Pores and [the Phenomenon of] Effusion. MARTIN KNUDSEN (*Ann. Physik*, 1909, [iv], 28, 999—1016. Compare this vol., ii, 216).—Measurements have been made of the rate of passage of hydrogen, oxygen, and carbon dioxide through small holes in a platinum plate 0.0025 mm. thick. Two apertures measuring respectively 5.2 and 66×10^{-6} square cm. were employed, and the dependence of the rate of diffusion on the pressure of the gas was examined.

The experimental results show that the rate of passage of the gas through a small aperture is inversely proportional to the square root of the density and directly proportional to the pressure difference on the two sides, provided that the diameter of the aperture is small in comparison with the mean free path of the molecules. When the ratio of these becomes smaller than $1:10$, the process no longer takes place according to the requirements of the molecular diffusion formula. For a given pressure difference on the two sides of the aperture the deviations from this formula increase as the ratio of this pressure difference to the mean pressure diminishes. When the diameter of the aperture is more than about ten times as large as the mean free path of the gas molecules, the rate of flow of the gas through the aperture agrees satisfactorily with the law of isothermal effusion.

H. M. D.

Diffusion of Chromium, Iron, and Aluminium Salts through Gelatin Jelly. HENRY R. PROCTER and DOUGLAS J. LAW (*J. Soc. Chem. Ind.*, 1909, 28, 297—299).—Results of experiments are given in which the rate of diffusion of metallic salt solutions was observed; the solutions were poured on the surface of 5% gelatin jelly contained in Nessler cylinders, and coloured pink by the addition of slightly alkaline phenolphthalein. Owing to the hydrolysis of the chromium salts employed, the penetration of the acid was much more rapid than that of the base. Solutions of normal salts and others rendered basic by the addition of definite quantities of sodium carbonate were employed, and it was noticed that in the case of chromium chloride the rate of diffusion and the apparent amount of hydrolysed acid was unaffected by these conditions, whilst with chrome alum, the diffusion of the chromium was rendered much slower, but without any corresponding influence on that of the acid. The rate of diffusion was

found to be quite independent of the bore of the tube. Striæ or layers of green were noticed, recalling the effects observed in the diffusion of potassium dichromate in gelatin containing traces of silver nitrate (compare Abstr., 1907, ii, 533). The phenomena in the case of iron and aluminium salts were very similar in character to those observed in the case of chromium salts. W. P. S.

Osmotic Pressure of Sucrose Solutions at 20°. HARMON N. MORSE and WILLIAM W. HOLLAND (*Amer. Chem. J.*, 1909, 41, 257—276. Compare this vol., ii, 216).—Twenty-seven measurements of osmotic pressure are recorded for the usual ten weight-normal solutions. The supply of sucrose, with which the measurements at 10°, 15°, and 25° were made, became exhausted before the series at 20° was completed, and the authors have experienced great difficulty in obtaining fresh material of the same degree of purity. The new material has given slightly higher values than had been expected according to the previous measurements. The data for the various temperatures are compared, and the authors state that the experimental evidence, which has now been accumulated, points to the substantial equivalence of the temperature-coefficients of osmotic and gas pressures. H. M. D.

Selective Permeability of the Coverings of the Seeds of *Hordeum vulgare*. ADRIAN J. BROWN (*Proc. Roy. Soc.*, 1909, 81, B, 82—93).—The permeability of the coverings of the seeds of a variety of barley, *Hordeum vulgare*, var. *cærulescens*, for dissolved salts and other substances, and the proportions of water taken up from different solutions, have been investigated. The property does not depend on the living protoplasm, as seeds killed by immersion in hot water are equally efficient. The membrane in question is confined to the testa of the seed.

The seeds contain a blue pigment turned red by acids, hence the entrance of the latter can readily be detected. When seeds are immersed in normal solutions of hydrochloric or sulphuric acid, water readily enters, but acid does not. On the other hand, acetic, formic, propionic, and trichloroacetic acids readily enter along with the water, as does ammonia in dilute solution. The seed-covering is impervious for most dissolved salts, but mercuric chloride and cyanide and cadmium iodide pass through, whilst mercuric nitrate and sulphate and cadmium nitrate and sulphate do not diffuse. In aqueous solution, sucrose, glucose, and glycerol do not pass through, but certain non-electrolytes of low molecular weight, such as ethyl alcohol, aldehyde, ethyl acetate, and acetone, readily pass through, as does iodine dissolved in an aqueous solution of potassium iodide. In the experiments in which the covering is permeable, it is shown that this is not due to destruction of the membrane; when, for example, seeds are immersed in a solution containing both acetic and sulphuric acids, only the former acid and water pass through.

The proportion of water absorbed from solution (expressed as a percentage calculated on the original weight of the dry seed), as well as the rate of absorption, depend largely on the nature of the solute.

After eleven days, the seeds have absorbed from a normal solution of sodium chloride 36—37% of water, as compared with 70% from water alone. About the same proportion is absorbed from other alkali chlorides and nitrates, but potassium nitrate gives a distinctly higher value. It is remarkable that the proportion absorbed from normal solutions of sucrose and dextrose is only a little greater than from normal sodium chloride. The amount of water taken up from solutions of substances which pass through the membrane is usually almost as great as from water alone. As regards the rate of absorption, the solution of ethyl alcohol enters at about the same rate as pure water, the solution of acetic acid more rapidly, and the solution of ethyl acetate still more rapidly, although the equilibrium point is the same in each case.

No satisfactory explanation of the semipermeable action in question has been obtained; it may be that the molecules of the two classes of substance are combined in a different way with the solvent. The only strong electrolyte which can traverse the membrane is trichloroacetic acid. G. S.

Origin of Osmotic Effects. II. Differential Septa. HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1909, 81, B, 94—96. Compare Abstr., 1907, ii, 13, 848, 849, 850; 1908, ii, 814—817; and Brown, preceding abstract).—An attempt to account for the results described in the previous abstract on the basis of the author's theories of solution and osmotic pressure. The measurements involve the study of a struggle for "hydrone" between a mass of fine particles of starch within the grain and the solution outside the grain. The concentrating efficiencies of the solutes are in general agreement with those obtained in other ways. The compounds which penetrate the membrane are presumably slightly, if at all, hydrated, whilst those which do not penetrate form stable hydrates. It is suggested that the colloidal surfaces of the intramolecular passages in the membrane are associated with water molecules ("hydrolated" and "hydronated"); solutes which are hydrolated would be retained in virtue of the attraction between them and the hydrolated membrane, whilst non-hydrolated solutes would pass through. Some isolated observations made by Brown, such as the action of ethyl acetate in promoting the entry of water into the grains, can also be readily accounted for on the author's theory. G. S.

Molecular Weight and Form of Substances. Work of Molecular Weight. MICHEL YÉGOUNOFF (*Centr. Bakt. Par.*, 1909, ii, 23, 1—10).—The form of a substance produced when two substances inter-diffuse depends on the respective molecular weights; similarly, the form of a microbe colony growing in the field of a diffusing substance depends on the molecular weight of the substance. Equations are deduced by means of which the molecular weight may be calculated in certain simple cases from the form of a substance produced under the influence of diffusion, and conversely, when the molecular weight is known, the form of the resulting substance can to some extent be foretold. The work of the molecular weight is,

however, usually masked by many other influences, such as movements of the medium, variation of temperature, and variation of concentration.
G. S.

Aqueous Solutions. CAM. GILLET (*Bull. Soc. chim. Belg.*, 1909, 23, 119—129).—Various properties of aqueous solutions are considered from the standpoint of the view that liquid water consists of molecules of dihydrol and hydrol in dissociation equilibrium corresponding with the equation $(\text{H}_2\text{O})_2 \rightleftharpoons \text{H}_2\text{O}^+ + \text{H}_2\text{O}^-$. Corresponding with the + and - signs, the hydrol molecule is supposed to exist in two forms which are related to one another in a similar way to that exhibited by tautomeric forms. Aqueous solutions of all substances are supposed to contain chemical compounds formed by union of the dissolved substance with the positive or negative hydrol. Corresponding with the increase in the dissociation of the dihydrol molecules with rise of temperature, the solubility of most substances in water increases. The changes in volume in the formation of a solution, the lowering of the vapour-pressure, and the osmotic pressure are discussed in relation to the dissociation equilibrium and the formation of compounds of hydrol with solute.
H. M. D.

Mutual Influence on Solubility in Aqueous Solutions of Ether, Chloroform, Phenol, etc. HERMANN FÜHNER (*Ber.*, 1909, 42, 887—889).—The fact that a clear saturated aqueous solution of chloroform when mixed with a similar solution of ethyl ether produced a turbidity due to the separation of a mixture of ether and chloroform led to the examination of the behaviour of a number of aqueous solutions of organic solvents. The solubility of ether in water at 20° is 6.48%, and that of phenol, 8.40%, yet 5% solutions when mixed become milky, although 4% solutions remain clear after mixing. These phenomena have also been examined by Traube's stalagmometer.
W. R.

Theory of Concentrated Solutions. J. TIMMERMANS (*Bull. Soc. chim. Belg.*, 1909, 23, 129—148).—The author is of the opinion that the anomalies exhibited by concentrated as compared with dilute solutions are to be explained by the application of the ideas of van der Waals and not by the assumption that compounds are formed. The influence of pressure on the mutual solubility of a pair of liquids is considered, and it is shown that, in general, a pair of liquids can be made to pass through all the stages of mutual miscibility by varying sufficiently the external pressure. It is thus possible to pass continuously from dilute to concentrated solutions by variation of the pressure, and, on the basis of this, the author proposes to elaborate a theory of concentrated solutions.
H. M. D.

Supposed Influence of Crystallisation in Modifying the Properties of the Solution of a Substance Prepared by Mixing two Solutions. DESIRÉ GERNEZ (*Compt. rend.*, 1909, 148, 537—541).—The author has repeated some experiments which were performed sixty years ago and appeared to show that the rotatory

power of a solution prepared by mixing equal volumes of equimolar solutions of sodium and potassium tartrates is different from that of an equally concentrated solution prepared from the crystalline double salt. Equimolar solutions of the two tartrates were mixed in equal volumes and the rotation observed; the solution was then allowed to crystallise completely, and a fresh solution of the same concentration was prepared from the separated crystals. The rotation of this solution was exactly the same as that of the original solution. The same result was obtained with sodium and ammonium tartrates.

H. M. D.

Existence and Properties of Dispersive Systems in the Region between Colloidal and Crystalloidal Solutions. THE SVEDBERG (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 168—175).—By the reduction of auric chloride solutions by means of hydrazine and an ethereal solution of phosphorus, employing solutions of gradually decreasing concentration, the author prepared colloidal solutions of metallic gold containing particles of gradually diminishing size. By the hydrolysis of ferric chloride solutions and by the action of hydrogen sulphide on solutions of arsenious acid, a similar series of colloidal solutions of ferric hydroxide and arsenious sulphide was obtained. The absorption of light by these solutions was examined, and it was found that the specific absorption (the absorption due to each particle of the suspended phase) diminishes as the size of the particles decreases, and approximates to the absorption which is characteristic of the crystalloidal solution.

H. M. D.

Crystal-like Arrangement of Fine Solid Particles. RUDOLF KRULLA (*Zeitsch. physikal. Chem.*, 1909, 66, 126—128).—Iron and tin were fused together in a graphite crucible under a layer of sodium hydrogen carbonate, the greater part of the sodium carbonate removed by washing, and the fused mass placed in a dish with water and stirred. After some time it was noticed that part of the metallic-looking dust on the surface of the water had arranged itself in the form of a star, and on stirring, new star-like groups were formed. The composition of the stars could not be determined, neither was it found possible to repeat the experiment. A number of the groups are figured.

G. S.

Inorganic Ferments. IV. Iridium Catalysis of Hydrogen Peroxide. G. A. BROSSA (*Zeitsch. physikal. Chem.*, 1909, 66, 162—180. Compare Bredig and co-workers, *Abstr.*, 1900, ii, 213; 1901, ii, 441, 442).—Fairly stable solutions of colloidal iridium have been prepared by Bredig's method, using a current of 20—25 amperes at 220 volts. The solutions are reddish-brown or black, depending on the conditions of preparation; a relatively small current favours the production of black solutions. The solution decomposes hydrogen peroxide rapidly; the reaction is unimolecular, and the rate is approximately proportional to the concentration of the catalyst. Unlike its effect on the catalytic action of other colloidal metals, alkali does not affect the rate of decomposition of hydrogen peroxide by iridium. Acids

accelerate the reaction in dilute solution, but some of them retard it in concentrated solution. The magnitude of the effect varies greatly with the nature of the iridium preparation, in some cases it is scarcely noticeable. The rate of the reaction is retarded by hydrogen sulphide, mercuric chloride, potassium cyanide, and certain other compounds, but not by iodine. The temperature-quotient for a change in temperature of 10° is 1.6. G. S.

Application of Nernst's Theorem to Certain Heterogeneous Equilibria. JOHN JOHNSTON (*Zeitsch. physikal. Chem.*, 1909, 65, 737—743).—The substance of a paper previously published (compare Abstr., 1908, ii, 812) is repeated in reply to Schottky's criticisms (Abstr., 1908, ii, 1016) of the author's work (Abstr., 1908, ii, 358). G. S.

Equilibria between the Liquid and Solid Phases in the System $\text{NaCl} + \text{H}_2\text{O}$. CAMILLE MATIGNON (*Compt. rend.*, 1909, 148, 550—553).—The eutectic temperature was found to be -21.3° , and the solution in equilibrium with the two solid phases contains 30.7 parts of sodium chloride per 100 parts of water. The freezing points of solutions containing 11, 15, 20, and 25 parts of sodium chloride per 100 of water are respectively -6.6° , -9.25° , -12.7° , and -16.66° . The solubility of the hydrate $\text{NaCl} \cdot 2\text{H}_2\text{O}$ at -12.25° corresponds with 32.9 parts of sodium chloride per 100 of water. H. M. D.

Dependence of the Reaction Velocity on the Temperature in Homogeneous Gaseous Systems. HANS GOLDSCHMIDT (*Physikal. Zeitsch.*, 1909, 10, 206—210).—A theoretical paper, in which the author has deduced a relationship between the rate of change in a gaseous system and the temperature. It is assumed that the molecules which undergo change are solely those which have velocities greater than a certain limiting value, and by applying Maxwell's distribution law, an equation is obtained which gives the connexion between the values of the velocity constants for two different temperatures. The equation involves three terms in which the two temperatures are involved, but two of these can be neglected in comparison with the third at temperatures not very different from the normal. The resulting equation is then identical with the empirical equation set up by Arrhenius to express the results of experimental measurements. H. M. D.

Equilibria in the System $(\text{CH}_3\text{CO})_2\text{O} - \text{B}_2\text{O}_3 - \text{H}_2\text{O}$ at 30° . M. DUKELSKI (*Zeitsch. anorg. Chem.*, 1909, 62, 118—122).—The solubility of boric acid in water is diminished by the addition of acetic acid, and in glacial acetic acid the solubility is very small. Addition of acetic anhydride now increases the solubility very greatly, new solid phases being formed. For the estimation of acetic acid in presence of boric acid, the best results are obtained by titration with

iodide-iodate solution, towards which boric acid is indifferent, and thiosulphate. The reaction is a very slow one, and it is necessary to keep the solutions forty to forty-four hours in stoppered vessels at 15—18° before titrating with thiosulphate (compare Gröger, *Zeitsch. angew. Chem.*, 1899, 12, 356, and Kux, *Abstr.*, 1893, ii, 307).

The products obtained from solutions containing acetic anhydride may also be prepared by decomposing the compound $B_2O_3 \cdot 3Ac_2O$ (Pictet and Geleznoff, *Abstr.*, 1903, i, 601). The regions of stability have been partly determined at 30° for the solid phases $B(OH)_3$, $B_2O_3 \cdot 2Ac_2O$, and $B_2O_3 \cdot 3Ac_2O$.
C. H. D.

Saponification in Stages of the Esters of Dibasic Acids.

I. JULIUS MEYER (*Zeitsch. physikal. Chem.*, 1909, 66, 81—125. Compare *Abstr.*, 1907, i, 462, 819).—The formulæ representing the saponification in stages of the esters of dibasic acids on different assumptions as to the relative values of the two velocity constants are deduced. In continuation of earlier work on the hydrolysis of the esters of glycol and glycerol in acid solution, the rate of hydrolysis of a number of acid and normal esters of tartaric, succinic, and camphoric acids in dilute (0.01—0.1*N*) hydrochloric acid have been determined at 18° and 25°, and also at higher temperatures for the esters of the last-mentioned acid.

In the case of all the esters of tartaric and succinic acid, the reaction is apparently unimolecular. The hydrolysis of the esters of the first two acids really proceeds in the two stages: (1) diester \rightarrow monoester + alcohol; (2) monoester \rightarrow acid + alcohol, but as the velocity constant for the first reaction is almost exactly double that of the second, the whole reaction is pseudo-unimolecular; in other words, the formula for unimolecular reactions applies when this relationship holds between the two velocity constants, as the mathematical deductions show.

The esters of camphoric acid, being scarcely soluble in water, were hydrolysed in a mixture of water and methyl alcohol containing different concentrations of hydrochloric acid. The two monoesters are designated as *V* and *E* respectively. In this case the hydrolysis of the diester does not give constants when calculated as a reaction of the first order; the constant for the hydrolysis of the *E* ester is about fifty times greater than that of the *V* ester at 45°; hence, when the diester is hydrolysed, one group is split off rapidly, the other slowly, and a mixture is obtained containing a large proportion of the *V* ester. The method may be used for the preparation of the *V* ester.

For one and the same acid, the rate of hydrolysis is not greatly influenced by the substituting alkyl group, but the velocity is greatly influenced by the nature of the acid. The temperature-quotient for 10° for all the reactions considered lies between 2.6 and 3.1. The rate of hydrolysis is throughout proportional to the concentration of the hydrochloric acid.

It is shown that the different theories of hydrolysis so far suggested are in many respects unsatisfactory, and an attempt is made to account for the above results on a kinetic basis.
G. S.

New Method of Mathematically Harmonising the Weights of the Elements, together with a Review of Kindred Work, and Some Observations Concerning the Inert Gases and Satellites. F. H. LORING (*Chem. News*, 1909, 99, 148—151).—Following a brief review of previous attempts to arrive at some plan or formula which would classify the elements, the author describes a newly-devised mathematical treatment of this question.

This method is based on two simple operations; the first being to arrange the elements in a regular series that passes through a zero, according to the empirical equation $\pm(4P) + K = W$, P representing a number of an integral series, 0, 1, 2, 3. . . etc., and K a constant of somewhat arbitrary selection. This equation gives the value W approximating to the true atomic weight by a plus or minus difference ranging from 0 to 0.9. The second operation consists in projecting the differences between the calculated and actual atomic weights, horizontally along a line, on which, by the above equation, the element is placed. By drawing curves through these points, the interesting fact is brought to light, that elliptical curves round two common foci are obtained which intersect practically all the elements and occur in groups of nine.

Nitrogen and glucinum are the only elements which do not fit into this system, the former giving a difference of 1.1 between the observed and the calculated atomic weights, and the latter falling away from any probable curve. It is suggested that these two elements, as well as iodine, each carry a satellite, which, by trial, is found to be about 0.2684. Subtracting this from the atomic weight of nitrogen and glucinum, these elements then fall on curves in a regular manner.

A more fitting position for iodine on one of the curves is found by assuming the true value for this element plus its satellite to be 126.9634 instead of 126.92; subtracting 0.2684 gives a value placing iodine on a curve symmetrical with bromine.

It is thought probable that the calculations made may be at best only approximate, and that some of the curves may require shifting; the agreement, however, between the observed and the corrected values are sufficiently close to make the probability of coincidence impossible.

J. V. E.

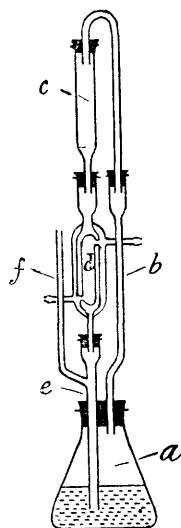
Streams of Gases through Vessels. NICOLAE TECLU (*J. pr. Chem.*, 1909, [ii], 79, 171—173).—An experiment designed to show that a gas only fills a vessel not of uniform diameter if the current is slow, is performed by bubbling air through a bromine solution, and then passing the bromine-laden air through a tube into a balloon provided with a similar tube diametrically opposite. If the current is slow, the vessel is gradually filled with bromine; if fast, the bromine is seen to pass through the balloon as a band, the diameter of which is equal to the diameter of the tube.

W. R.

A Porcelain Vacuum Reservoir for Liquid Air. ERNST BECKMANN (*Zeitsch. angew. Chem.*, 1909, 22, 673).—The well-known glass vacuum reservoir (Dewar's flask) is replaced by one made of porcelain, as there is less danger of breakage during transport.

L. DE K.

An Apparatus for Continuously Extracting Solids. NORMAN L. GEBHARD and F. BRYAN THOMPSON (*Chem. News*, 1909, 99, 124).—The extracting liquid is placed in the flask, *a*, and heated to boiling, when the vapour passes up the tube *b* and enters *c*, which contains the solid to be extracted. After passing through the solid, which is supported on a perforated porcelain disk, the vapour enters the double-surface condenser *d*, where it is condensed and returned to the flask *a*. To guard against the generation of pressure in the apparatus, the return tube, *e*, carries a side-tube, *f*, which is open to the air. If the position of *c* and *d* are interchanged, the solid substance may be extracted by percolation of the cold liquid condensed in *d*. J. V. E.

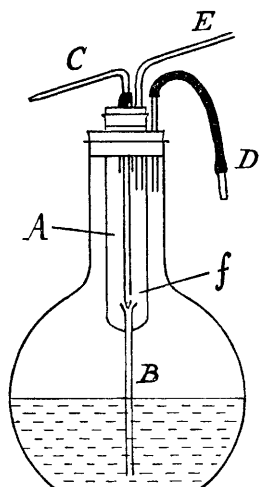


Some Time- and Labour-saving Apparatus in American Chemical Laboratories. VICTOR SAMTER (*Zeitsch. Chem. Apparatenkunde*, 1908, 3, 569—573).—These papers contain figures and brief descriptions of mechanical pulverising, ore-sampling, and filtering apparatus in use in certain American analytical laboratories. F. M. G. M.

Arrangement for Filtering Liquids Maintained at Constant Temperature in a Thermostat. EUGENIO MORALES CHOFÉ (*Anal. Fis. Quim.*, 1909, 7, 50—53).—The liquid, for example a solution in equilibrium with its solid, is contained in a cylindrical lamp-glass, closed at both ends with corks, and immersed in the thermostat. The liquid is kept in motion by a stirrer passing through the upper cork. Through the lower cork a small glass tube passes, which is provided with a wad of filter-paper or glass-wool, and connects by means of india-rubber tubing with a larger glass tube arranged in the thermostat parallel to the lamp-glass. This second tube receives the filtered liquid, which is drawn into it by connecting the upper orifice with a vacuum; the level of the filtered liquid is regulated so as to be below that of the water in the thermostat, so that it is uniformly heated. The receiving tube can be graduated as a pipette to hold a known volume. W. A. D.

A Simple Lecture Experiment to Illustrate Simultaneously Three Stages of Oxidation. JOHN E. MACKENZIE (*Chem. News*, 1909, 99, 146).—A somewhat striking demonstration of the change lead peroxide undergoes when heated is effected by sprinkling a thin layer of this substance on to a flat-bottomed, porcelain basin, which is supported on a pipe-clay triangle, and then heating the dish by a Bunsen flame. Where the heat is most intense, litharge is produced, the parts screened by the triangle change to red lead, and in the cooler regions of the dish the unaltered peroxide remains. J. V. E.

A Pipette Wash-bottle. P. B. DALLIMORE (*Pharm. J.*, 1909, [v], 527).—The advantage of the apparatus described and figured is



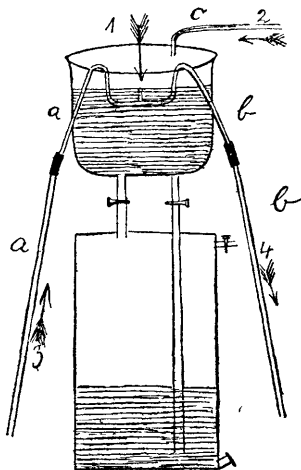
that it renders the washing of a precipitate, etc., by a known quantity of water far more practicable. A small wash-bottle A, conveniently made from glass tube, has a piece of ordinary tubing fused through the bottom, the top end of which is slightly opened out above the fused joint so as to allow tube C to be ground into it. The latter tube is sealed off at the bottom, and a small hole, *f*, is blown about three-eighths of an inch above the ground glass joint. A slightly larger piece of glass tubing is fastened in the cork for C to work in, and a piece of rubber tube is placed over the two so as to form a spring to keep C down in its place. To use the wash-bottle, tube C is slightly raised, and water is forced up B into the inner reservoir by blowing down D until any desired graduation mark is reached. C is then released, the rubber

spring making the ground joint water-tight, and by blowing down E the measured water may be discharged down to the zero hole *f*.

J. V. E.

Arrangement for Preventing an Overflow in Open Water-fed Gas-holders. HERMANN WUSTENFELD (*Chem. Zeit.*, 1909, 33, 412).—It is difficult to arrange a gas-holder so that a long continued, slow current of gas is obtained from it. The following arrangement has been found to obviate the difficulties of regulating the water-supply. An inverted W-shaped glass tube, *a* and *b*, has at the centre a small vertical tube. The end *a* of the glass tube is connected with a water-supply, the end *b* with the outflow, and the apparatus is then suspended in the reservoir of the gas-holder, into which a constant stream of water is also flowing; a constant, moderately strong stream of water is then passed through the system *a a b b*.

The outflow carries away constant streams of air-bubbles, and the suction thus caused in the small tube suffices to remove from time to time any excess of water in the reservoir.



L. DE K.

Inorganic Chemistry.

Behaviour of Fluorine towards Nitrogen, Oxygen, and Chlorine at the Temperature of the Electric Arc and the Induction Discharge. OTTO RUFF and JULIAN ZEDNER (*Ber.*, 1909, 42, 1037—1046).—Two special pieces of apparatus are described which make it possible to heat fluorine and mixtures of fluorine with other gases at the temperature of the electric arc or of the induction discharge. Fluorine was heated with nitrogen, with oxygen, and with chlorine, but in no case did any reaction take place. E. F. A.

Quadrivalency of Oxygen. JOHN C. THOMLINSON (*Chem. News*, 1909, 99, 185).—The conclusions drawn by Redgrove (this vol., ii, 308) are criticised. The increment of oxygen atoms in a molecule accompanied by a lower molecular heat of combustion than would be expected by theory is considered to be probably due to experimental error, and not a valid argument for the quadrivalency of oxygen.

J. V. E.

Phosphorescence and Combustion Flames of Sulphur. LÉON BLOCH (*Compt. rend.*, 1909, 148, 782—783).—The phosphorescence exhibited by sulphur at about 200° is accompanied by the formation of considerable quantities of ozone, but not by any ionisation phenomena. Attempts to isolate a lower oxide of sulphur by passing air over gently heated sulphur and then through a tube immersed in liquid air were unsuccessful. The combustion flame, which replaces the phosphorescence effect when the temperature of sulphur is raised to 360°, is non-conducting, and the oxidation of sulphur dioxide by air in contact with spongy platinum is also unaccompanied by the production of ions. Attention is directed to the difference in the phenomena of oxidation of sulphur and phosphorus. H. M. D.

Purification of Hydrated Sulphuric Acid from Arsenic by Cooling. MORANCÉ (*Compt. rend.*, 1909, 148, 842—843).—The author exposed Glover tower acid of 63·5° Baumé, prepared from Spanish pyrites, to a temperature varying from -8° to 2° for twenty-four hours. It was then found that, of 3730 grams of acid taken, 1895 grams had solidified in the form of crystals, whilst the rest remained liquid. The impurities present in these two forms, calculated as grams per 100 grams of monohydrated acid, were:

	Solid.	Liquid.
Residue at a red heat.....	0·281	0·829
Iron and aluminium	0·029	0·119
Arsenic.....	0·033	0·368

T. H. P.

Synthesis and Formula of Caro's Acid (Monopersulphuric Acid). HERMANN AHRLE (*J. pr. Chem.*, 1909, [ii], 129—164. Compare Lowry and West, *Trans.*, 1900, 77, 950; Baeyer and Villiger, *Abstr.*, 1901, ii, 380; Armstrong and Lowry, 1902, ii, 558; Price, *Trans.*, 1906, 89, 53).—The results of previous investigations has led

to the conclusion that Caro's acid is either H_2SO_5 or $\text{H}_2\text{S}_2\text{O}_8$, the acid in the former case being monobasic, and in the latter, dibasic. This uncertainty would be removed if the acid or one of its salts could be obtained in a state of purity. The present investigation deals with an attempt to prepare the free acid from hydrogen peroxide and either sulphuric acid or sulphur trioxide, as Price (*loc. cit.*) failed to obtain a pure potassium salt. The reaction $\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{SO}_5 + \text{H}_2\text{O}$ is a reversible one, and if the free acid is to be obtained, water must be carefully excluded. This has been done as far as possible by mixing sulphur trioxide and 100% hydrogen peroxide; above -10° the action becomes visible, the crystals gradually disappear with development of heat. In this way a 92.3% monopersulphuric acid was obtained, and which also contained 6% of hydrogen peroxide. Experiments in which the materials were added in molecular proportions gave an 80–85% acid.

Further experiments to show the equilibrium between hydrogen peroxide and sulphuric acid gave the result that equilibrium is reached when two-thirds of the monopersulphuric acid is formed.

The synthesis and kinetic experiments lead to the conclusion that the acid has the constitution $\text{O} \gg \text{S} \begin{matrix} \text{OH} \\ \text{O-OH} \end{matrix}$, the hydrogen of the hydroxyl attached to the sulphur being the replaceable hydrogen atom. At the ordinary temperature, monopersulphuric acid is a mobile liquid, and above 0° slowly decomposes. It decomposes explosively with catalysts, such as finely-divided platinum or silver, but lead or zinc dust are without vigorous action. Cellulose and wool are instantaneously decomposed.

Full details are given for the preparation of 100% hydrogen peroxide.
W. R.

Hydroxylamine. FRITZ HABER (*J. pr. Chem.*, 1909, [ii], 79, 173–176. Compare Abstr., 1897, ii, 23).—The observation of the author that hydroxylamine is reduced quantitatively to ammonia by alkaline ferrous solution has been contradicted by Ebler and Schott (Abstr., 1908, ii, 1029), who found that nitrogen and nitrous oxide were also evolved. This discrepancy is explained by the fact that the author used dilute hydroxylamine solution, whereas Ebler and Schott probably used concentrated. Further experimental evidence is given in support of the quantitative production of ammonia in such dilute solutions, and the conclusion is drawn that this result is in harmony with the aminoxide structure $\text{O}:\text{NH}_3$, and against the constitution $\text{NH}_2\cdot\text{OH}$.
W. R.

Anhydrous Hydronitric Acid [Azoimide]. I. Electrolysis of a Solution of Potassium Trinitride [Azoimide] in Hydronitric Acid [Azoimide]. ARTHUR W. BROWNE and G. E. F. LUNDELL (*J. Amer. Chem. Soc.*, 1909, 31, 435–448).—Since anhydrous ammonia and hydrazine are poor conductors of electricity and are capable of acting as ionising solvents, it has been considered of interest to study the behaviour of anhydrous hydronitric acid [azoimide].

Anhydrous hydronitric acid has been prepared by Dennis and Isham's method (Abstr., 1907, ii, 165), and experiments are described which indicate that the pure substance offers a very high resistance to the electric current and has a specific conductivity approximately equal to that of pure ammonia. On dissolving potassium trinitride in the anhydrous acid, the conductivity is greatly increased, and when such a solution is electrolysed, nitrogen and hydrogen are evolved in a ratio which is approximately 3:1, but somewhat less under certain conditions. Ammonia is formed during the electrolysis, but hydrazine is not produced. In the course of the experiments, certain phenomena were observed which might have been caused either by traces of ozone or by the formation of small quantities of a polymeride of nitrogen, N_3 or N_6 (compare Szarvasy, Trans., 1900, 77, 607). E. G.

Atomic Weight of Arsenic. Analysis of Silver Arsenate. GREGORY P. BAXTER and FLETCHER BARKER COFFIN (*J. Amer. Chem. Soc.*, 1909, 31, 297—309).—The method depends on the conversion of silver arsenate into silver chloride or bromide. Samples of the arsenate were prepared by adding to a dilute $N/15$ -solution of silver nitrate an equivalent amount of an alkali arsenate in corresponding dilution in a room lighted only with ruby light. There is some evidence that in these circumstances trisodium arsenate gives rise to a slightly basic silver triarsenate, whilst disodium ammonium arsenate and disodium hydrogen arsenate give rise to the normal salt. The precipitates were washed by decantation, partly dried by centrifugal action, and then heated in an electric oven at 130° for some time.

Two methods were employed in converting the silver arsenate into chloride. By the first method, the arsenate, in a quartz tube, was heated for seven to eight hours in a stream of dry air at 250° , then weighed, and finally heated in a current of dry hydrogen chloride for some hours until the reaction was practically complete. Small corrections had to be made for the traces of arsenic still remaining after prolonged heating, and also for the traces of moisture remaining after heating the arsenate for some hours at 250° . The second method consisted in heating the arsenate in a platinum boat, and, after weighing, dissolving in nitric acid and precipitating as silver chloride or bromide. In this case, a small residue insoluble in dilute nitric acid was found to be soluble in concentrated acid.

The specific gravity of silver arsenate was determined by displacement of toluene; D_4^{25} 6.657.

The ratio $3AgCl : Ag_3AsO_4$ has been determined in 15 analyses, and the ratio $3AgBr : Ag_3AsO_4$ in 11 analyses. The mean of the most trustworthy results gives $As = 75.02$ for $Ag = 107.93$; $As = 74.96$ for $Ag = 107.88$, and $As = 74.92$ for $Ag = 107.85$ [$O = 16$]. G. S.

The System Sulphur-Arsenic. W. P. A. JONKER (*Zeitsch. anorg. Chem.*, 1909, 62, 89—107).—Arsenic remains unmelted at about 800° . A mixture having the composition of realgar, As_2S_3 , melts at 321° to a thin liquid; the freezing point is lowered by the addition of either sulphur or arsenic, the viscosity being greatly increased at the

same time, the addition of 5% of sulphur rendering the mass so viscous that crystallisation does not take place on cooling. On the arsenic side, the eutectic point is at 310° . Natural orpiment, As_2S_3 , melts at about 310° ; an artificial preparation of this composition does not crystallise on cooling. A few points on the sulphur side of the curve have been determined by mixing sulphur and realgar, and measuring the temperature at which the mass becomes rigid on cooling. This does not give the freezing point, but the curve has a similar form to the freezing-point curve.

The sublimation point of arsenic in an open vessel is 616° (Krafft and Knocke, this vol., ii, 211, give $554\text{--}556^{\circ}$). A saturated solution of arsenic in realgar boils at 534° , and natural or artificial orpiment at 707° . By analysing the vapour in contact with the boiling liquid, the sublimation curve has been determined, and its form shows that As_2S_2 is very largely dissociated in the vapour (compare Szarvasy and Messinger, Abstr., 1897, ii, 404). On the other hand, As_2S_3 distils unchanged. The curves do not indicate the formation of As_2S_5 .

A diagram is given in which the above results are collected.

C. H. D.

Preparation of a Boron Carbide. SAMUEL A. TUCKER (D.R.-P. 206177).—A boron carbide corresponding with the formula B_6C was prepared by heating at about 2500° in the electric furnace a mixture of carbon and boric anhydride containing excess of the latter; when the current was gradually diminished, so that the material was cooled very slowly, the product was obtained in a crystalline form.

F. M. G. M.

Action of Gaseous Hydrogen Chloride on Amorphous Silicon. ADOLPHE BESSON and L. FOURNIER (*Compt. rend.*, 1909, 148, 555—557).—When dry hydrogen chloride is passed over heated amorphous silicon, products are obtained which are condensed with difficulty. It was found convenient to absorb these in silicon tetrachloride cooled by means of solid carbon dioxide. By fractional distillation of the solution, the compounds SiH_3Cl , which boils at about -10° , and SiH_2Cl_2 , which boils at about $+12^{\circ}$, were obtained in appreciably pure condition. Both these chlorides are colourless, mobile liquids, which have a large coefficient of expansion, and are decomposed by water and alkalis with evolution of hydrogen. A sulphur compound boiling at about -25° was also obtained in small quantity; the formation of this is attributed to the presence of sulphur as an impurity in the amorphous silicon.

With the object of preparing the above compounds, silicon tetrachloride vapour was passed over calcium hydride heated to a temperature below redness. The products obtained, however, were hydrogen, hydrogen chloride, silico-chloroform, calcium chloride, and either calcium silicide or amorphous silicon, depending on the temperature. At a relatively low temperature and with excess of calcium hydride, calcium silicide is formed, whereas at a higher temperature and with excess of silicon tetrachloride amorphous silicon is obtained.

H. M. D.

Preparation of Silicon Chlorides of the Silicomethane Series.

ADOLPHE BESSON and L. FOURNIER (*Compt. rend.*, 1909, 148, 839—842). From the mixed silicon chlorides obtained by the action of an electric discharge on a mixture of hydrogen and silicomethane, the authors have separated the following compounds. (1) Silicon tetrachloride. (2) Hexachlorosilicoethane. (3) Octachlorosilicopropane, b. p. 215—218° (Gattermann and Weinlig, *Abstr.*, 1894, ii, 414, gave b. p. 210—215°), which, after solidification, has m. p. - 67°. (4) *Dodecachlorosilicopentane*, $\text{Si}_5\text{Cl}_{12}$, which is a colourless, oily liquid, b. p. about 150°/15 mm., fumes in the air, is readily decomposed by water, giving a white product resembling silica, and often gives off sparks and ignites when gently rubbed. (5) *Tetradecachlorosilicohexane*, $\text{Si}_6\text{Cl}_{14}$, which is a white solid, m. p. 170° (decomp.), subliming in a vacuum at about 200°, giving crystals which later assume a waxy consistency; it is readily decomposed by water, giving a white, combustible substance.

After the above compounds have been removed by prolonged heating at 200—210° in a vacuum, there remains a solid, reddish-yellow, glassy mass, which is almost entirely soluble in light petroleum or carbon tetrachloride, and is apparently a mixture of a number of chlorides.

T. H. P.

Thermal Effects of the Musical 'Arc. Probable Fusion of

Carbon. M. LA ROSA (*Compt. rend.*, 1909, 148, 475—478).—As there is some evidence that the singing arc is more powerful than the ordinary arc, the author has attempted to fuse carbon by means of the former. Sugar charcoal was exposed to the musical arc between carbon electrodes for some hours, and in the residue particles of graphite, showing under the microscope no trace of the contours of the original charcoal, were observed. This appears to indicate the fusion of carbon, more particularly as the ordinary arc under corresponding conditions did not produce the same effect (compare this vol., ii, 311). G. S.

Decomposition of Carbon Tetrachloride Vapour in the High

Tension Electric Arc. CARL SCHALL (*Zeitsch. physikal. Chem. Unterr.*, 1908, 21, 385—387).—An apparatus suitable for demonstration purposes, in which a high-tension electric arc is passed through the vapour of carbon tetrachloride, is described and figured. Clouds of soot are immediately formed, and a considerable proportion of free chlorine is obtained. In one experiment, 100 grams of the pure tetrachloride were subjected for a considerable time to the action of the arc, and, besides chlorine and carbon, hexachlorobenzene was detected in the residue.

G. S.

Formation of Graphitic Acid and the Definition of Graphite.

GEORGES CHARPY (*Compt. rend.*, 1909, 148, 920—923).—For the preparation of graphitic acid, Brodie's reagent, fuming nitric acid, and potassium chlorate may be replaced by other oxidising mixtures, such as concentrated sulphuric acid with potassium permanganate or chromic acid. The reaction proceeds at the ordinary temperature, and is accelerated by heat, although with loss of carbon as carbon dioxide. Specimens of carbon hitherto considered amorphous (carbon from steel

and the product obtained by heating graphitic acid) also yield graphitic acid on oxidation. The definition of graphite, which depends on the action of these oxidising agents, is therefore unsatisfactory.

The density of the above specimens of carbon was found to be 2.25 after compression; they should consequently be classed as true graphites (compare Le Chatelier and Wologdine, *Abstr.*, 1908, ii, 177).

W. O. W.

Atomic Weight of Potassium. GUSTAVE D. HINRICHS (*Compt. rend.*, 1909, 148, 484—485).—From the recent experiments of Lenher (this vol., ii, 230) on the atomic weight of tellurium by the decomposition of potassium telluribromide, the author shows that on his theory (compare *Abstr.*, 1907, ii, 945) the atomic weight of potassium is $39\frac{1}{8} = 39.125$.
G. S.

Alcoholic Potash. A. VAN RAALTE (*Chem. Weekblad*, 1909, 6, 252—253. Compare Scholl, *Abstr.*, 1908, ii, 425; Rabe, *Abstr.*, 1908, ii, 689).—Alcoholic potash, prepared by Rabe's method, may keep in Batavia, but not in Holland. By suspending 35 grams of potassium hydroxide sticks in a muslin bag in a litre of 96% alcohol until solution is complete, filtering, and preserving the solution in a brown stoppered bottle, alcoholic potash, which remains colourless for at least six months, is obtained. At the end of that period its titration value was unaltered.
A. J. W.

Impossibility of Judging of Relative Stabilities of Corresponding Compounds of Silver and Lead from Thermochemical Data. ALBERT COLSON (*Compt. rend.*, 1909, 148, 837—839).—The relations between the heats of formation of silver and lead carbonates and nitrates, either from their constituent elements or from the oxides into which they decompose on heating, indicate that lead nitrate and carbonate should be more stable than the corresponding silver compounds. This is found to be the case with lead carbonate, which attains a dissociation pressure of 760 mm. at 285°, whilst the silver salt gives this pressure at 220°.

The nitrates, however, exhibit different behaviour. Lead nitrate does not decompose at 200°, as is stated in the text-books. When it is perfectly dried by prolonged heating in a vacuum at a temperature higher than 200°, it shows no trace of decomposition when heated at 260° under a pressure of 2 mm., and it is not until a temperature of 283° is reached that the salt is observed to decompose. Dry silver nitrate, on the other hand, undergoes no decomposition when heated at 350° in a vacuum.

The heat of formation of lead nitrate is less in the dissolved than in the free state, but it is found that the stability of the salt is increased considerably by dissolving it in silver nitrate. T. H. P.

Alloys of Calcium and Silicon. S. TAMARU (*Zeitsch. anorg. Chem.*, 1909, 62, 81—88).—The alloys were prepared from calcium and silicon in an atmosphere of nitrogen, some calcium nitride being always formed. The vessels used were of carbon or of porcelain, lined

in either case with a layer of magnesia mixed with a little tar and burnt. Silicon is practically insoluble in molten calcium at 900° . At 990° a reaction takes place, having a maximum value in the alloy containing 60% Si corresponding with the compound CaSi_2 . The formula of the compound was not certainly established, and it is possible that another silicide is also formed. The alloys rich in calcium always contained magnesium, derived from the lining by reduction.

The alloys are scarcely attacked by alkalis, more readily by acids. Those containing 38–52% Si react violently with dilute acids, yielding a spontaneously inflammable gas, which, if collected over water, loses its power of spontaneous ignition in a few minutes. Concentrated acids give a gas which is not spontaneously inflammable.

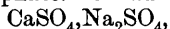
C. H. D.

Dissociation of Calcium Carbonate. D. ZAVRIEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, i, 34–56. Compare Abstr., 1907, ii, 768).—Further experiments on this reaction show that within the limits of temperature 700 – 950° no intermediate phase is formed, as might have been expected from Raoult's experiments (Abstr., 1881, 348; 1882, 695), and from the fact that the reaction is completely reversible within these limits. At low temperatures the reaction proceeds slowly, the velocity depending greatly on the condition of the surface of the lime, so that accurate investigation is impossible. It cannot be stated with certainty that intermediate products are not formed at 500 – 600° , at which temperatures, also, solid solutions may be formed. With a considerable excess of lime, when presumably solid solutions with a small content of carbon dioxide are formed, the dissociation pressure is very much less than when calcium carbonate alone is used.

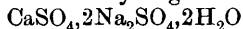
T. H. P.

Calcium Alkali Sulphates. JOH. D'ANS [with O. SCHREINER] (*Zeitsch. anorg. Chem.*, 1909, 62, 128–167. Compare Abstr., 1906, ii, 751; 1907, ii, 168, 459; 1908, ii, 104, 182, 590).—The regions of existence of all the calcium alkali sulphates have been determined between 0° and 100° . Sodium occupies a separate position in the alkali metal series; ammonium takes its place between potassium and rubidium.

The solubility curve of sodium sulphate is little altered by saturation with calcium sulphate. In addition to glauberite,



a labile double salt exists, and is always formed first under the conditions of formation of glauberite. It may remain long in a metastable condition, but changes into glauberite if inoculated with crystals of the latter. Direct analysis gives the composition



for the labile salt (compare Cameron, Bell, and Robinson, Abstr., 1907, ii, 648).

The results with potassium calcium sulphates are in agreement with those of van't Hoff (Abstr., 1905, ii, 319). Experiments at 140 – 170° failed to indicate the formation of a potassium dicalcium sulphate, which has been isolated from mixtures of the fused salts.

Ammonium forms double salts of all the three types, syngenite, pentacalcium sulphate, and dicalcium sulphate. Of the five transition points, two have been determined by tensimetric measurements, and two more from the results of solubility measurements; the fifth probably lies below the eutectic point. Two of the three transition points have also been determined for the calcium rubidium sulphates.

In view of the fact observed by van't Hoff (Abstr., 1904, ii, 34) that gypsum does not form syngenite in a solution saturated with sodium and potassium chlorides, the author has studied the influence of various salts on the solubility of syngenite at 25°. The limit gypsum-syngenite is found to be 3.223 mols. K_2SO_4 and 0.223 mol. $CaSO_4$ in 1000 mols. solution. Potassium salts lower the SO_4 -concentration. The "activity" of potassium salts in equal concentrations follows the diminishing order KOH , $C_2H_3O_2K$, the three halides, KNO_3 , $KClO_3$, $KClO_4$, $K_4Fe(CN)_6$. The order of activity of sodium salts and of acids is exactly the opposite of that of potassium salts; it depends in these cases on the affinity of the anion. Other sulphates give irregular results. Sucrose is practically without influence.

The results are represented graphically and discussed theoretically.

C. H. D.

Occluded Gases present in Certain Common Metals.

B. DELACHANAL (*Compt. rend.*, 1909, 148, 561—564).—The metals were heated to a bright red heat in an exhausted porcelain tube and the gases pumped off for analysis. From aluminium, prepared by the reduction of the double fluoride of sodium and aluminium, hydrogen alone was obtained; from magnesium, hydrogen and carbon monoxide; from zinc, hydrogen, carbon monoxide, and carbon dioxide; from tin, platinum sponge, commercial platinum and platinum-iridium, hydrogen, methane, carbon monoxide, carbon dioxide, and nitrogen.

H. M. D.

Action of Magnesium on Carbon Monoxide. CAMILLE MATIGNON (*Bull. Soc. chim.*, 1909 [iv], 5, 269—270).—Conflicting statements have been made in the literature regarding this reaction. The author finds that burning magnesium powder reacts very vigorously with carbon monoxide, carbon and magnesium oxide being produced.

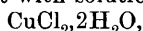
C. S.

Hardness of Magnesium-Silver Alloys. WLADIMIR I. SMIRNOFF and NICOLAI S. KURNAKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 108. Compare Kurnakoff and Schemtschuschny, Abstr., 1908, ii, 932).—The minimum conductivity (36×10^{-4}) for magnesium-silver alloys occurs at the composition Mg_3Ag , with which also corresponds the maximum hardness, 180 kilos. per sq. mm. In consequence of the formation by the argentide $MgAg$ of solid solutions with excess of magnesium (36—50% atom silver) and silver (50—60% atom silver) (compare Schemtschuschny, Abstr., 1906, ii, 539), this substance exhibits a relative minimum hardness, namely, 76 kilos. per sq. mm. The formation of solid solutions of magnesium in silver (*loc. cit.*) is accompanied by an increase of the hardness from 26 (pure silver) to 109 kilos. per sq. mm. (70.16% atom silver).

T. H. P.

The System Silicon-Magnesium. PAUL LEBEAU and P. BOSSUET (*Rev. Métallurgie*, 1909, 6, 272—278).—Alloys of magnesium and silicon have been prepared by fusing the components together under a layer of potassium silicofluoride, or by heating magnesium with potassium silicofluoride. Microscopical examination shows that only one silicide is formed having the formula Mg_2Si , and a slate-blue surface colour; D 2. It decomposes water slowly at the ordinary temperature, liberating hydrogen, whilst in acids a mixture of hydrogen and hydrogen silicide is formed. The two eutectics of the series contain about 2% and 50% of silicon respectively. C. H. D.

The System: Copper Sulphate, Copper Chloride, Ammonium Sulphate, Ammonium Chloride and Water at 30°. FRANS A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 11, 615—620).—A method is described for the special representation of the various saturated solutions which are formed from the above four-component system. The substances which may occur as solid phases at 30° in contact with solution are: $CuSO_4 \cdot 5H_2O$,



$(NH_4)_2SO_4$, NH_4Cl , and the double salts $CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ and $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$. From the solid figure it follows that the double salt $CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ can co-exist with $(NH_4)_2SO_4$, NH_4Cl , $CuSO_4 \cdot 5H_2O$, and $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$, but not with $CuCl_2 \cdot 2H_2O$. Similarly, $CuSO_4 \cdot 5H_2O$ can co-exist with $CuCl_2 \cdot 2H_2O$, and each of the double salts, but not with $(NH_4)_2SO_4$ or NH_4Cl . Both double salts behave in regard to each other and to water as single substances; for each there is a series of saturated solutions, and there is a particular solution which is saturated with respect to both.

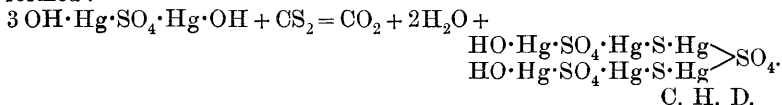
H. M. D.

Influence of Small Quantities of Elements in Copper on its Reactions with Nitric Acid. JOHN H. STANSBIE (*J. Soc. Chem. Ind.*, 1909, 28, 268—274).—The investigation is a continuation of previous work (Abstr., 1908, ii, 497), and deals particularly with the influence of small quantities of arsenic, phosphorus, and lead on the reactions of alloys of these elements with copper when the alloys are dissolved in nitric acid, D 1.2, the reactions taking place at a temperature of 65°. The results confirm the view that the chief cause of the decrease in the volume of nitric oxide liberated by the dissolution of copper alloys in nitric acid is the formation of a solid solution of the added element, or of a compound of that element, in the excess of copper. The maximum effect of phosphorus on the chemical relations of copper appears to be produced by a phosphorus-content of about 0.025%. Small percentages of lead exert little or no influence on the reactions of copper with the acid, so that lead acts similarly to bismuth in this respect, and it is also shown that a small quantity (0.1%) of copper in lead has little or no influence on the reactions of lead itself. It may be noted that the quantities of phosphorus, arsenic, antimony, and bismuth which produce the maximum effect are in the order of

their atomic weights, and it may be that the atomic volume of the added element is a factor in the influence it exerts upon the copper.

W. P. S.

A Thiobasic Mercuric Sulphate. KNUD ESTRUP (*Zeitsch. anorg. Chem.*, 1909, **62**, 168—170).—When a solution of mercuric sulphate, prepared by dissolving 10 grams of yellow mercuric oxide in 10 c.c. of concentrated sulphuric acid and 40 c.c. of water, is shaken with one-fourth its volume of carbon disulphide and allowed to remain for several weeks, large crystals are obtained. After washing with dilute sulphuric acid, alcohol, and ether, snow-white, hexagonal plates are obtained, having the composition $4\text{HgO}, 2\text{HgS}, 3\text{SO}_3, 4\text{H}_2\text{O}$. On boiling with potassium iodide, mercuric sulphide is precipitated and two equivalents of alkali are set free. Assuming the constitution given by Biilmann (*Abstr.*, 1900, **i**, 431) for mercuric sulphate, the new compound is thus formed :



Extraction of Rare Earths from Mariupolite. JÓZEF MOROZEWICZ (*Bull. Acad. Sci. Cracow*, 1909, 207—213).—The dyke modification of the rock mariupolite (*Abstr.*, 1902, **ii**, 668; 1905, **ii**, 177) contains rare earths of the cerium group and of the tantalum group, the former being present in beckelite (which forms about 0.3% of the rock) and the latter in pyrochlore (0.2%). The fact that beckelite is decomposed by dilute hydrochloric acid enables the cerium earths to be readily separated and converted into the oxalates, and by digesting the insoluble portion with sulphuric and hydrofluoric acids the tantalum and columbic acids and also the zircon can be isolated. Full details of the method of procedure are given. The yields were :

(Ce, La, Di, Y, Er) $_2\text{O}_3$, 0.21 and 0.07% ; Cb_2O_5 , 0.16% ; zircon, 1.70%.

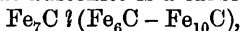
L. J. S.

The Odour of Clay. PAUL ROHLAND (*Zeitsch. physiol. Chem.*, 1909, **59**, 325—326).—The odour and taste of clay are due to organic admixture, and are least noticeable in clays most free from such impurity. In some of the Saxon clays this is of a fatty nature, whilst in others from Silesia it is in the form of hydrocarbons, the variable nature of the organic matter influencing the odour of the clay. That it is not chemically united to the clay is shown by the fact that it can be transferred to another (colloidal) substance. If clay is shaken with a solution of ferric succrate ($y\text{C}_{12}\text{H}_{22}\text{O}_{11}, x\text{FeH}_6\text{O}_6$), the clay loses both odour and taste, which are acquired by the succrate solution.

W. D. H.

Structure of Tempered Steel. W. A. KURBATOFF [in part, with M. M. MATVÉEFF] (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1—17).—Metallographic study of steels treated in various ways leads to the following results.

The best method of preparing austenite is to temper steel containing 1.8—2.2% of carbon, heated nearly to its melting point, either in mercury at 130° or in mercury at the ordinary temperature with subsequent softening at 130°. The substance between the crystals of austenite consists of troostosorbite (*fer de lance*), and that forming a network from the centres of crystallisation, troostite. The old scheme representing the transformation of austenite \rightarrow martensite \rightarrow troostite \rightarrow sorbite \rightarrow perlite is inaccurate. The equilibrium austenite \rightleftharpoons sorbite is displaced from right to left at 90—150° and above 1000°, whilst the opposite change takes place at 150—750°, the velocity of this transformation passing through its first maximum at 250°. It is probable that austenite is a carbide of iron,



the molecules of which are stable at 1000°, whilst troostite and sorbite are apparently solutions (β and α) of carbon in iron.

T. H. P.

Action of Coke on Ferric Chloride and Auric Chloride in Solution. ALFRED TINGLE (*J. Amer. Chem. Soc.*, 1909, 31, 461—463).—It has been stated by Oechsner de Coninck (*Abstr.*, 1900, ii, 485) that when solutions of auric, platinic, or ferric chloride are filtered through animal charcoal or powdered coke, the metal is completely retained by the filter. Experiments are now described on the action of powdered coke on solutions of auric chloride, ferric chloride, and basic ferric chloride. In some instances, the coke was first purified by washing with hydrochloric acid, and in others it was not so treated. In the case of the ferric chloride solutions, the iron was always partly reduced to the ferrous state, whilst in the case of the auric chloride solution a large proportion of the gold was retained by the filter. These results are considered to be due, chiefly or entirely, to the sulphur compounds present in the coke.

E. G.

Ferric Nitrates at 25°. FRANK K. CAMERON and WILLIAM O. ROBINSON (*J. Physical Chem.*, 1909, 13, 251—255).—Ferric nitrate solutions were shaken with freshly precipitated ferric hydroxide or with excess of nitric acid for four months at 25°. The liquid and solid phases were then analysed.

Application of the graphic method to the results shows that there are no definite basic nitrates of iron; the various compounds which have been described as such were solid solutions of ferric oxide, nitric acid, and water. When nitric acid is in excess, the yellow, crystalline hydrate, $\text{Fe}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_5 \cdot 18\text{H}_2\text{O}$, is formed. In two cases a colourless, crystalline pernitrate, apparently $\text{Fe}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_5 \cdot 18\text{H}_2\text{O}$, was obtained, but later attempts to produce this salt failed.

R. J. C.

Action of Carbon Monoxide on Chromium, Nickel, Manganese, and their Oxides and Alloys. GEORGES CHARPY (*Compt. rend.*, 1909, 148, 560—561).—The action of carbon monoxide on the metals and oxides was investigated at 1000°. Nickel is practically unaltered, although carbonisation appears to take place to a very small extent; the oxide is completely reduced to metal. Manganese and

ferro-manganese are oxidised with formation of manganous oxide, carbon being deposited; at first the gas is completely absorbed, carbon dioxide being evolved at a later stage. The oxide, Mn_3O_4 , is reduced to manganous oxide. Chromium behaves like manganese, but the action takes place much more slowly; chromic oxide is unacted on. In the case of steel containing a small percentage of chromium, both metals are acted on by the carbon monoxide as they would be if the metals were separate. A portion of the carbon liberated in the oxidation of the chromium is used up in the carbonisation of the iron. When the amount of chromium present exceeds 7%, this action does not take place. H. M. D.

Speed of Oxidation, by Air, of Uranous Solutions. Volumetric Estimation of Uranium. HERBERT N. MCCOY and HERBERT N. BUNZEL (*J. Amer. Chem. Soc.*, 1909, 31, 367—373).—The rate of oxidation by air of an acid solution of uranous sulphate has been measured by drawing a current of air through the solution, and titrating portions of it at intervals with permanganate. The velocity is proportional to the concentration of the salt, inversely proportional to the square of the hydrogen ion concentration, and is only slightly diminished by the addition of zinc sulphate.

The oxidation-reduction potential of a solution containing uranous and uranyl salt and some free sulphuric acid has been measured.

In estimating uranium salts by reduction to uranous salts with zinc and acid, and titration with permanganate, oxidation by free oxygen is a source of error, but accurate results are obtained by the following procedure. Fifty c.c. of pure uranyl sulphate solution (=about 0.3 gram uranium), 55 c.c. of water, and 20 c.c. of concentrated sulphuric acid ($D=1.84$) are poured on 100 grams of zinc in sticks, the solution is heated nearly to boiling, after fifteen minutes it is filtered, the zinc washed with cold 3*N*-acid, the solution made up to 300 c.c., and titrated with *N*/10-permanganate. G. S.

Titanium Nitride. OTTO RUFF (*Ber.*, 1909, 42, 900).—Although the estimation of nitrogen in the easily decomposable titanium halogen nitrides (compare Abstr., 1908, ii, 700) can be carried out either by Dumas' method or by decomposing the nitride with boiling potassium hydroxide, the latter method is not applicable when pure titanium nitride is used, as the action is very slow.

Pure titanium nitride is best prepared from the dioxide and ammonia by heating in a porcelain tube at 1400—1500° during four to six hours. W. R.

Hydrolytic Dissociation of Bismuth Chloride. RENÉ DUBRISAY (*Compt. rend.*, 1909, 148, 830—832).—The author has studied the course of the hydrolytic dissociation of bismuth chloride, in order to ascertain whether this reaction is rightly expressed by the equation: $BiCl_3 + H_2O = BiOCl + 2HCl$. The reaction should be divariant, and, since it is exothermic, a rise of temperature should correspond with a diminution in the degree of dissociation.

Investigation of the equilibria at 18°, 80°, and 85° and for various

concentrations, leads to curves which are continuous, and thus show that only one oxychloride is formed; the curves also indicate a fall in the dissociation as the temperature rises. T. H. P.

Action of Ammoniacal Hydrogen Peroxide on Bismuth Salts. ALEXANDER GUTBIER and R. BÜNZ (*Chem. Zentr.*, 1909, i, 732—733; from *Sitzungsber. physikal. med. Soz. Erlangen*, 1909, 40, 90—95. Compare Abstr., 1906, ii, 174, 234, 551, 678; 1907, ii, 181; 1908, ii, 701).—The yellow, or orange, precipitate obtained by adding a large excess of hydrogen peroxide to an acid solution of bismuth nitrate, and filtering in small portions into concentrated ammonia, is not a peroxide, as stated by Hasebroek (Abstr., 1887, 340), since it is completely soluble in concentrated nitric acid, and contains only traces of active oxygen, whether dried at 120° or at a low temperature. It contains 95% Bi_2O_3 . The yellow colour indicates that it is not a basic hydroxide, $\text{BiO}\cdot\text{OH}$. C. H. D.

[Preparations containing Colloidal Gold.] LES ETABLISSEMENTS POULENC FRÈRES (D.R.-P. 206343).—The aromatic amines, such as aniline and α -naphthylamine, reduce solutions of auric chloride, giving precipitates of pulverulent black gold.

When this chloride is reduced with sodium sulphanilate, naphthionate, or *p*-aminophenylarsinate (atoxyl) in solutions rendered slightly alkaline with sodium hydrogen carbonate, a stable solution of colloidal gold is produced. The grey residue obtained by evaporating the solution to dryness in a vacuum dissolves completely in water to a solution having the ruby-red colour characteristic of colloidal gold. The solution obtained with atoxyl (10%), gold chloride, and sodium hydrogen carbonate is of therapeutic interest. These colloidal solutions are stable towards dilute alkalis, but the carbonates and chlorides of the alkaline-earth metals, and the salts of the heavy metals induce precipitation of the gold. F. M. G. M.

Atomic Weight of Palladium. I. Analysis of Palladosammine Chloride. ALEXANDER GUTBIER, A. KRELL, and M. WOERNLE (*J. pr. Chem.*, 1909, [ii], 79, 235—252).—After a careful examination of numerous palladium compounds, the authors select palladosammine chloride, $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$, as being the only suitable material for the determination of the atomic weight of palladium. It is easily obtained by various methods, is readily purified, and does not retain a trace of water. For its preparation, pure palladium is dissolved in hydrochloric and nitric acids, and the solution is evaporated repeatedly on the water-bath with hydrochloric acid. The residue is dissolved in the smallest possible quantity of hydrochloric acid, and the solution filtered into a platinum basin containing an excess of ammonium hydroxide. By prolonged warming on the water-bath, the precipitated Vauquelin's salt is redissolved. The clear yellow solution is saturated with hydrogen chloride, and the yellow, crystalline palladosammine chloride washed thoroughly with water. The process of solution in ammonium hydroxide, reprecipitation by hydrochloric acid and washing, is thrice repeated, and the resulting chloride is dried for seventy hours in a vacuum and finally at 105—110° to constant weight.

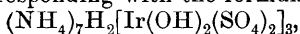
In the first set of experiments, palladosammine chloride is decomposed by ignition in a current of hydrogen (from platinised zinc and dilute sulphuric acid), and the hydrogen retained by the spongy palladium is removed by heating to a temperature exceeding 150° in a current of carbon dioxide. The mean of five experiments gives the value 106.64 ± 0.03 .

A second set of experiments is performed by Amberg's electrolytic method. The cathode is a weighed platinum dish, the anode a polished disk of platinum-iridium (10% Ir). The electrolyte is palladosammine chloride dissolved in dilute sulphuric acid at $60-65^{\circ}$. The current is $0.05-0.04$ ampere, and the potential 0.75 volt, which must not exceed 1.25 volts. The platinum dish after being washed with water and alcohol is dried at $110-120^{\circ}$. The mean of five experiments gives the value 106.65 ± 0.02 ($O = 16$). C. S.

Iridium Ammonium Disulphates. MARCEL DELÉPINE (*Compt. rend.*, 1909, 148, 557-560. Compare Abstr., 1906, ii, 551).—When ammonium iridochloride is boiled with moderately concentrated sulphuric acid, a yellow powder is obtained, which dissolves slowly in the acid, giving a green solution. If the solution is mixed with an equal weight of water and left in the cold for some days, a mixture of star-shaped crystals and of rectangular needles separates out.

The dark green, star-shaped crystals correspond with the formula $\text{NH}_4 \cdot \text{H}_3[\text{Ir} \cdot \text{OH}(\text{H}_2\text{O})(\text{SO}_4)_2]_2$. In aqueous solution, this is transformed into the compound $(\text{NH}_4)_3\text{H}[\text{Ir} \cdot \text{OH}(\text{H}_2\text{O})(\text{SO}_4)_2]_2$, which crystallises in dark green needles, soluble in 210 parts of water at 16° . This salt is also obtained by adding a solution of the more acid salt to a solution of ammonium chloride or sulphate.

If excess of ammonia is added to the green solution, the colour changes to reddish-brown, and, on the addition of alcohol, an olive-brown substance, corresponding with the formula



is precipitated. An aqueous solution of this substance, when acidified, exhibits a green colour, and gives no precipitate with barium chloride.

When heated at 100° , the substance loses one-seventh of its ammonia, and the colour changes from olive-brown to grass-green. The formulæ of these complex salts can be adapted either to the notation of Werner or that of Blomstrand-Jürgensen. H. M. D.

Mineralogical Chemistry.

The Borderland between Colloidal Chemistry, Mineralogy, and Geology. CORNELIO DOELTER and FELIX CORNU (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 189—190).—A series of brief notes on the genesis and synthesis of colloidal magnesite, on the phenomenon of

shrinkage in minerals, on the analogy between mineral hydrogels and the organic colloids, and on natural colloidal molybdenum sulphide (jordisite).

Magnesite results from the weathering of serpentine or peridotite in presence of opal, gymnite, picrolite, and dermatine.

The mother substance of ilsemannite is jordisite.

H. M. D.

Colloidal Colouring Matters in the Mineral Kingdom.

CORNELIO DOELTER (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 188—189).

—The same substance may impart different colours to a mineral according as it is present in the crystalline or colloidal form. The minerals, which are coloured by isomorphous admixture, are changed very little in comparison with the minerals which owe their colour to the presence of colloids when heated or subjected to the action of various gases, radium, or ultra-violet rays. The colour of ruby, emerald, tourmaline, and aquamarine is due to a crystalline admixture; that of citrine, smoky topaz, rose quartz, fluorspar, topaz, and most sapphires is probably due to a colloidal colouring constituent. In certain minerals, colouring substances of both kinds are present, and since the colloidal colouring matter is much less stable than the other, changes in the colour of the mineral can be easily effected.

An experiment is described in which the author covered a plate of smoky quartz with a layer of gold, and then placed it between 220 volt-terminals at a temperature of 900—1000°. The quartz plate was found to have acquired a rose-red colour, due to the presence of colloidal gold particles.

H. M. D.

Hatchettite from Bonarka, near Cracow. JÓZEF MOROZEWICZ (*Bull. Acad. Sci. Cracow*, 1908, 1067—1072).—The material forms small nests in Cretaceous marl; it is pearl-white with a tinge of yellow, and has a lamellar structure. Hardness 1; D 0.961. There is a perfect cleavage parallel to the surface of the lamellæ, and the material is brittle. The optical characters point to orthorhombic symmetry, the acute, positive bisectrix being perpendicular to the cleavage. Analysis gave C 85.25, H 14.59%. No bromine is taken up, so that the compound is saturated and belongs to the paraffin series. From the m. p. of 79.4°, the formula $C_{38}H_{78}$ is deduced. The molecular weight, determined in benzene, is about 554, which would correspond with 39 atoms of carbon.

The dark brown ozocerite of Boryslaw, with m. p. 70—83°, was examined, and is, no doubt, a mixture of hatchettite with other hydrocarbons.

L. J. S.

Hydrogels of the Mineral Kingdom in the Groups of the Elements, Sulphides and Halides. FELIX CORNU (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 187—188. Compare this vol., ii, 222).—According to the author, carbon (as anthracite), sulphur, gold, and silver, and the sulphides of silver, cadmium, mercury, copper, arsenic, and antimony, occur in nature in the form of hydrogels. So-called “buttermilk silver” represents the hydrogel form of silver chloride, and the name *Ostwaldite* is suggested for this mineral.

H. M. D.

Regular Intergrowth of Carnallite and Hæmatite. ARRIEN JOHNSEN (*Centr. Min.*, 1909, 168—173).—Carnallite crystals from Stassfurt are colourless to dark red with a metallic schiller, the red colour and schiller being due to the inclusion of minute scales of hæmatite (0.55%). The scales of hæmatite are arranged with the basal plane parallel to the basal plane of the pseudo-hexagonal carnallite, or occasionally parallel to the faces of the form {130}. The origin of the hæmatite is discussed; it is unlikely that the scales were caught up and enclosed in parallel position by the growing crystals of carnallite, and owing to their wide difference in solubility they could not have been both deposited together. The suggestion is made that the iron was originally present in the carnallite as ferrous chloride isomorphously replacing magnesium chloride, and that this by a series of changes (for which equations are given) gave rise to secondary hæmatite.

L. J. S.

Two New Magnesite Occurrences in Carinthia. KARL A. REDLICH (*Zeitsch. prakt. Geol.*, 1908, 16, 456—458).—On account of its economic value, magnesite is much sought for in the Eastern Alps. The two new localities now recorded in Carinthia are the Millstätter Alpe and St. Oswald. At the latter, the mineral has the same mode of occurrence and the same composition as that of Veitsch, in Styria (compare following abstract).

MgO.	CaO.	Fe ₂ O ₃ .	Mn ₂ O ₄ .	SiO ₂ .	Al ₂ O ₃ .	CO ₂ .
40.66	2.00	9.81	1.80	1.60	0.15	43.98
39.65	1.60	11.56	0.40	1.44	0.30	45.05

L. J. S.

Minerals of the Magnesite Deposits of Veitsch, Styria. FELIX CORNU (*Zeitsch. prakt. Geol.*, 1908, 16, 449—456).—These magnesite deposits have been formed by the action of solutions of magnesium hydrogen carbonate on the limestones of the Palæozoic sediments. The primary minerals include magnesite, dolomite, pyrites, and talc, and amongst secondary minerals are quartz, dolomite, ankerite, aragonite, calcite, rumphite, pilolite, pyrolusite, and pyrites. The magnesite is also traversed by metalliferous veins containing quartz, copper-pyrites, fahlore, and pyrites, and the alteration of these primary vein minerals has given rise to several other secondary minerals. The magnesite forms coarsely-crystalline masses of a white to yellowish-white colour. The following analyses prove it to be the ferriferous variety, breunnerite.

MgCO ₃ .*	CaO.	Fe ₂ O ₃ .	Mn ₂ O ₄ .	SiO ₂ .	Al ₂ O ₃ .	CO ₂ + H ₂ O.
87.56	1.76	9.96	0.62	1.34	0.76	49.86
90.07	1.33	8.60	0.72	1.28	0.00	50.60
89.86	2.89	8.15	0.76	0.26	0.08	50.87
88.08	0.96	8.74	0.70	0.75	0.95	50.30
85.53	3.52	7.43	0.51	0.79	2.22	50.48

* In original, given as MgO.

L. J. S.

Turanite and Alaité, Two New Vanadium Minerals. K. A. NENADKEVITSCH (*Bull. Acad. Sci. St. Pétersbourg*, 1909, 185—186).—In the uranium and vanadium mines close to the Alai Mountains and south of Andijan, Siberia, the author has found the following new vanadium minerals: (1) *Turanite*, which is a copper vanadate, $V_2O_5 \cdot 5CuO \cdot 2H_2O$, and occurs in compact or spongy form, or as radio-spheroidal aggregates. (2) *Alaité*, which is a hydrated vanadium pentoxide, $V_2O_5 \cdot H_2O$, and occurs in thick, soft, mossy masses having a blood-red colour and a silky lustre.

T. H. P.

Alum from Mormugao, India. LEWIS LEIGH FERMOR (*Rec. Geol. Surv. India*, 1908, 36, 312—314).—The mineral occurs as a snow-white efflorescence on the surface of a decomposed argillaceous rock exposed in a cliff section. It owes its origin to the weathering of iron-pyrites contained in the rock. Analysis proves the material to be kalinite, or potash-alum.

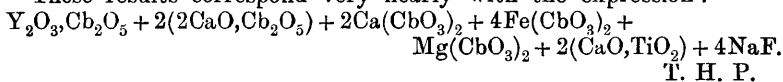
K ₂ O.	Al ₂ O ₃ .	SO ₃ .	H ₂ O.	Insol.	Total.
7.69	9.74	36.04	46.23	0.30	100.00

L. J. S.

Chemical Investigation of a Caucasian Pyrochlore. G. P. TSCHERNIK (*Bull. Acad. Sci. St. Pétersbourg*, 1909, 365—370).—The sample of Caucasian pyrochlore examined by the author occurred in octahedral crystals, D¹⁷ 4.308, hardness 5, and had the percentage composition:

Cb ₂ O ₅ (and Ta ₂ O ₅).	TiO ₂ .	Y ₂ O ₃ (and Ce ₂ O ₃).	CaO.	FeO (and MnO).	MgO.
64.75	3.73	5.56	10.55	6.73	0.92
Na ₂ O (and K ₂ O).	F.	SnO ₂ .	SiO ₂ .	Total (less O = F).	
5.90	1.78	trace	trace	99.17	

These results correspond very nearly with the expression:



T. H. P.

Formation of Nontronite by the Action of Solutions of Iron Sulphate on Wollastonite. ALFRED BERGEAT (*Centr. Min.*, 1909, 161—168).—Nontronite occurs abundantly as a mineral of recent formation in the levels of the copper mines at Aranzazú, near Concepción del Oro in Mexico. The veins of copper-pyrites are associated with wollastonite, garnet, and other contact minerals at the contact of limestone with granodiorite. The wollastonite is usually much altered; the freshest material (anal. I) is flesh-red with a fibrous to columnar structure; it is often altered to yellowish-green nontronite, and pseudomorphs of nontronite after wollastonite were found. Anal. II is of the nontronite, purified by washing the powdered material in water and separating with a heavy liquid; this material (dried at 110°) still contained some limonite, garnet, and magnesium silicate, but probably no opal, and the composition calculated for the pure

material is given under III, agreeing with the formula $H_8Fe_4Si_9O_{23}$ (compare Abstr., 1897, ii, 413).

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	CaO.	MgO.	H ₂ O.	Total.	Sp. gr.
I.*	46·71	0·69	—	2·62	34·25	0·85	4·66	95·76	2·88
II.	57·64	4·09	26·14	—	2·27	1·90	6·90	98·94	2·29
III.	59·40	3·08	29·68	—	—	—	7·84	100·00	—

* Also FeO, trace; K₂O, 0·08; Na₂O, 0·18; SO₃, 1·15; CO₂, 4·57.

The alteration of the copper-pyrites has given rise first to bornite and then to copper-glance, whilst the iron it contains passed into solution as sulphate, which acted on the wollastonite with the formation of nontronite. Wollastonite when placed in a solution of ferrous sulphate causes the precipitation of iron hydroxide, and some calcium passes into solution.

L. J. S.

Cæsium in Felspar. WLADIMIR I. VERNADSKY (*Bull. Acad. Sci. St. Pétersbourg*, 1909, 163—164).—Orthoclases from Murzinki and Shajtanki contain, besides lithium, rubidium and cæsium in quantities sufficient to allow of their separation as platinichlorides, whilst some of those from Murzinki show the presence of thallium when examined spectroscopically. The presence of rubidium is seen clearly, and that of cæsium less clearly, in the spectrum of microcline from the Ilmen Mountains.

T. H. P.

Jadeite in the Kachin Hills, Upper Burma. ALFRED WILLIAM GUSTAV BLEECK (*Rec. Geol. Surv. India*, 1908, 36, 254—285).—A description is given of the jadeite mines and of the geology of the district. At Tawmaw the jadeite occurs with albite in an igneous dyke traversing serpentine. It is suggested that the rock of this dyke was originally a nepheline-albite-rock, which has been altered by dynamometamorphism, the change $NaAlSi_3O_8$ (nepheline) + $NaAlSi_3O_8$ (albite) = $2NaAlSi_2O_6$ (jadeite) being accompanied by a diminution in volume. The albite has sometimes precisely the appearance of jadeite, being pure white to light grey with pale green spots, translucent, and compact, with a splintery fracture; such material ("pseudojadeite") was proved by analysis I to be albite. Fragments of a dark green (emerald-green in thin sections) mineral, containing a few small crystals of chromite, are also abundant in the Tawmaw quarry; they have the optical characters of epidote, and gave analysis II; for this chromiferous epidote, the name *tawmawite* is proposed.

	SiO ₂ .	Al ₂ O ₃ .	Cr ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.	Sp. gr.
I.	67·10	20·42	—	0·23	—	8·93	3·20	—	99·80	2·577
II.	37·92	12·83	11·16	9·93	25·35	—	—	2·38	99·57	—

At the neighbouring localities of Hwéka and Mamon the jadeite is quarried in a conglomerate and in alluvial deposits.

L. J. S.

Physiological Chemistry.

Physico-chemical Relations of Red-blood Corpuscles. IVAR BANG (*Biochem. Zeitsch.*, 1909, 16, 255—276).—A repetition, correction, and extension of the older observations of others, chiefly as regards agglutination and the permeability of red-blood corpuscles. The erythrocytes of the calf are not agglutinated by treatment with sugar solution, but those of the ox are. This apparent discrepancy is due to the different method of bleeding, the calf's blood being arterial and containing less carbon dioxide. If the carbon dioxide in ox blood is first washed away, ox corpuscles are no longer agglutinated in sugar solution. Ox corpuscles have a fairly considerable permeability to salts. The rate of diffusion of carbon dioxide is, however, much greater, and must be taken into account when considering the isotonic coefficient of the blood. When blood is diluted with sodium chloride solution, the variable quantity of carbon dioxide in the erythrocytes is partly replaced by hydrochloric acid, making the isotonic coefficient somewhat variable and indeterminate. G. B.

Metabolism in the Infant. WALTHER FREUND (*Biochem. Zeitsch.*, 1909, 16, 453—472).—A number of observations on infants are recorded, the chief points examined being the amount of fat and soaps in the fæces during different diets. Some details regarding calcium metabolism are also given. No general conclusions are drawn.

W. D. H.

Protein Metabolism. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1909, 59, 177—193).—A discussion of Voit's well-known theory of the difference between "organ protein" and "circulating protein." The comparatively high output of urinary nitrogen during the first few days of starvation is attributed by the theory to the breakdown of the "circulating protein." It is pointed out that it is a pure assumption that the source of this extra nitrogenous waste is protein. It may be mere worthless ballast in non-protein form which is broken up and excreted. Some experiments on dogs are recorded at length, which show that the course of nitrogenous excretion during inanition is much the same, whether the animal had been previously fed on excess of protein food or not.

W. D. H.

Rôle of the Ash Constituents of Wheat Bran in the Metabolism of Herbivora. EDWIN B. HART, ELMER V. MCCOLLUM, and G. C. HUMPREY (*Amer. J. Physiol.*, 1909, 24, 86—103).—Details are given of the relative amounts of potassium, magnesium, etc., in fæces and urine in accordance with differences in the intake. Magnesium, when supplied as a chloride or phytin compound, was largely excreted in the gut. Variations in the intake of various ash constituents or of phytin did not influence the composition of the milk. Phytin causes diuresis, probably because of the high potassium intake. Absence of phytin leads to constipation.

W. D. H.

Influence of Alcohol on Metabolism in Animals during Inanition. MARTIN KOCHMANN and WALTER HALL (*Pflüger's Archiv*, 1909, 127, 280—356).—In moderate doses, subcutaneous administration of alcohol in rabbits during inanition increases the period during which they live, but large doses hasten death. The favouring action is due to protein sparing, and to the retention of water. Death is accelerated by large doses owing to increase of protein catabolism, especially of proteins poor in sulphur, as evidenced by the N:S ratio. Alcohol produces a diuretic action only when given in large doses.

W. D. H.

Protein Absorption. OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1909, 59, 239—246).—Experiments on fishes are recorded into the intestine of which protein cleavage products were introduced. These are partly absorbed as ammonia, partly deamidised during absorption, and the remainder are absorbed in an unknown way.

W. D. H.

Peptolytic Enzymes in the Stomach. II. EMIL ABDERHALDEN and ALFRED SCHITTENHELM (*Zeitsch. physiol. Chem.*, 1909, 59, 230—232. Compare Abstr., 1908, ii, 1049).—Glycyl-*l*-tyrosine, or peptone from silk, which is rich in tyrosine, may be employed for the detection of peptolytic enzymes. They are absent from pure gastric juice, and when present in the stomach are due to regurgitation from the intestine, which may be increased by the administration of oil. Their presence may be employed for diagnosis of such regurgitation in disease.

W. D. H.

Chemical Mechanism of Gastric Secretion. J. SYDNEY EDKINS and M. TWEEDY (*J. Physiol.*, 1909, 38, 263—267).—By a specially devised method, the fundus and pyloric ends of the stomach in cats were functionally separated. Different substances were placed in the pyloric end or in the duodenum; the fundus responded by a marked secretion, although the same substances placed in the fundus itself provoked none. The effectiveness of the substances used was in the following order: meat extracts, dextrose, dextrin, and least of all hydrochloric acid.

W. D. H.

Action of Certain Hitherto Unknown Constituents of the Pancreas on Sugar. I. ERNST VAHLEN (*Zeitsch. physiol. Chem.*, 1909, 59, 194—222).—The theory propounded is that the cleavage of sugar is the result of the catalytic action of certain substances formed in the pancreas. In support of this, certain substances are stated to have been separated from the pancreas, one of which produces a breakdown of sugar and evolution of carbon dioxide, and also favours alcoholic fermentation, whilst another produces the opposite results. No details are given either of the mode of preparation or chemical nature of the substances in question.

W. D. H.

Action of Secretin and Receptive Substances. WALTER E. DIXON and P. HAMILL (*J. Physiol.*, 1909, 38, 314—336).—Enzymes

exist in the pancreas as precursors: protrypsinogen, proamyllopsin, and prosteapsin. Secretin combines chemically with these and liberates the active enzyme in the two last cases, but only liberates trypsinogen in the first, which in its turn is converted into trypsin by the entero-kinase of the succus entericus.

No evidence that vegetable alkaloids exert a specific effect in the body by combining with "receptive substances" was obtained; but it is suggested that the physiological activity of muscle and gland is due in all cases to the liberation of specific hormones, which combine with "receptive substances."

The statement that secretin and choline are identical is criticised.

W. D. H.

The Rôle of the Small Intestine in the Formation of Glycogen from Dextrose. KARL GRUBE (*Pflüger's Archiv*, 1909, 127, 529—532).—Croftan (this vol., ii, 328) has stated that the small intestine produces some preliminary condensation of sugar molecules, without which the liver is unable to make glycogen from dextrose. The present experiments show that the injection of dextrose into a mesenteric vein leads to glycogen formation in the liver.

W. D. H.

A Mucoid in the Intestinal Mucous Membrane of the Horse. HUBERT W. BYWATERS (*Proc. physiol. Soc.*, 1909, xlii—xliii; *J. Physiol.*, 38).—About 20 grams of a mucoid, believed to be identical with sero-mucoid, were separated from 20 kilos. of moist mucous membrane. It contains from 5.68 to 7.91% of ash.

W. D. H.

Transformations in the Phosphorised Compounds of the Hen's Egg during Development. R. H. ADERS PLIMMER and FREDERICK H. SCOTT (*J. Physiol.*, 1909, 38, 247—253).—The following table gives the distribution of phosphorus in (1) the unincubated egg, and in (2) the newly-hatched chick:

	(1.)	(2.)
Inorganic phosphate	trace	60.0 per cent. of total
Water soluble organic compounds ...	6.2	8.6 " "
Ether soluble substances	64.8	19.3 " "
Nuclein-like substances	1.9	12.0 " "
Vitellin	27.1	0.0 " "

Ether soluble and other organic compounds must therefore have been transformed into inorganic phosphates; this change begins markedly about the sixteenth or seventeenth day of incubation. Glycero-phosphoric acid is believed to give rise to inorganic phosphates only. There is also a probable transformation of the phospho-protein (vitellin) into nucleo-protein as well as into inorganic phosphate.

W. D. H.

Fatty Infiltration of the Liver in Hunger. V. H. MOTTRAM (*J. Physiol.*, 1909, 38, 281—313).—After twenty-four hours' inanition in rabbits and guinea-pigs (but not in hedgehogs, pigeons, or rats), the percentage of fat in the liver increases; this is sometimes due to the

shrinkage of the liver, but in other cases, especially in rabbits, is produced by a migration of fat into the liver from other parts, and in the process the fat undergoes a change in the direction of desaturation.

W. D. H.

Desaturation of Fatty Acids in the Liver. JOHN B. LEATHES and J. MEYER-WEDELL (*Proc. physiol. Soc.*, 1909, xxxviii—xl; *J. Physiol.*, 38).—By feeding rats on various fats, it is shown that the liver as well as the connective tissue takes up fats conveyed to it by the blood. Other organs do not do the same to any extent. The connective (adipose) tissue stores the fat as brought to it; the liver, however, changes it so as to increase its power of absorbing iodine. This furnishes additional evidence in support of the view that one function of the liver is to prepare fat for oxidation in other tissues, and that the preparatory treatment consists, in part, of a desaturation process.

W. D. H.

The Behaviour of the Liver to Foreign Proteins. FELIX REACH (*Biochem. Zeitsch.*, 1909, 16, 357—363).—Iodoprotein perfused through the liver was taken up by that organ. A cleavage of the protein was only recognisable in small measure.

W. D. H.

Liver Ferments, with Special Reference to the Gelatinolytic Enzyme. S. HATA (*Biochem. Zeitsch.*, 1909, 16, 383—390).—This is a contribution to the subject of intracellular enzymes in the liver, and deals especially with the details of action (time, quantity, etc.) of liver extracts in liquefying gelatin.

W. D. H.

Pressor Substances in Placental Extracts. OTTO ROSENHEIM (*J. Physiol.*, 1909, 38, 337—342).—The pressor substances which are obtainable from human placenta are products of initial putrefaction; the autolytic enzymes without the aid of micro-organisms are unable to produce them, that is, they are unable to split off the terminal carboxyl group of the amino-acids. The most active substance separated out was identified as *p*-hydroxyphenylethylamine; the identity of another with *iso*amylamine is probable. The bases are identical with those found by Barger and Walpole in putrid meat (see next abstract).

W. D. H.

Pressor Substances in Putrid Meat. GEORGE BARGER and GEORGE S. WALPOLE (*J. Physiol.*, 1909, 38, 343—352. Compare this vol., ii, 254).—In the putrefaction of horse-flesh, bases are formed which cause a rise of arterial blood-pressure when injected intravenously; they are derived from amino-acids by the loss of carbon dioxide. The following were isolated: *iso*amylamine (from leucine), *p*-hydroxyphenylethylamine (from tyrosine), and probably phenylethylamine (from phenylalanine). The second is the most powerful. The pressor base previously obtained from putrid meat by Abelous and his colleagues is probably *iso*amylamine.

W. D. H.

Lipoids of the Adrenal. OTTO ROSENHEIM and M. CHRISTINE TEBB (*Proc. physiol. Chem.*, 1909, liv—lvi; *J. Physiol.*, 38).—The anisotropic substance of the adrenal cortex is not, as Powell White

suggests, a mixture of cholesterol and fatty acids, although such a mixture readily produces anisotropic globules. Free cholesterol is absent, but cholesterol esters (palmitic and stearic) as well as free stearic and other fatty acids are present. In the brain and other organs, cholesterol exists in a free state. A small quantity of sphingomyelin was also separated.

Whether the function of the adrenal cortex is the neutralisation of toxins is a subject to be pursued. The present analyses tend to support this view.

W. D. H.

The Human Pituitary. WILLIAM D. HALLIBURTON, J. P. CANDLER, and A. W. SIKES (*Proc. physiol. Soc.*, 1909, xxxvii; *J. Physiol.*, 38).—The human pituitary weighs about 0.5 gram, and contains 76% of water. A single pituitary will, however, make sufficiently strong extracts to test their physiological action. Extracts of the anterior lobe are inactive or produce an insignificant fall of blood-pressure, such as is caused by tissue extracts generally. Extracts of the posterior lobe produce, as was found by Schäfer and his colleagues in their work on the pituitary of other mammals, (1) a rise of arterial pressure at the first injection, (2) a constriction of peripheral vessels, but (3) prolonged dilatation of the kidney vessels, accompanied by (4) diuresis. The pituitaries used came from asylum cases, but in nearly all cases the structure was normal. The number and size of the colloid cysts vary a good deal, but the colloid material does not appear to be the substance to which the extracts owe their activity. In man and ox, the pituitary contains no iodine.

W. D. H.

Heat Coagulation in Smooth Muscle. The Connexion between Protein Coagulation and Heat Rigor. EDWARD B. MEIGS (*Amer. J. Physiol.*, 1909, 24, 1—13, 178—186. Compare this vol., ii, 251).—Lactic acid formation is an accompaniment of heat coagulation in smooth muscle; this is believed to cause the fibre cells to swell in such a way that they lengthen.

The view is advanced that the heat shortening of tissues is not due to coagulation of their protein constituents, but to some other process, the nature of which is left vague.

W. D. H.

Hydrolysis of Muscle of Scallop (*Pectens viradians*). THOMAS B. OSBORNE and D. BREESE JONES (*Amer. J. Physiol.*, 1909, 24, 161—169).—The amounts of amino-acids obtained are not vastly different from those previously given for the muscle of halibut and chicken. Glycine is absent in the muscle of halibut and scallop, but present in small amount in chicken's muscle. Ox muscle, on the other hand, yields a larger amount. The scallop contains relatively a good deal of free glycine.

W. D. H.

Chemico-physical Investigations on the Crystalline Lens. FILIPPO BOTTAZZI and NOÈ SCALINCI (*Atti. R. Accad. Lincei*, 1909, [v], 18, i, 225—228. Compare this vol., ii, 162).—Lenses of dogs' eyes, immersed in aqueous or vitreous humour, were found in one case,

first to diminish and then increase, and in another, first to increase and then diminish in weight. The diminution in weight may be explained as due to the diffusion outwards of the protein substances of the lens surpassing the penetration of liquid into the lens. The increase of weight can only be the effect of an increase in the degree of imbibition of the lens in consequence of a diminution of the elasticity of the capsule. In all the experiments, the body of the lens remained quite transparent, not only when the uninjured capsule limited the imbibition, but even for nineteen hours after the capsule had been removed. Hence a much longer period is necessary for the increase of the degree of imbibition of the crystalline lens, immersed in normal ocular liquids, to produced opacity of the lens.

T. H. P.

The Influence of Electrolytes on the Rhythmical Movements of Medusæ. II. ALBRECHT BETHE (*Pflüger's Archiv*, 1909, 127, 219—273. Compare Abstr., 1908, ii, 969).—Medusæ continue to live and move in artificial mixtures of salts provided they are present in the same proportions as in sea-water.

Sodium chloride alone hastens, then paralyses their movements; this action is reversible; potassium chloride stimulates in large doses; calcium chloride strengthens the systole, and in large doses lessens its frequency, and finally stops it, producing inexcitability. Magnesium chloride and sulphate have primary paralysing action; aluminium has the same action, only more markedly. The accelerating action of sodium salts is as follows: $\text{Na}_2\text{SO}_4 > \text{NaCl} > \text{NaI} > \text{NaBr} > \text{NaNO}_3$, and the potassium salts: $\text{K}_2\text{SO}_4 > \text{KCl} > \text{KNO}_3$; the paralysing action of magnesium sulphate is greater than that of the chloride. Increase of hydrogen ions stimulates, of hydroxyl ions, paralyses. The membrane of the medusæ is probably not permeable to hydrogen and hydroxyl ions.

W. D. H.

Formation of Silk. EMIL ABDERHALDEN and H. R. DEAN. EMIL ABDERHALDEN and WOLFGANG WEICHARDT (*Zeitsch. physiol. Chem.*, 1909, 59, 170—173, 174—176).—Silk contains much tyrosine, glycine, and alanine. On the view that these acids are present in the silk-worm in abundance, the mono-amino-acids were estimated in the body of the silk-worm and in the moth after silk formation, with the following results.

	In silk-worm.	In moth.
Glycine	10.2 %	3.5 %
Alanine	8.7	3.2
Valine	1.7	1.7
Leucine.....	4.8	8.5
Aspartic acid	1.6	2.7
Glutamic acid	3.5	5.7
Phenylalanine.....	2.4	2.7
Tyrosine	4.3	1.6
Proline	1.5	4.0

In the first column the high percentage of glycine, alanine, and tyrosine is noteworthy, so also is the fall in each in the second column.

W. D. H.

Connexion between Changes of Permeability and Stimulation. RALPH S. LILLIE (*Amer. J. Physiol.*, 1909, 24, 14—44).—A number of experiments are given on the influence of salts on the contraction of *Arenicola* larvæ. Solutions which produce contraction, and these only, produce a diffusion outwards of a yellow pigment in the larvæ; stimulating agents increase the normal permeability; their effect is considered to depend essentially on their influence in varying the rate at which carbon dioxide leaves the cell. W. D. H.

Sugar Formation in Pupæ. OTTO KRUMMACHER and ERNST WEINLAND (*Zeitsch. Biol.*, 1909, 52, 273—279).—The experiments were performed with the pupæ of *Calliphora*. Calorimetric observations are recorded, and the general conclusion is drawn that sugar is formed from protein and not from fat. W. D. H.

Physiology of Mollusca. IV. Purine Substance of Sycotypus. LAFAYETTE B. MENDEL and H. GIDEON WELLS (*Amer. J. Physiol.*, 1909, 24, 170—177).—The purine bases obtained by acid hydrolysis of the liver of the gastropod, *Sycotypus canaliculatus*, are the same as those derived from the comparable tissues of the higher animals, namely, adenine, guanine, hypoxanthine, and xanthine. The amino-purines preponderate; hence it is probable that the nucleoprotein complexes are much the same in molluscs as in vertebrates. Nuclease, adenase, and guanase are present in the molluscan liver; xantho-oxydase, the uricolytic enzyme, and uric acid were not found. W. D. H.

Chemical Processes in Worms. II. ERNST J. LESSER (*Zeitsch. Biol.*, 1909, 52, 282—297. Compare Abstr., 1908, ii, 309).—In anoxybiosis the chief product formed by the earth worm is volatile fatty acid, probably a valeric acid. During the process, the alcoholic fermentation of sugar does not occur. The parent substance of the fatty acid is probably carbohydrate (glycogen). In the first eight days of inanition, during six hours anoxybiosis, 1 molecule of fatty acid is formed per 3 molecules of carbon dioxide. W. D. H.

Creatinine Output in Man. PHCEBUS A. LEVENE and L. KRISTELLER (*Amer. J. Physiol.*, 1909, 24, 45—65).—In pathological conditions of the muscular system, the rate of catabolism of ingested creatine is lowered, and part of the creatine is removed in the form of creatinine. In some forms of muscular disease, the creatinine output is normal, in others it is altered; in others, ingestion of meat increases the output of both creatine and creatinine.

These facts are considered inexplicable by any of the current theories, and two factors are stated to be of importance: (1) the formation of creatinine, and (2) its further oxidation; disturbances of either factor will lead to an abnormal creatinine output. W. D. H.

Hypno-anæsthetics. A. BRISSEMORET and J. CHEVALIER (*Compt. rend.*, 1909, 148, 731—733).—A description of the physiological action of $\beta\beta$ -dichloropropane and $\beta\beta$ -diethoxypropane.

The experiments, which were carried out on dogs by intraperitoneal injection, show that the hypno-anæsthetic properties of the former compound are not sufficiently well marked to render it of practical value. In its pharmacodynamic action $\beta\beta$ -diethoxypropane resembles the acetals already studied. The accelerating influence it exerts on the heart restricts its field of useful application. W. O. W.

The Effect on the Animal Organism of Chloroform and Cocaine or Strychnine. JOH. DOGIEL (*Pflüger's Archiv*, 1909, 127, 357—442).—A large number of experiments on the effect of chloroform on the heart, pulse, and circulation generally, on the respiration, nervous system, reflexes, etc., are recorded. The cessation of respiration so often observed in the preliminary induction of chloroform anæsthesia is attributed to a reflex action from the respiratory passages and lungs. In many points cocaine, like strychnine, acts antagonistically to chloroform, and the main outcome of the research is a recommendation to employ cocaine with chloroform, in order to lessen the danger of the latter. W. D. H.

[Physiological Action of Optical] Isomerides of Adrenaline. ARTHUR R. CUSHNY (*J. Physiol.*, 1909, 38, 259—262. Compare Abstr., 1908, ii, 720).—The minimal lethal dose of *l*-adrenaline in rats is 1—2 mg. per 100 grams of body-weight; that of *d*-adrenaline is 12 to 15 more. The same relationship in activity is seen in the effects on blood-pressure and in producing glycosuria. No evidence was obtained suggesting that adrenaline acts elsewhere than on the "receptive substances" of the sympathetic myo-neural junction. W. D. H.

Physiological Action of *l*-, *d*-, and *dl*-Adrenalines. III. EMIL ABDERHALDEN and SLAVU (*Zeitsch. physiol. Chem.*, 1909, 59, 129—137. Compare this vol., ii, 333; also Cushny, preceding abstract).—The present experiments confirm the conclusions previously arrived at, that *d*-adrenaline is less active physiologically than *l*-adrenaline; the points specially referred to are: (1) contraction of the pigment cells of the frog's skin; (2) lowering of body temperature, and (3) fatal dose. W. D. H.

Glycine as a Detoxicating Agent. HENRY D. DAKIN (*J. Biol. Chem.*, 1909, 5, 413—418).—When benzoic acid is introduced into the body, it is promptly converted into hippuric acid and excreted. It is not clear whether this union with glycine is protective, as the toxic action of benzoic acid is not known.

The glycine compounds of phenylpropionic acid, cinnamic acid, and β -hydroxyphenylpropionic acid are non-toxic, but the acids themselves are poisonous. The glycine compounds are much more resistant to oxidation than the acids. W. D. H.

Behaviour of Atoxyl in the Organism. J. IGRSHEIMER and A. ROTHMANN (*Zeitsch. physiol. Chem.*, 1909, 59, 256—280. Compare Abstr., 1908, ii, 1061).—The undecomposed atoxyl in the circulating blood appears to have a strong action on cells (trypanosomes or tissue

cells), with the formation of toxic products; this is not certain, but what is regarded as certain is that the toxic action of atoxyl is determined by two factors: (1) the formation of a reduction product, and (2) the liberation of arsenic in inorganic combination.

W. D. H.

Chemo-therapeutic Experiments with Some New Atoxyl Preparations in Spirochaete Diseases, with Special Reference to Experimental Syphilis. PAUL UHLENHUTH and MANTEUFEL (*Chem. Zentr.*, 1909, i, 782; from *Zeitsch. Immunitätsforsch. exp. Therap.*, 1908, 1, 108—132. Compare also following abstract).—The acid mercuric salt of *p*-aminophenylarsinic acid (of which atoxyl is the sodium salt) works better than atoxyl derivatives containing iodine, which are more toxic than atoxyl. Mercuric iodophenylarsinate is less toxic than the corresponding sodium salt. The action of arsenophenylglycine has also been examined.

G. B.

Constitution and Toxicity of Various Substances of the Atoxyl Group. FERDINAND BLUMENTHAL (*Chem. Zentr.*, 1909, i, 782; from *Med. Klin.*, 1908, Heft 44, 2 pp.).—Although acetylatoxyl is much less poisonous than atoxyl, the same does not hold for the corresponding mercury salts. *p*-Iodophenylarsinic acid is more toxic than atoxyl, but the mercury salt of the former acid is less toxic than the mercury salt corresponding with atoxyl (compare preceding abstract). The cause of this change in toxicity is not due to greater difficulty of absorption, for most of the iodine appears in the urine within twenty-four hours.

G. B.

The Detection and the Course of Excretion of Atoxyl in Urine. Observations on the Paper by Lockemann and Paucke. FERDINAND BLUMENTHAL (*Chem. Zentr.*, 1909, i, 949; from *Deutsch. med. Woch.*, 1908, 34, No. 52).—Polemical against Lockemann and Paucke (this vol., ii, 167). The precipitate obtained by these authors with β -naphthylamine in the diazotised urine of patients after treatment with atoxyl consisted only to a small extent of an atoxyl-dye; over 80% was impurity. The author does not agree with Lockemann and Paucke's conclusion, that arsenious oxide is set free, and maintains his position as regards the duration of arsenic excretion after the administration of atoxyl.

G. B.

The Excretion of Atoxyl through the Urine. Reply to the Observation of F. Blumenthal. GEORG LOCKEMANN (*Chem. Zentr.*, 1909, i, 949; from *Deutsch. med. Woch.*, 1909, 35, No. 5).—Reply to Blumenthal (compare preceding abstract), and criticism of his gravimetric arsenic estimation.

G. B.

Acapnia and Shock. III. YANDELL HENDERSON (*Amer. J. Physiol.*, 1909, 24, 66—85).—A further development of the author's views with special reference to abdominal operations. Local acapnia, due to direct exhalation of carbon dioxide, is a factor in the loss of tonus of exposed viscera. Carbon dioxide tension in the nerve centres and in the tissues and fluids of the body is a factor in the maintenance of tonus. Restoration of the body's store of carbon dioxide is effective as a method of relief.

W. D. H.

Protein Metabolism in Carbon Monoxide Poisoning. CHARLES G. L. WOLF and EMIL OSTERBERG (*Biochem. Zeitsch.*, 1909, 16, 476—485).—Experiments on dogs are recorded with very complete urinary analyses, especially in relation to nitrogen and sulphur. The most remarkable feature in some cases as the result of poisoning by carbon monoxide is the excretion of creatine in amounts exceeding that found in inanition. This was not, however, always found.

W. D. H.

Effect of Hydrogen Peroxide on Gonionemus. O. P. TERRY (*Amer. J. Physiol.*, 1909, 24, 117—123).—The rhythmical contractions of the bell of the jelly-fish gonionemus cease when the margin of the bell containing the nerves is removed. Hydrogen peroxide will initiate pulsations in the marginless bell in normal sea-water by increase of oxidation processes.

W. D. H.

Mineral Constituents of Bone in Osteomalacia. CÆSARE CAPPEZZUOLI (*Biochem. Zeitsch.*, 1909, 16, 355—356).—In this disease, the percentage quantity of ash is lessened; the diminution of calcium is greater than that of magnesium. The alterations are more marked in flat than in long bones.

W. D. H.

The Diastatic Enzyme of Paramœcium in Relation to the Killing Concentration of Copper Sulphate. AMOS W. PETERS and OPAL BURRES (*J. Biol. Chem.*, 1909, 6, 65—73).—The data given show a uniform correlation between the concentration of copper sulphate required to kill *Paramœcia* instantly and that which markedly inhibits the action of their diastase. This suggests the more general conclusion that the injurious action of certain poisons which act in low concentrations may be due to the inactivation of protoplasmic enzymes.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Bacillus Infantilis. ARTHUR I. KENDALL (*J. Biol. Chem.*, 1909, 5, 419—438); CHRISTIAN A. HERTER and A. I. KENDALL (*ibid.*, 439—442).—This new bacillus is found in certain chronic intestinal infections, and is believed by Herter to be related to what he terms “infantilism,” in which, in addition to intestinal troubles, there is an arrest of bodily development and a slight retardation of cerebral development. Large amounts of indican and phenolic substances occur in the urine; indoleacetic and aromatic hydroxy-acids are also often in excess. The bacillus is a powerful alkali producer, ammonia and a primary amine being the chief basic substances found in cultures. It does not produce indole, scatole, or phenolic substances. Whether it produces “infantilism” is left open, but the observations recorded are considered to prove that irritant products produced by its growth may cause diarrhoea.

W. D. H.

Constituents of Emmenthal Cheese. IV. ERNST WINTERSTEIN and ALBERT KÜNG (*Zeitsch. physiol. Chem.*, 1909, 59, 138—140. Compare Abstr., 1906, ii, 248).—The present experiments show the occurrence of *p*-hydroxyphenylethylamine in Emmenthal cheese; its presence is attributed to bacterial action. W. D. H.

Oxidation by Fungi. II. REGINALD O. HERZOG and A. MEIER (*Zeitsch. physiol. Chem.*, 1909, 59, 57—62. Compare Abstr., 1908, ii, 1063).—The oxidation by fungi of the two antipodes of hydroxy-acids containing an asymmetric carbon atom takes place with different velocities. It is a ferment action, for the fungus can be killed with alcohol, acetone, etc., or by liquid air. Acids without an asymmetric carbon atom are scarcely attacked. Intermediate products have not as yet been isolated, although the oxidation does not proceed at once to carbon dioxide. G. B.

Specificity of Peptolytic Enzymes in Different Fungi. EMIL ABDERHALDEN and HANS PRINGSHEIM (*Zeitsch. physiol. Chem.*, 1909, 59, 249—255).—A comparison of the action of the enzymes of various moulds in the cleavage of certain polypeptides shows that there are differences of degree and of kind in their actions. W. D. H.

The Function of Septic Tanks in the Biological Purification of Sewage. ACHILLE MÜNTZ and E. LAINÉ (*Compt. rend.*, 1909, 148, 597—601).—Before passing to the oxidising beds, sewage is generally first placed in deep reservoirs, where it forms a reducing medium, characterised by putrid emanations. The chief use of these reservoirs is to allow suspended matter to settle down; they do not further aid in the oxidation of the organic substances in the sewage. G. B.

The Effect of Ammonium Salts on the Fermentation of Wines. W. BIERBERG (*Centr. Bakt. Par.*, 1909, ii, 23, 12—32).—It is known that yeast can utilise the nitrogen in ammonium salts as food, and the author investigates the effect of adding ammonium salts to wines undergoing fermentation. The most striking result is the influence of the initial content of alcohol. The larger the amount of alcohol present originally the smaller the amount of ammonium salt necessary in order to produce a strong fermentation. Reasons are adduced for supposing that the ammonium salt acts rather as a stimulant than as a nutrient. E. J. R.

The [Carbon] Assimilation Process [in Plants]. HANS EULER (*Zeitsch. physiol. Chem.*, 1909, 59, 122—124).—Oxalic acid is not, as supposed by Baur, an intermediate product in carbon assimilation, but rather an oxidation product of sugar, and due to respiration. The author's experiments support Ewarts' criticism (Abstr., 1908, ii, 217) of Usher and Priestley's conclusion (Abstr., 1906, ii, 299, 881) that formaldehyde is formed from carbon dioxide and a chlorophyll extract in the light. G. B.

Photodynamic Action of Chlorophyll and its Relation to the Photosynthetic Assimilation of Plants. WALTHER HAUSMANN (*Biochem. Zeitsch.*, 1909, 16, 294—312).—Tappeiner (Abstr.,

1908, ii, 867) and his pupils have shown that certain fluorescent substances, such as eosin, under the influence of light hæmolyse a suspension of red-blood corpuscles and kill *Paramæcia*. The author now shows that chlorophyll, including the crystallised chlorophyll of Willstätter, has the same effect on both objects. This "photodynamic" action takes place in the same regions of the spectrum as photosynthesis, so that there appears to be an intimate connexion between assimilation and the photodynamic action of chlorophyll. The photodynamic action of phylloporphyrin is identical with that of hæmatoporphyrin.

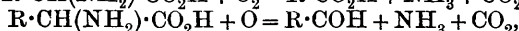
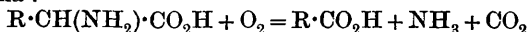
G. B.

The Effect of Light on the Formation of Protein in Plants. W. ZALESKI (*Ber. deut. bot. Ges.*, 1909, 27, 56—62).—The fact that plants can form protein in absence of light, provided sugar and nitrates are supplied, indicates that light plays only an indirect part in protein formation; certain physiologists have, however, recently supposed that light acts directly and supplies energy. The author's experiments are entirely opposed to the latter view.

Portions of etiolated bean seedlings were grown on culture solutions containing respectively 5 and 10 per cent. of sugar for five and ten days under aseptic conditions. Some of the experiments were made in ordinary light, others in yellow light (light which has passed through saturated potassium dichromate solution), others in blue light (light passed through 2% cuprammonium hydroxide solution). No difference was observed between yellow and blue light, and protein formation is therefore independent of the wave-length of the light. It is noteworthy, however, that protein formation was more intense in coloured than in white light.

E. J. R.

Ammonia as a Decomposition Product of the Nitrogenous Compounds in Higher Plants. WL. BUTKEWITSCH (*Biochem. Zeitsch.*, 1909, 16, (6), 411—452).—A general discussion, with copious references to the literature of the subject. The production of ammonia goes on even after the protoplasm has been killed; it is, however, bound up with an oxidation process. This observation appears to rule out of court several of the hypotheses which have been advanced to account for the decomposition, and lends support to the view that ammonia is produced by the oxidation of a proteolytic substance. In this connexion Dakin's observation is of interest, that amino-acids on oxidation with hydrogen peroxide give rise to fatty acids, aldehydes, and ammonia:



but it is not clear that oxidation is an indispensable condition, and it is possible that even in one and the same cell ammonia may be formed by several different processes, as by oxidation of an amino-acid or by addition of hydrogen to an amide.

E. J. R.

Cyanogenetic Plants. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1909, 28, 24—41).—Treub has shown (*Abstr.*, 1896, ii, 327) that

the leaves of *Pangium edule* contain hydrogen cyanide, partly as a stable compound hydrolysed by an enzyme also present in the leaves, and probably also in a free or very loosely combined condition, since a greater or less quantity is evolved when the leaves are treated with boiling absolute alcohol.

The stable compound isolated from the leaves is shown to be identical with the glucoside gynocardin discovered by Power and Lees (Trans., 1905, 87, 349) in the seeds of *Gynocardia odorata*.

When an absolute alcoholic solution of gynocardin cooled to -10° is treated with sufficient aqueous gynocardase solution to dilute the alcohol to the same extent as that effected by the moisture contained in the leaves of *Pangium edule*, the solution after one hour is found to contain a very small amount of hydrogen cyanide (estimated by adding a known excess of potassium hydroxide solution containing a chloride and titrating with $N/100$ -silver nitrate solution, correction being made for the retardation in the appearance of the opalescence by the excess of alkali), but as the quantity remains constant the conclusion is drawn that enzyme action is inhibited by alcohol of such strength at -10° , and that the trace of hydrogen cyanide detected is liberated before the aqueous enzyme solution is completely mixed with the alcoholic glucoside solution. In order, therefore, to determine whether the evolution of hydrogen cyanide when the leaves of *Pangium edule* are treated with boiling alcohol is due to enzyme action, experiments were carried out at -10° . When fragments of the leaves are immersed in absolute ethyl alcohol at -10° , hydrogen cyanide is liberated in amounts almost equal to those evolved by the treatment with boiling alcohol, and 50—100 times as great as that observed in the experiment (above) with alcoholic gynocardin solution. The conclusion is drawn that the hydrogen cyanide extracted from the leaves by alcohol occurs either in a free or very loosely combined condition, possibly as a cyanohydrin. Since Ult  e (this vol., i, 293) has shown that the cyanohydrins do not precipitate silver nitrate solution, a series of determinations were made of the amounts of hydrogen cyanide extracted from the leaves by absolute alcohol at -10° , both by direct titration as described above (determining the total hydrogen cyanide, free and as cyanohydrin, if any) and by precipitation with excess of silver nitrate solution and determination of the cyanide in the precipitate. The results show that for the most part the hydrogen cyanide is present in the free state, but they do not indicate with certainty whether a small quantity occurs in the form of an unstable compound. It is pointed out that in cyanogenetic plants a state of equilibrium exists between the aldehyde or ketone, the sugar, and the hydrogen cyanide, and the latter will be found in a free state when it is produced by the plant in a relatively larger proportion than the aldehyde or ketone and the sugar.

The author has isolated from the leaves of the *Phaseolus lunatus* the glucoside phaseolunatin obtained by Dunstan and Henry (Abstr., 1904, ii, 71) from the seeds of the same plant, and in agreement with these authors (Abstr., 1907, ii, 572), but contrary to the observation of Kohn-Abrest (Abstr., 1906, ii, 625), he has obtained it also from Java beans.

E. H.

Biochemical Investigations on the Development of Anthocyanin in Plants. R. COMBES (*Compt. rend.*, 1909, 148, 790—792).—It is known that anthocyanin is formed in leaves under the action of strong light or of low temperatures. Overton has shown, also, that it is formed when plants grow in culture solutions containing sugar, and he suggests that its formation is in all cases due to excess of sugar in the cell sap. The author has examined a number of leaves which had turned red under the influence of autumn frosts or of strong light and compared them with green leaves. In all cases the red leaves contained more sugar (estimated after hydrolysis) and more glucosides than the green leaves; these results are quite in accordance with Overton's view. It does not appear that the insoluble carbohydrates have much to do with the formation of anthocyanin, since they are sometimes more and sometimes less in red than in green leaves. The plants examined were *Ampelopsis hederaceae*, *Rosa canina*, *Mahonia aquifolium*, *Sorbus latifolia*, and *Spirea paniculata*.

E. J. R.

Scatole and Indole in Wood of *Celtis reticulosa*. CHRISTIAN A. HERTER (*J. Biol. Chem.*, 1909, 5, 489—492).—*Celtis reticulosa* is a tree which grows in Java. It is termed "filth wood" by the natives on account of the faecal odour of the wood. Scatole has been obtained from it by Dunstan (*Abstr.*, 1890, 191); this is confirmed; indole was also found in less amount; although indoleacetic acid was not found, the substances mentioned are believed to originate from tryptophan, and not to be synthesised from simpler substances.

W. D. H.

Oil of Colocynth Seeds. CARLO GRIMALDI and L. PRUSSIA (*Boll. Chim. Farm.*, 1909, 48, 93—95).—The constants of colocynth oil, which is best extracted from the seeds by means of carbon tetrachloride, are as follows: D_{15}^{15} 0.9289; D_{15}^{100} 0.8733; solidifying point, 14°; refractive index on Zeiss's butter refractometer, 78.2 at 15°, 72.3 at 25°, and 63.5 at 40°; thermal degree on the Tortelli thermoleometer, 86.4; acid number, 2.7; Hehner number, 90.72; saponification number, 191.7; Hübl iodine number, 120.37; Reichert-Meissl number, 0.32. The fatty acids of the oil give the following constants: D_{15}^{100} 0.8537; m. p. 29.2—30°; solidifying point, 26.2—27.2°; refractive index on Zeiss's butter refractometer, 56.7 at 30°, 51.5 at 40°, and 48.3 at 45°; acid number, 192.6; saponification value, 198.2; Hübl iodine number, 121.0; absolute iodine number (Tortelli and Ruggeri), 150.0; mean molecular weight of the insoluble fatty acids, 272.0. The liquid fatty acids constitute 56.2%, and the solid ones 43.8%, of the whole.

The oil has slight drying properties, and is similar in all its characters to the oils of other cucurbitaceous seeds.

The colour reactions of the oil are given.

T. H. P.

A Simple Method for Detecting Benzoic Acid in Cranberries. ANTON NESTLER (*Ber. deut. bot. Ges.*, 1909, 27, 63—70).—The amount of benzoic acid in cranberries (*Vaccinium vitis idaea*) is surprisingly large, in view of the fact that it acts as a preservative,

and has been estimated at 0.05 to 0.08% in the fresh berry and 0.45% in the dried. The dried berries are placed in a covered watch-glass and warmed with a small flame; free benzoic acid sublimes, condenses on the cover, and may be recognised by its appearance under the microscope and its behaviour towards sodium hydroxide followed by hydrochloric acid. The method is so sensitive that even a single berry, which would contain about 0.0001 gram of benzoic acid, gives a distinct reaction. Larger quantities of benzoic acid are readily obtained by extracting a number of berries with ether, evaporating the extract, and subliming the residue.

Benzoic acid was found in all parts of the fruit and in the seeds, but not in the leaves or stalks. *Vaccinium oxycoccus* also contained benzoic acid, although in smaller quantity than *V. vitis idaea*. *V. myrtillus* (bilberry) and *V. uliginosum* contained none. E. J. R.

Stachyose from White Jasmine. J. VINTILESCO (*J. Pharm. Chim.*, 1909, [vi], 29, 336—339).—From the twigs of white jasmine a sugar has been isolated, the properties of which point to its being identical with Tanret's stachyose, $C_{24}H_{42}O_{21}$; a direct comparison of the two sugars confirms the correctness of the supposition. C. S.

The Constants of Jasmine Flower Wax. LIONEL G. RADCLIFFE and J. ALLEN (*J. Soc. Chem. Ind.*, 1909, 28, 227).—Jasmine flower wax is obtained by extracting the petals with light petroleum of low b. p. and then macerating the crude wax obtained with alcohol so as to extract the odoriferous matters. After drying, a specimen of the wax gave the following constants: solidifying point, 56—57°; refraction in Zeiss's butyrometer, 30 at 84°, 33 at 74°, 36 at 70°, 38 at 65°, 40 at 62°, 42 at 60°, 44 at 56°; acid value, 0.28; saponification value, 6.58; the saponification had to be carried out in the presence of amyl alcohol. Iodine value by Wys's method, 52—53°.

The fatty acids after having been freed from unsaponifiable matter by repeated treatment with light petroleum in the presence of an alkali show a mean mol. weight of 398 and an iodine value of 39%. The mixed fatty acids when crystallised from boiling alcohol melt between 57° and 65°.

The unsaponifiable matter when crystallised from ether melts sharply at 64°. It probably contains alcohols, but it has not yet been successfully investigated. L. DE K.

"Oleuropein" from Olive Leaves. FREDERICK B. POWER and FRANK TUTIN (*Pharm. J.*, 1908, iv, 27, 714—715. Compare Abstr., 1908, i, 994).—Bourquelot and Vintilescu are wrong in supposing that the authors had not given proof of the existence of a glucoside in olive bark (*Trans.*, 1908, 93, 891). The "oleuropein" obtained from olive leaves by Bourquelot and Vintilescu is not homogeneous and is not a chemical individual. G. B.

Fruit of *Viburnum nudum*. ROBERT H. LOTT (*Chem News*, 1909, 99, 169).—The fruit of this shrub was gathered about the end

of August, 1907, in the swampy district around Sylvan Beach, New York. An alcoholic extract of the berries reacted acid towards litmus, and when freed from alcohol by distillation left a dark thick syrup and a blue, resinous, gummy substance. The amount of sugar found present in the sugar extract was 42.85%, and probably consisted of dextrose and lævulose. An average of four estimations gave 4.3% of ash, the composition of which was :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	SO ₃ .	P ₂ O ₅ .
2.11	3.88	3.88	7.66	1.87	12.87	16.79	27.14	12.89

The dried berries from the sugar extraction were digested with ether and the ethereal extract treated with bone charcoal, when an amber-coloured oil was obtained, having D 0.9353, b. p. 82°, and an odour resembling olive oil. Saponification results indicate that this oil is one of the oleins in the same group as castor oil and olive oil; the acids separated were probably oleic and linoleic. Albumin containing sulphur was also present, and tests for acids made on the sugar extraction showed the presence of tartaric acid, a small quantity of malic acid, and larger quantities of citric acid. J. V. E.

Composition of Volcanic Soil from Java. JAKOB M. VAN BEMMELEN (*Chem. Weekblad.*, 1909, 6, 199—215, 254).—The author gives the results of analyses of a number of samples of volcanic soil from Java. A. J. W.

Nitrification of Soils in situ. ISIDORE POUGET and GUIRAUD (*Compt. rend.*, 1909, 148, 725—727).—Determinations were made of the amount of nitrates present in two uncultivated and uncropped plots at the School of Agriculture, Maison-Carrée, Algeria. A colorimetric method was used. During the wet months (January to April) the soil is almost depleted of nitrates, but nitrification does not at once begin when drier, warmer weather sets in. Throughout May, very little nitrate was found. Later on, the authors consider that denitrification takes place. E. J. R.

Production of Nitric Acid in Humus and Peat Soils. FR. WEIS (*Bied. Zentr.*, 1909, 38, 145—148; from *Forstl. Forsögsväsk*, 1908, 257—296).—Results of monthly determinations of nitrates in two typical Danish humus soils from beech woods, free from calcium carbonate, showed (with one exception in July) that nitrates were invariably present, sometimes in considerable quantity. The greatest amounts of nitrates were found in the coldest months (November to February). The comparatively low results obtained in the warmer months are probably attributed to the absence of sufficient moisture for nitrification, or to the nitrates being to a great extent taken up by the trees. N. H. J. M.

Soil Fatigue. OSWALD SCHREINER and M. X. SULLIVAN (*J. Biol. Chem.*, 1900, 6, 39—50).—The fatigue of soils, due to the growth of one kind of crop, is not altogether due to using up of ash constituents. The present experiments with the cow-pea show that organic substances

are produced which cause infertility; one of these toxic materials was crystallised out. W. D. H.

The Action of Iron on Wine. J. AUGUSTE TRILLAT (*Compt. rend.*, 1909, 148, 792—795).—Iron, whether in the metallic state or in the form of certain salts, has an injurious effect on wine, causing a deposition of the colouring matter and the production of an odour and taste resembling that produced by age. The author has already shown that acetaldehyde is formed in red wine, and he finds that the effect of iron is simply to hasten this action and cause it to go on to a much greater extent. Acetal or ethyl acetate are formed at the same time. The deposit of colouring matter is brought about by the aldehyde. Other factors, such as the amount of air present and the composition of the wine, also influence the reaction, but in the main it appears that iron simply accelerates the processes naturally taking place, and thus brings about an artificial “ageing” of the wine. The processes are, however, sufficiently distorted to spoil the wine.

E. J. R.

Effect of Mineral Manures on Certain Cyperaceae. J. B. GÈZE (*Compt. rend.*, 1909, 148, 727—730).—The experiments show that nitrogenous manures increased the yield of *Carex riparia* and *C. stricta*. Phosphates and potassium had no decided influence. E. J. R.

Feeding Value of Cereals as Calculated from Chemical Analyses. JOSEPH S. CHAMBERLAIN (*U.S. Dept. Agric., Bureau Chem. Bul.* 120, 1909).—Cereal grains may be divided into three groups, represented by (1) oats, as a typical muscle or energy producing food, (2) wheat, and (3) maize as a fat or heat producing food. The oats group includes emmer (*Triticum dicoccum*) and einkorn (*T. monococcum*), which are nearly equal to oats in food value, whilst the maize group includes broom-corn millet (*Panicum miliaceum*) and the non-saccharine sorghum (*Andropogon sorghum*), which are lower in food value than maize itself, but equal the oat group. The wheat group, including barley and rye, which are nearly equal to wheat in food value, is intermediate between the oats and maize groups.

The introduction of foreign varieties of cereals into the United States has resulted in increased amounts of protein in oats and barley.

Detailed analytical and calculated results are given.

N. H. J. M.

Nitrogen Compounds in Rain and Snow. FRANK T. SHUTT (*Trans. Roy. Soc. Canada*, 1909, [iii], 2, Sect. III., 181—185. Compare Abstr., 1908, ii, 422).—Analyses of rain and snow during the year March, 1907, to February, 1908. The average results for the year are as follows:

Rainfall, inches.	Nitrogen per million.			Nitrogen per acre (lbs.).			Total.
	As ammonia.	As nitrates.	Albu- minoid.	As ammonia.	As nitrates.	Albu- minoid.	
37.35	0.296	0.134	0.082	2.502	1.134	0.692	4.328

The percentages of nitrogen as ammonia and as nitrates in the total nitrogen (excluding organic N) were 68·8 and 31·2 respectively.

The actual amount of rain was 24·05 inches, the rest, 13·3 inches, being snow (equivalent to 133 inches), and it is estimated that about 75% of the total nitrogen was supplied by the rain and 25% by snow.

Separate analyses of rain (46) and of snow (32) showed that both contain about the same amount of nitrogen as nitrates and nitrites, whilst the rain was found to contain nearly twice as much ammonia, and three times as much albuminoid ammonia as snow.

Results were obtained indicating that snow has a slighter solvent or absorbent action than rain. A fall of snow, 8·75 inches (=0·875 inch of rain), early on December 30 contained 0·09, 0·115, and 0·086 per million of nitrogen as ammonia, as nitrates, and as organic matter respectively. This was followed shortly afterwards, 10·30 a.m., by 0·15 inch of rain containing 0·238, 0·582, and 0·271 per million of nitrogen in the respective forms.
N. H. J. M.

Nitric Acid and Agriculture. L. GRANDEAU (*Bied. Zentr.*, 1909, 38, 148—150; from *Ann. sci. agron.*, 1906, II, 256—277).—Experiments with various crops grown in plots of five are, without manure, with minerals alone, and with minerals and nitrogen respectively. The soil was a poor sand containing N, 0·005; P_2O_5 , 0·063; K_2O , 0·173, and $CaO + MgO$, 0·180%. The average yields during eight years were 10,500 kilos, without manure, 11,840 kilos, with minerals only, and 17,700 kilos. per hectare with nitrogenous and mineral manure; so that whilst minerals alone gave an increase of only 11·3%, minerals in conjunction with nitrogen increased the yield 40·1%.

In an experiment with potatoes manured with calcium and sodium nitrates, it was found that whilst sodium nitrate more than doubled the yield, the calcium salts produced a still greater increase.

N. H. J. M.

Can Calcium Cyanamide with a large Amount of Calcium Carbide Act Injuriously on Vegetation? HJALMAR VON FEILITZEN (*Deut. landw. Presse*, 1909, 36, 327. Compare Aeby, *Chem. Zeit.*, 1909, 145, and Haselhoff, *Landw. Versuchs-Stat.*, 1908, 68, 189).—Pot experiments, in which oats were grown in sand, showed that only about half or two-thirds of the seeds produced plants when Norwegian cyanamide, containing 5·5% of carbide, and Swedish cyanamide, containing 0·1%, were applied at the same time. When the two preparations of calcium cyanamide were applied fourteen days before sowing the seed, no injurious action was observed. Even considerable amounts of unchanged calcium carbide are therefore harmless, provided that the manure is applied in good time.
N. H. J. M.

Analytical Chemistry.

Substitute for Forceps and for Triangles in Desiccators: Article for General Laboratory Use. C. W. EASLEY (*J. Amer. Chem. Soc.*, 1909, 31, 463—464).—A crucible holder is described which consists of a brass ring and handle, and enables the crucible to be readily removed from the desiccator without employing forceps or taking off the lid of the crucible. Three adjustable brass screws, 120° apart, pass through the ring near the lower edge; the top of each screw is bored, and a short piece of platinum wire, 1 mm. in diameter, is inserted; it is on these that the crucible rests. The holder can also be used as a substitute for the platinum triangle. E. G.

New Forms of Percolating and Extraction Apparatus. KARL VON DER HEIDE (*Zeitsch. Nahr. Genussm.*, 1909, 17, 315—320).—In the first apparatus described, the solution to be extracted by percolation is placed in a wide tube, the lower end of which is drawn out and fits into the neck of the boiling flask. The ether vapour coming from the latter passes up a side-tube, reaching nearly to the top of the apparatus, and then downwards through a tube surrounding the side-tube and entering the bottom of the tube containing the solution. The ether vapour bubbles through the solution, and the condensed ether flows back again into the flask through a central tube reaching downwards below the surface of the solvent in the flask. A spiral condenser which fits into the apparatus is also described. In another form of the apparatus, the ether vapour passes up into a condenser, and the ether then falls through a central tube to the bottom of the wide tube containing the solution to be extracted. Perforated inverted cups fitted round the outside of the central tube cause the ether to mix with the solution, and a side-tube allows the ether to flow from the top of the apparatus back into the flask. A modified form of this apparatus is described, which may be used with either ether or chloroform as the solvent. A modified Soxhlet apparatus shown consists of the ordinary wide tube for containing the cartridge; this tube is surrounded by another tube, and the syphon is arranged in the space between the two. The ether vapour also passes up this space and enters the inner tube through a series of holes at the top of the inner tube. W. P. S.

Munroe Crucible. WALTER O. SNELLING (*J. Amer. Chem. Soc.*, 1909, 31, 456—461).—Munroe (Abstr., 1888, 1333) has recommended a crucible of the Gooch pattern, in which the asbestos filtering medium is replaced by platinum felt. As this crucible possesses many advantages and is not yet generally known, the methods of preparing the felt and using the crucible are again described. E. G.

A System of Qualitative Analysis for the Common Elements. [IV.] **Analysis of the Alkaline Earths and Alkali Groups.** WILLIAM C. BRAY (*Tech. Quart.*, 1908, 21, 450—489. Compare Abstr., 1908, ii, 538).—The barium, calcium, strontium, and

also the magnesium are precipitated jointly as carbonates by adding an excess of ammonia and ammonium carbonate and some alcohol. The filtrate is evaporated to dryness, and the residue heated to expel ammonium salts. After dissolving in a little water, one-third of the solution is mixed with sodium hydroxide and phosphate, also with some alcohol, which causes a precipitate of lithium phosphate. The filtrate is then tested for potassium with sodium cobaltinitrite. The remainder of the solution is evaporated with hydrofluoric acid to remove any lithium as fluoride, and sodium is then tested for with potassium metantimoniate.

The carbonates are dissolved in acetic acid, and the barium is precipitated with potassium chromate. The strontium is then also precipitated as chromate by adding ammonia and some alcohol, and to the filtrate ammonium oxalate is added to remove the calcium. Finally, the magnesium is precipitated with ammonia and sodium hydrogen phosphate.

For minute details, and a large number of interesting test experiments, the original article should be consulted. L. DE K.

Estimation of Acids Contained in Hydrogen Peroxide. HERMANN ENDEMANN (*Zeitsch. angew. Chem.*, 1909, 22, 673—674).—The author states that when titrating commercial hydrogen peroxide with standard alkali and phenolphthalein in the cold, only half of the acidity present is found, so, consequently, the result must be multiplied by two. Better results are obtained by adding to 50 c.c. of the sample 10—15 c.c. of *N*/5-sodium hydroxide and heating until no more oxygen is evolved; this may be much accelerated by adding some pieces of platinum wire. When cold, the excess of alkali is titrated with *N*/5-hydrochloric acid.

A qualitative analysis will reveal the nature of the acid impurity.

L. DE K.

Application of Urine to the Detection of Oxidising Substances. JUAN FAGES VIRGILI (*Anal. Fis. Quim.*, 1908, 6, 519—523; *Ann. Chim. anal.*, 1909, 14, 129—132).—The following procedure is recommended as a test for minute traces of certain oxidising agents. To a small quantity of the substance in a test-tube (a fragment to 1 gram, if solid, or a drop to 1 c.c., if liquid), 1 c.c. of urine is added, and four times the volume of hydrochloric acid, *D* 1.12; on mixing, a purple coloration appears more or less rapidly, depending on the nature and amount of the oxidising agent present. As traces of ferric chloride (or chlorine) are often present in hydrochloric acid in sufficient quantity to produce a faint purple coloration, even when other oxidising substances are not present, the test should always be made by comparison with a blank, using urine and hydrochloric acid alone. Relatively large quantities of oxidising agents either do not produce the purple coloration, or it is fugitive, giving place to a clear yellow colour; the purple substance is easily oxidised to higher oxidation products.

By means of the test, 0.000003 gram of potassium chlorate can be detected, and about the same weight of hydrogen peroxide. It is

more delicate than the method based on the use of aniline hydrochloride (this vol., ii, 179), with which it may be advantageously combined as a means of detecting either very small or larger quantities of oxidising substances as follows. To the solution prepared for the test as above, 4 volumes of the hydrochloric solution of aniline hydrochloride are added. Traces of an oxidising agent produce a purple colour, larger quantities a blue or green coloration, following the purple.

The urine test responds to the oxidising compounds to which aniline hydrochloride is sensitive (*loc. cit.*), and, in addition, to traces of bromine, nitrites, nitrates, free nitric acid, ferric chloride, and molybdates (slowly). Bromides, which hinder the aniline test, do not affect the urine test, but iodides must not be present in either case.

W. A. D.

Detection and Estimation of Chlorates in Urine. JUAN FAGES VIRGILI (*Anal. Fis. Quim.*, 1909, 7, 56—63).—The facts recorded in two previous papers (this vol., ii, 179, and preceding abstract) are applied to the detection and estimation of chlorates in urine.

Detection.—To 1 c.c. of urine, 4 c.c. of the solution *A* or *B* of aniline hydrochloride are added. If chlorates are absent, no change of colour occurs, but minute traces of a chlorate produce a purple colour, due to the action of the chlorate and hydrochloric acid on the chromogenic substances present in the urine; when a chlorate is present in larger proportion, the purple colour, if produced at first, is soon destroyed by the excess of chlorate, but in this case the aniline hydrochloride betrays the presence of this excess by producing a characteristic blue coloration. When the proportion of chlorate in a urine is very small, the test for chlorate can be carried out by adding hydrochloric acid (4 vols.) to the urine, when the purple coloration is developed, changing to yellow if more than a trace of chlorate be present. The colour test is not available in the presence of the oxidising compounds enumerated in the previous papers.

Estimation.—This is effected colorimetrically by a method analogous to that already described (*loc. cit.*). One c.c. of urine (suitably diluted if necessary), containing not more than 0.0025 gram or less than 0.0020 gram of chlorate, is mixed with 5 c.c. of water, and 25 c.c. of solution *A* or 20 c.c. of solution *B* added. The colour is compared (after twenty minutes in the case of *A* or ten minutes in the case of *B*) with that of a series of solutions freshly prepared by mixing 1 c.c. of urine free from chlorate with 5, 4.75, 4.5, 4.25, and 4 c.c. of a solution of 0.5 gram potassium chlorate per litre, in each case diluting exactly to 6 c.c., and adding 25 c.c. of solution *A* (or 20 c.c. of *B*). The results obtained are very good.

Another method suitable for very small quantities of chlorate (0.1 to 0.5 gram KClO_3 per litre) consists in adding sufficient of the dilute standard solution of potassium chlorate to make the coloration equal in intensity to that given by a urine containing a known proportion of chlorate; the quantity of chlorate originally present is then obtained by difference.

W. A. D.

The Reduction and Estimation of Perchlorates. VICTOR ROTHMUND (*Zeitsch. anorg. Chem.*, 1909, 62, 108—113).—Perchlorates are not reduced by the ordinary reducing agents, or by electrolytic means. Reduction has been performed by Tommasi (*Ber.*, 1879, 12, 1701) with hyposulphites, and by Sjollesma (Abstr., 1905, ii, 21) with ferrous hydroxide, but neither of these methods gives accurate quantitative results. A practically complete reduction is obtained by using titanous sulphate, about twice the theoretical quantity of which is boiled with the perchlorate solution in a current of carbon dioxide. The excess of titanous sulphate is then removed by means of permanganate, and the chlorine titrated by Volhard's method. The titanous salt remaining may also be titrated with ferric alum (Knecht, Abstr., 1908, ii, 627), but this method is less convenient, as it requires the complete exclusion of air.

Nitrates, if present, must first be removed, for instance, by electrolytic reduction. In addition to titanium salts, the lower salts of vanadium and molybdenum reduce perchromates, tungsten salts act much more slowly, and chromous salts only to a minute extent after many hours' boiling.

The difference between reducing agents in this respect is entirely one of specific velocity, and not of potential; thus in the series zinc-chromium-vanadium-titanium, the first two ions, with a high reduction potential, are the least active, whilst titanium, the potential of which lies below that of hydrogen, acts most rapidly. The reaction furnishes an additional example of a reduction process accelerated by the presence of metals capable of existing in more than one state of oxidation.
C. H. D.

Acidimetric Estimation of Alkali Iodides. ERWIN RUPP and F. PFENNING (*Arch. Pharm.*, 1909, 247, 108—110).—A method of estimating alkali iodides has been devised, based on the reactions: $2\text{Hg}(\text{CN})_2 + 2\text{KI} = \text{Hg}(\text{CN})_2, \text{HgI}_2, 2\text{KCN}$; $\text{Hg}(\text{CN})_2, \text{HgI}_2, 2\text{KCN} + 2\text{HCl} = \text{Hg}(\text{CN})_2 + 2\text{KCl} + \text{HgI}_2 + 2\text{HCN}$ (compare Rupp and Goy, this vol., i, 295).

The estimation is performed as follows: the neutral solution of 0.5—1.5 grams of the iodide is added to a solution of 1—2 grams of mercuric cyanide in 30—50 c.c. of water, together with a small quantity of potassium chloride and 25 c.c. of *N*/2-hydrochloric or sulphuric acid. The total volume is made up to 100 c.c., filtered, and the excess of acid in 50 c.c. of the filtrate ascertained by means of standard alkali, using methyl-orange as indicator: 1 c.c. of *N*/2-acid = 0.0635 gram of iodion.

W. H. G.

Apparatus for Estimating Oxygen in Peroxides. GEORGE F. JAUBERT (*Rev. gen. Chim. pure app.*, 1909, 12, 63—67).—The peroxide is weighed or measured into a conical flask, furnished with a side-tube or appendix, into which manganese dioxide has been previously introduced. A little water is added together with the peroxide. The flask is closed by a perforated stopper, through which passes a glass tube which can be joined by means of stout indiarubber tubing to a calibrated, cylindrical gas-holder standing in a cylinder of water. At

the commencement of the experiment, the water within and without the gas-holder is at the same level, which is indicated by zero on the gas-holder. This vessel and the flask are now joined by means of the indiarubber tubing, and the manganese dioxide is rinsed, by means of the water first added, into the body of the flask with the peroxide which it decomposes, and the liberated oxygen displaces some of the water in the gas-holder. When the water levels are again adjusted, the reading on the graduated gas-holder indicates the volume of active oxygen evolved from the peroxide.

F. M. G. M.

Estimation of Sulphur in Coals and Cokes. MAX DENNSTEDT (*Zeitsch. angew. Chem.*, 1909, 22, 677—678).—A reply to Holliger's criticisms (this vol., ii, 343). The author upholds the accuracy of his own process.

L. DE K.

Estimation of Sulphuric Acid as Barium Sulphate. ERNST RUPPIN (*Chem. Zeit.*, 1909, 33, 398. Compare this vol., ii, 180).—The author attributes the discrepancy between the results obtained by Sacher (this vol., ii, 344) and by Folin (*Abstr.*, 1906, ii, 123) to the fact that, although the solubility of barium sulphate in cold water is 2.5 mg. per litre, this solubility becomes less in presence of barium chloride, but in the hot washings it dissolves to a slightly larger extent. The solubility is increased also by several chlorides (alkalis, alkaline earths).

L. DE K.

Quantitative Separation of Sulphates and Fluorides. RICHARD EHRENFELD and A. INDRA (*Chem. Zeit.*, 1909, 33, 375—376).—The mixed sodium fluoride and sulphate is heated in a Rose's crucible with ten times its weight of zinc dust for half an hour over a powerful burner in a current of hydrogen or purified coal gas. After cooling in the reducing gas, the crucible is at once placed in a suitable distilling apparatus, a little precipitated silica and alumina are added, and the sulphide formed is decomposed by heating with dilute sulphuric acid in a current of carbon dioxide. The hydrogen sulphide is absorbed in a ten-bulb tube containing standard iodine, and to guard against loss of iodine another bulb tube is attached containing standard thiosulphate, which is afterwards united with the iodine solution. The excess of thiosulphate is then titrated with iodine.

L. DE K.

Mitscherlich's Method for Estimating Very Small Quantities of Nitrogen. D. J. HISSINK (*Chem. Weekblad*, 1909, 6, 229—231. Compare Ringer and Klingen, *Abstr.*, 1908, ii, 320).—A method for estimating small quantities of nitrogen is described. It is accurate to ± 0.01 mg. of nitrogen. 250—800 c.c. of the liquid are placed in a litre flask, 3 grams of Devarda's alloy added, and the flask closed with a Hugershoff's delivery tube, the open end of which dips into a solution of 10 c.c. of *N*-sulphuric acid in 50 c.c. of water contained in a $\frac{1}{2}$ -litre flask. The liquid in the first flask is heated with 50 c.c. of concentrated sodium hydroxide until distillation is complete, the nitrogen from the ammonia, nitrates, and nitrites passing over as ammonia, and the organic nitrogen remaining behind. The organic nitrogen is

heated with a mixture of 50 c.c. of water and 60 c.c. of concentrated sulphuric acid, the reaction being complete thirty minutes after foaming has ceased. After mixing, the contents of the two flasks are distilled with 120 c.c. of concentrated sodium hydroxide into a mixture of 10 or 25 c.c. of *N*/50-sulphuric acid with 50 c.c. of water. The distillate is titrated back with *N*/50-sodium hydroxide, with a 1/10% solution of Congo-red in 50% alcohol as indicator. A. J. W.

Estimation of Total Nitrogen by Mitscherlich's Method. E. MERRES (*Zeitsch. angew. Chem.*, 1909, 22, 631—632).—The process, which is intended for small quantities of nitrogen, is briefly as follows. The substance is heated in a Kjeldahl flask, fitted with a Hegershoff cooling arrangement, with 200 c.c. of water and 50 c.c. of aqueous sodium hydroxide and a few grams of Devarda's alloy. The nitric nitrogen is converted into ammonia, and this, together with some ammonia derived from organic matter, is absorbed in a second Kjeldahl flask containing 100 c.c. of pure sulphuric acid, D 1.6. When some 50 c.c. are left, the flask is allowed to cool, when the sulphuric acid will be drawn into the flask. The operation of boiling and cooling is repeated three times. The contents are then boiled until the liquid assumes a bluish-green colour, showing the complete destruction of the organic matter, and consequent conversion of the organic nitrogen into ammonia. When cold, the mass is dissolved in water, the liquid is distilled with excess of alkali, and the ammonia titrated in the usual manner. Silica condensing tubes are recommended. L. DE K.

Method for the Estimation of Nitrogen in Organic Substances, and, in particular, for the Estimation of Hide Substance in Leathers and of Dissolved Hide Substance in the Soak Liquors and Lime Liquors of the Leather Factory. HUGH GARNER BENNETT (*J. Soc. Chem. Ind.* 1909, 28, 291—292).—In the method proposed, the organic matter is decomposed with sulphuric acid as in the ordinary Kjeldahl process, and the ammonia formed is titrated after the addition of formaldehyde, as described by Ronchèse (*Abstr.*, 1907, ii, 651). The substance is digested with sulphuric acid until a colourless solution is obtained, and the excess of acid is then neutralised by the addition of sodium hydroxide, using phenolphthalein as indicator. Neutral formaldehyde solution is next added, and the sulphuric acid, set free by the combination of the aldehyde with the ammonia, is titrated with *N*/10-sodium hydroxide solution. Each c.c. of *N*/10-sodium hydroxide is equivalent to 0.0014 gram of nitrogen. W. P. S.

Estimation of Nitrates by Grandval and Lajoux's Method. MAURICE LOMBARD and J. LAFORE (*Bull. Soc. chim.*, 1909, [iv], 5, 321—323).—The estimation depends on the formation of coloured derivatives of phenol by the action of free nitric acid. The product is not picric acid or a picrate. Lajoux noted that his method is not accurate in presence of chlorides. As the quantity of chloride increases, the coloration decreases. The authors consider that some nitric acid

is carried away by the hydrogen chloride evolved, and reject the theory of Perrier and Farcy (this vol., ii, 344), that hydrogen chloride attacks the nitrophenols produced.
R. J. C.

Estimation of Phosphoric Acid in Manures by Pemberton's Modified Process and by von Lorentz's Method. D. J. HISSINK (*Chem. Weekblad*, 1909, 6, 181—191).—A series of experiments showing that the results obtained by the author's modification of Pemberton's process (titration of the molybdate precipitate, *Abstr.*, 1905, ii, 419) and by von Lorentz's gravimetric process (direct weighing of the yellow precipitate) are both equally satisfactory.
L. DE K.

Volumetric Estimation of Small Quantities of Arsenic. LAUNCELOT W. ANDREWS and HENRY V. FARR (*Zeitsch. anorg. Chem.*, 1909, 62, 123—128).—Arsenic is best estimated, when present in more than traces, by a modification of Bettendorff's method (*Zeitsch. anal. Chem.*, 1869, 9, 105). The carrying down of tin in that process is prevented by the addition of tartaric acid.

The solution containing arsenic is neutralised, evaporated to 15—20 c.c., and transferred to a flask of 80—100 c.c. capacity with ground-in stopper. Forty to fifty c.c. of a solution, prepared by dissolving 20 grams of crystallised stannous chloride and 40 grams of tartaric acid in 1 litre 40% hydrochloric acid, is added. The stopper is inserted, and the flask kept in a warm place until all the arsenic is precipitated. This requires two to three hours at 40°. The arsenic is collected on an asbestos filter, and washed first with a little hydrochloric acid, which must be free from chlorine, and then with water. The filter is then transferred to the flask with an excess of *N*/10- or *N*/100-iodine solution, calculated from the equation $\text{As} + 5\text{I} + 7\text{NaHCO}_3 = \text{Na}_2\text{HAsO}_4 + 5\text{NaI} + 7\text{CO}_2 + 3\text{H}_2\text{O}$, sodium hydrogen carbonate being added to maintain neutrality. When all is dissolved, the excess of iodine is titrated with arsenite solution. A number of test analyses are given. The method may be applied to arsenic mirrors obtained by the Marsh process.
C. H. D.

Micro-sublimation Test for Arsenic Trioxide. C. HARTWICH and F. TOGGENBURG (*Chem. Zentr.*, 1909, i, 580; from *Schweiz. Woch. Chem. Pharm.*, 1908, 46, 831—834).—A glass tube of about 12 mm. diameter and 10 mm. in height is placed on a watch-glass. Into the tube is introduced the arsenical substance. The watch-glass is placed over a micro-burner, and the cylinder is covered with a plate of glass 50 mm. square. The flame should not exceed 5 mm. in height, and should be at 30—40 mm. distance from the watch-glass. After heating for ten to fifteen minutes, the whole is allowed to cool slowly, and the glass slide is then examined; even 0.01 mg. of arsenic trioxide gives a visible sublimate. The sublimate may be further identified by the silver reaction.

L. DE K.

New Apparatus for the Estimation of Carbon. A. KLEINE (*Chem. Zeit.*, 1909, 33, 376).—*Carbon Flasks.*—These are distinguished
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from the well-known Corleis flasks, not only by a superior cooling arrangement, but also by having a flat bottom and no lateral tube. Above the orifice of the air-tube is introduced a hole, which prevents an explosion in case of an obstruction occurring. To the air-tube is fixed a hook with an elevation in the middle. The long wire of the little bucket containing the substance is pushed over the elevation, the bucket is suspended to the point of the hook, and the cooling arrangement is inserted. After passing a current of purified air, the apparatus is slightly shaken and inclined, thus causing the bucket to slide from the point of the hook and empty its contents into the chromic acid mixture; it, of course, remains suspended to the long wire, and is readily removed from the flask.

Soda-lime Tubes.—These differ from the ordinary pattern in so far that into the middle of the left arm is inserted a glass disk containing three tubes, on which rests the asbestos, which is then covered with a layer of phosphoric anhydride. The other part of the tube is filled with soda-lime. The advantage of this arrangement is that no liquefied acid can come into contact with the soda-lime. L. DE K.

Examination of Carbon Tetrachloride. LIONEL G. RADCLIFFE (*J. Soc. Chem. Ind.*, 1909, 28, 229—230).—After trying experiments to estimate the amount of carbon disulphide in commercial carbon tetrachloride by fractional distillation, density, and refraction, the following slight modification of Gastine's method was found to give satisfactory results. A flask containing 25 c.c. of alcoholic potassium hydroxide, and loosely corked, is accurately weighed, about 1 c.c. of the sample is introduced, and the flask is re-weighed. After five minutes, the mixture is rendered slightly acid with dilute acetic acid, using phenolphthalein as indicator. Water is added and then an excess of solid sodium hydrogen carbonate, and the milky liquid is titrated with *N*/10 iodine, using starch as indicator. Two atoms of iodine = 1 mol. of carbon disulphide. L. DE K.

Estimation of Carbon Dioxide in the Atmosphere. SAMUEL H. DAVIES and BASIL G. McLELLAN (*J. Soc. Chem. Ind.*, 1909, 28, 232—234).—A modification of the Lunge-Zeckendorf process. Fresh air is forced through 25 c.c. of barium hydroxide solution, coloured with phenolphthalein of such strength that it will be decolorised by 15 strokes (being one over 14 actually required) of a pump delivering 50 c.c. per stroke. Having thus standardised the barium hydroxide, the apparatus may then be used for testing the air in rooms, etc.

A table is given showing the amount of carbon dioxide per 10,000 parts of air corresponding with the number of strokes (+ 1) required in the experiment. L. DE K.

Application of Alkaline Phosphate Solutions in Analysis. HERMANN GROSSMANN (*Chem. Zeit.*, 1909, 33, 385—386).—An adverse criticism of the analytical course for the separation of metals proposed by Pozzi-Escot (*Abstr.*, 1908, ii, 892). L. DE K.

The Iodometric Estimation of Silver, Potassium Chromate being Employed as Precipitating Agent. FRANK A. GOOCH and ROLAND S. BOSWORTH (*Zeitsch. anorg. Chem.*, 1909, 62, 74—76).—It

has been shown that silver is precipitated quantitatively by an excess of potassium chromate (this vol., ii, 346). The excess of potassium chromate remaining in the filtrate may be estimated by adding potassium iodide and sulphuric acid, and titrating the iodine set free with thiosulphate. Since a large excess of chromate is necessary when the silver is present as nitrate, more rapid results are obtained by dissolving the precipitate of silver chromate in ammonia, boiling to re-precipitate, and dissolving the washed crystalline chromate in a concentrated solution of potassium iodide, diluting, acidifying with sulphuric acid, and titrating with thiosulphate. C. H. D.

Assay of Commercial Magnesite. Estimation of Small Quantities of Calcium in Presence of much Magnesium. FRANZ HUNDESHAGEN (*Zeitsch. öffentl. Chem.*, 1909, 15, 85—93).—A criticism of the oxalate process, which the author asserts to be unsuitable for the estimation of calcium in magnesite. The following process is recommended: One gram of the mineral is ignited, the residue is dissolved in dilute hydrochloric acid, and the filtrate is evaporated to dryness on the water-bath to expel the excess of acid. The residue is then dissolved in 30 c.c. of water with addition of 4 grams of sodium sulphate crystals, and 40 c.c. of strong alcohol are added. After remaining for four to five hours (in the covered basin), the calcium is precipitated completely as sulphate, which is then washed with dilute alcohol. To free it completely from magnesium, etc., it is re-dissolved in hydrochloric acid and treated with ammonia and ammonium oxalate as usual.

The joint magnesium and calcium may be estimated by boiling 0.5 gram of the mineral with standard sulphuric acid and titrating the excess of acid with standard sodium carbonate. The calcium may then be precipitated as sulphate by adding a sufficiency of alcohol.

L. DE K.

Colour Test for Salts of Zinc. ANGEL DEL CAMPO (*Anal. Fis. Quim.*, 1909, 7, 63—69).—The production of a deep blue colour by the interaction of resorcinol and an ammoniacal solution of a zinc salt (Carobbio, *Abstr.*, 1906, ii, 809) serves as a means of detecting traces of zinc salts. To the ammoniacal solution containing zinc, 1 c.c. of a 0.5% ethereal solution of resorcinol is added, so as to form a separate layer; with quantities of zinc exceeding 0.0005 gram per c.c. of solution, a deep blue coloration develops at the junction of the two layers instantly or in a few minutes. The test serves to detect as small a quantity as 0.000005 gram of zinc per c.c., but in this case the coloration develops only after about an hour.

Cadmium salts produce a green colour instead of blue with resorcinol, and copper salts a black precipitate. Traces of zinc can be detected in presence of copper by one of the following methods: (a) The solution containing copper is decolorised by potassium cyanide, ammonia added, and then the ethereal solution of resorcinol. A blue coloration is produced only when traces of zinc are present; when the quantity of zinc is very small, the coloration is green. (b) Hydrochloric acid is added after the blue coloration has been formed on

adding the ethereal solution of resorcinol to an ammoniacal solution of the copper salt; if zinc is present, a red colour is developed and a red precipitate separates, which, when dissolved in amyl alcohol, develops an intense blue colour with ammonia. W. A. D.

Rapid Electro-analysis. H. FILIPPO, jun. (*Chem. Weekblad*, 1909, 6, 226—229. Compare Smith, Abstr., 1903, ii, 755; Kollock and Smith, Abstr., 1905, ii, 198, 859; 1906, ii, 194; 1907, ii, 719; Stoddard, this vol., ii, 347).—The author has devised a modification of Smith's method of rapid electro-analysis for estimating metals which has the advantage of allowing larger quantities of liquid to be manipulated. Thirty to sixty grams of distilled mercury are weighed out into a round-bottomed flask of moderate capacity. Through the bottom of the flask is sealed a platinum wire 0.5 mm. in diameter and 2 cm. long, the end of the wire being flush with the inside surface of the flask. The anode is a spiral of platinum wire, and its end is 1 cm. above the surface of the mercury cathode. A difference of potential of 6—10 volts and a current of 2—4 amperes are employed. The electrolysis requires twenty to seventy minutes, and has been applied to the estimation of mercury, silver, copper, and zinc. A. J. W.

Volumetric Estimation of Mercuric Salts. LAUNCELOT W. ANDREWS (*Zeitsch. anorg. Chem.*, 1909, 62, 171—172).—A reply to the criticisms of Morawitz (Abstr., 1908, ii, 185) of the author's method (Abstr., 1903, ii, 695). The proposed modification has no advantage over the original process. C. H. D.

Estimation of Clay in Soils. EMIL ARNTZ (*Landw. Versuchs-Stat.*, 1909, 70, 269—306).—The finely-ground soil (5 grams) is heated with 50 c.c. of water and 2 c.c. of hydrochloric acid (or more in the case of calcareous soils). The solution is filtered off, and the soil washed into a 300 c.c. beaker (12 cm. high and 6 cm. in diameter) and gently boiled for half an hour with 30 c.c. of 18—20% ammonia. When cold, water is added until it reaches a mark 11 cm. above the soil, and after twenty-four hours the liquid is removed by means of a pipette, turned up at the end, to within 1 cm. of the soil. The residue is rubbed with a little water, in a porcelain dish until the water remains clear, and both the residue and the decanted liquid are then boiled for fifteen minutes with 20 c.c. of ammonia. After cooling, water is added to the mark, the whole left for twenty-four hours, and removed as described above. The process is repeated three times, and the turbid liquid treated with ammonium chloride to precipitate the clay. The latter is added to the precipitate, containing iron and alumina from the first hydrochloric acid extract, washed, ignited, and weighed. The results obtained from soils containing 1—15, 15—30, and 30—50% of clay are divided by 0.99, 0.98, and 0.97 respectively.

When time permits, the washing process may be continued to the end, and, when necessary, the alumina can be determined in the product.

The method is considered sufficiently exact, and can be carried out in a relatively short time. N. H. J. M.

Estimation of Nickel in Nickel Steels by the Electrolytic Method and the Methods of Brunck and Grossmann. AUGUST PRETTNER (*Chem. Zeit.*, 1909, 33, 396, 411—412).—A full investigation as to the respective merits of the electrolytic process of estimating nickel in nickel steels and the processes recommended by Brunck (separation by means of dimethylglyoxime) and Grossmann (dicyanodiamidine sulphate reagent).

The author favours the Brunck or the Grossmann methods particularly when cobalt is present in some quantity, and where the direct cyanide titration process cannot be applied. L. DE K.

Volumetric Estimation of Uranium. HERBERT N. MCCOY and HERBERT H. BUNZEL (*J. Amer. Chem. Soc.*, 1909, 31, 367—373). See this vol., ii, 406.

Estimation of Vanadic and Arsenic Acids and of Vanadic and Antimonic Acids, when present together. GRAHAM EDGAR (*Zeitsch. anorg. Chem.*, 1909, 62, 77—80).—Arsenic and vanadium are commonly associated in minerals, and their quantitative separation presents difficulties. The following method permits the estimation of both metals without separation.

The solution, containing arsenic and vanadic acids, is divided into two parts. One part is boiled with tartaric or oxalic acid until the vanadium is completely reduced to the blue tetroxide. After cooling, and nearly neutralising with potassium hydrogen carbonate, an excess of iodine solution is added. After addition of an excess of potassium hydrogen carbonate, the solution is allowed to remain one-quarter to one-half hour, and the remaining iodine titrated with arsenious acid. The oxidation with iodine takes place according to the equation $V_2O_4 + I_2 + H_2O = V_2O_5 + 2HI$.

The second portion is heated with sulphurous acid in a pressure flask for one hour in a water-bath, so as to reduce both the arsenic and the vanadic acids. After boiling off the sulphur dioxide in a current of carbon dioxide, the solution is oxidised with iodine as described above: $As_2O_3 + V_2O_4 + 3I_2 + 3H_2O = As_2O_5 + V_2O_5 + 6HI$. The difference between the two results gives the arsenic.

The same method is applicable to solutions containing vanadic and antimonic acids. C. H. D.

Determination of the Heating and Illuminating Values of Gas. NICOLAE TECLU (*J. pr. Chem.*, 1909, [ii], 79, 165—171).—The method depends on the assumption that the force of an explosive mixture of gas and air is determined by the heating value of a gas. The apparatus consists of a litre flask provided with three openings, the upper fitted with a glass tube for igniting the gas, the lower for admission of air and gas, and a broad side-tube constricted at one end, on which rests loosely an aluminium cup of a pendulum. Gas is admitted to the apparatus and ignited at the upper tube, the supply is then cut off, the flame descends from the tube into the flask, where an explosion takes place, and an aliquot portion of the explosive wave is measured by the amplitude of the swing of the pendulum. A comparison of ordinary town gas and a mixture of hydrogen and marsh gas gave

a superiority in heating value to the town gas of from 0.36 to 9.6%. The time which the flame remains at the top of the tube depends on the density of the gas and therefore on its illuminating power. This has also been measured, and the illuminating value of gas examined found to be 26 to 29% better than the mixture of marsh gas and hydrogen. The duration of burning and amplitude of swing are in close relationship, the ratio of the two values being a constant.

W. R.

A Colour Reaction for Colophony. J. SANS (*Ann. Chim. anal.*, 1909, 14, 140—141).—A very small quantity of colophony is placed in a test-tube, 1 or 2 c.c. of neutral methyl sulphate are added, and the whole is heated gently. A coloration is noticed passing from rose and violet to deep violet; on heating more strongly, the colour fades to a slight brown. The test may serve for the detection of colophony in soaps; other resins and gum resins do not give the test provided the reagent contains no free sulphuric acid.

L. DE K.

Detection of Reducing Sugars. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1909, 5, 485—488).—The alkali of Fehling's solution has a destructive influence on dextrose and other carbohydrates. Sodium carbonate does not have this disadvantage. Rochelle salt is objectionable on account of the change it may undergo; it should be replaced by sodium citrate. The following test solution is therefore recommended:

Copper sulphate	17.3 grams
Sodium citrate	173.0 "
Sodium carbonate (anhydrous)	100.0 "
Water	to 1000.0 c.c.

This is more sensitive than Fehling's solution, and has none of its disadvantages.

W. D. H.

Titration of Diabetic Sugar. ERWIN RUPP and F. LEHMANN (*Chem. Zentr.*, 1909, i, 876; from *Apoth. Zeit.*, 24, 73—75).—Of urine, D 1023 or less, 50 c.c. are diluted to 100 c.c.; of urine, D 1023—1033, 25 c.c. are made up to 100 c.c., and of urine, above D 1033, 10 c.c. are taken. The urines, however, are at first diluted to about 85 c.c., 2—3 c.c. of basic lead acetate are added, and then 6—8 c.c. of sodium carbonate solution (1 + 4) to precipitate the excess of lead; water is then added up to 100 c.c. The titration is carried out as follows: 15 c.c. of Fehling's solution are heated to boiling, 20 c.c. of the filtrate of the urine are run in, the boiling is continued for two minutes, and the whole is cooled rapidly. The solution is then added to a solution of 2 grams of potassium iodide in 25 c.c. of dilute sulphuric acid, and the iodine liberated, which represents the excess of copper, is titrated with *N*/10-thiosulphate, using starch as indicator.

L. DE K.

Estimation of Reducing Substances in Blood. JOHN J. R. MACLEOD (*J. Biol. Chem.*, 1909, 5, 443—452).—The methods of Waymouth Reid and Schenck are compared. The latter gives lower

values for dog's blood than the former. This deficit is probably due to the mercuric chloride precipitating some reducing substances (glycuronic acid, jecorin, pentose (?), and combined dextrose) which are not precipitable by phosphotungstic acid. Reid's method is therefore recommended. W. D. H.

Glycogen Analyses by the Use of Dilute Potassium Hydroxide. BERNHARD SCHÖNDORFF, PETER JUNKERSDORF, and GEORG FRANCKE (*Pflüger's Archiv*, 1909, 127, 274—279).—Treatment of organs with dilute alkali for periods as long as seventy-two hours does not destroy their glycogen. Subsequent treatment with 30% potassium hydroxide gives a full yield of glycogen. W. D. H.

Estimation of Furfuroids in Presence of Pentosans. D. H. BRAUNS (*Pharm. Weekblad*, 1909, 46, 326—331).—The total percentage of pentosans, including furfuroids, in cocoa was found to vary between 1.6 and 0.06%, and that in the shell of cocoa-beans between 6.7 and 1.4%, hydrolysis being effected by heating with 2% sulphuric acid. The shell contains a cellulose-like substance, which is insoluble and either non-hydrolysable or difficult to hydrolyse. To this substance the name furfuroid has been given. A. J. W.

The Detection of Mineral Acids in Vinegar. FRANZ UTZ (*Oesterr. Chem. Zeit.*, 1908, [ii], 11, 321—328).—The author gives a résumé of the methods previously employed in detecting mineral acids in vinegar, and indicates the following process. About 10 c.c. of the vinegar is mixed with 4 to 5 grams of sucrose, and the latter inverted on the water-bath. The solution is extracted with ether, the extract evaporated, and the thoroughly dried residue treated with a few drops of a 10% solution of resorcinol in concentrated hydrochloric acid (D 1.19). A cherry-red coloration betokens the presence of small amounts of mineral acid in the original samples of vinegar. Large quantities lead to the development of a deep red coloration. In the absence of mineral acid the solution either remains colourless or develops merely a lemon-yellow tint. G. T. M.

Buignet's Method for the Estimation of Hydrocyanic Acid and the Titration of Cherry-Laurel Water; Correction and Modification. GABRIEL GUÉRIN and L. GONET (*J. Pharm. Chim.*, 1909, [vi], 29, 234—236).—Buignet's method for the estimation of hydrocyanic acid (*ibid.*, 1859, [iii], 35, 168), depending on titration with a standard solution of cupric sulphate in presence of ammonia, has become obsolete, owing to the difficulty of ascertaining the end-point, a rose colour changing gradually to mauve being obtained in place of the sky-blue tint due to excess of ammoniacal copper sulphate. This difficulty can be avoided by adding sodium sulphite to the liquid under titration. The equation representing the reaction as given by Buignet is inaccurate, and should be $\text{CuSO}_4 + 3\text{NH}_4\text{CN} = [\text{NH}_4]_2\text{SO}_4 + \text{Cu}(\text{CN})_2 + \text{NH}_4\text{CN}$. In titrating cherry-laurel water a small amount of sodium hydroxide should be added to prevent the formation of hydrobenzamide. T. A. H.

Partition-coefficient and its Application to the Estimation of Volatile Acids in Wines. PHILIPPE MALVEZIN (*Compt. rend.*, 1909, 148, 784—787; *Bull. Soc. chim.*, 1909, [iv], 5, 332—335; *Bull. Assoc. chim. suc. dist.*, 1909, 26, 848—851).—The author finds that the coefficient of distribution for the volatile aliphatic acids between the solvents ether and 10% alcohol varies with the concentration of the acids, but is independent of the concentration of the non-volatile acids. Taking advantage of this, he has devised a rapid and accurate method for estimating the amount of volatile acids in wines. The wine is extracted with ether, which under certain conditions, for which the original should be consulted, dissolves 72% of the volatile acids present. Results obtained by this method were practically identical with those arrived at by the method of Duclaux (*Abstr.*, 1896, ii, 504). W. O. W.

Estimation of Succinic Acid in Wine. KARL VON DER HEIDE and H. STEINER (*Zeitsch. Nahr. Genussm.*, 1909, 17, 291—307).—The authors have submitted the method described by Kunz (*Abstr.*, 1903, ii, 701) to a critical examination, and consider it to be, with certain slight modifications, the most trustworthy one for the estimation of succinic acid. The modified process is carried out as follows: Fifty c.c. of the wine are evaporated in a basin to remove the alcohol, and the residual solution is treated with 1 c.c. of 10% barium chloride solution. Finely powdered barium hydroxide is then added, in small quantities at a time, until the mixture is neutral, a drop of phenolphthalein solution being added as indicator. The whole is then evaporated to a volume of 20 c.c., carbon dioxide is passed over the surface of the residue in order to remove any excess of barium hydroxide, and 85 c.c. of 96% alcohol are added, with constant stirring. Barium succinate, tartrate, malate, and other salts are precipitated quantitatively, whilst barium acetate and lactate remain in solution. After the lapse of two hours, the supernatant liquid is poured through a filter, the precipitate is washed once with 80% alcohol, and then rinsed back again into the basin with hot water. The contents of the basin are heated on the water-bath to expel the alcohol, and to the hot mixture is added 5% potassium permanganate solution until a red coloration is obtained. After the lapse of five minutes, a further 5 c.c. of permanganate solution are added, and the mixture is placed aside for fifteen minutes. Should the permanganate be reduced completely at the end of this time, more must be added. The excess of permanganate is destroyed by the addition of sulphurous acid, the mixture is then acidified with 25% sulphuric acid, and a further quantity of sulphurous acid is added until the precipitated manganese dioxide has re-dissolved. After evaporating to a volume of about 30 c.c., the solution is treated with 40% sulphuric acid, so that it shall contain about 10% of free acid, and is then extracted with ether in a percolating apparatus for twelve hours. The ethereal solution is evaporated, the residue is neutralised by the addition of chlorine-free *N*/10-sodium hydroxide solution, 20 c.c. of *N*/10-silver nitrate solution are added, the whole is diluted to a volume of 100 c.c., and filtered. The excess of silver is then titrated

in a definite volume of the filtrate according to Volhard's process; 1 c.c. of $N/10$ -silver nitrate solution = 0.0059 gram of succinic acid.

W. P. S.

Estimation of Malic Acid in Wine. KARL VON DER HEIDE and H. STEINER (*Zeitsch. Nahr. Genussm.*, 1909, 17, 307—315).—In the method proposed, the malic and succinic acids are separated together after the tartaric, acetic, and lactic acids have been removed, and their quantity estimated from the alkalinity of the ash of their alkali salts. Fifty c.c. of the wine are treated with 1 c.c. of glacial acetic acid, 0.25 c.c. of 20% potassium acetate solution, 7.5 grams of potassium chloride, and 7.5 c.c. of 95% alcohol. The mixture is well stirred, and, after fifteen hours, the crystalline precipitate is collected on a filter and washed three times with a small quantity of a solution containing 15 grams of potassium chloride, 20 c.c. of 95% alcohol, and 100 c.c. of water. The filter and precipitate are then washed three times with water, using not more than 10 c.c. in all, and the filtrate and washings are evaporated to a volume of a few c.c. When most of the acetic acid has been expelled, the residue is dissolved in a little water, 5 c.c. of 10% barium chloride solution are added, and then powdered barium hydroxide until the mixture is neutral. Carbon dioxide is introduced to remove any excess of barium hydroxide, the whole is evaporated to a volume of 20 c.c., and 85 c.c. of 96% alcohol are added. After two hours, the precipitate is collected on a filter, washed with 80% alcohol, redissolved in hot water, and the solution evaporated almost to dryness. The moist residue is treated with from 2.5 to 3 c.c. of 40% sulphuric acid, and sufficient anhydrous sodium sulphate is added to form a dry powder, which is then transferred to a cartridge and extracted with ether for six hours. From 10 to 20 c.c. of water are added to the ethereal extract, the ether is evaporated, and the remaining aqueous solution is treated with 3 grams of animal charcoal, the mixture being kept on a water-bath for one hour. The solution is next filtered, the precipitate, consisting of tannin, charcoal, etc., is washed with hot water, the filtrate is neutralised exactly, and evaporated to dryness. The residue is then ignited, and the resulting carbonates titrated. From the quantity of acid required for the titration, the amount of malic acid may be calculated, the quantity of succinic acid having been estimated previously by the method described by the authors in the preceding abstract.

W. P. S.

Estimation of Some of the Organic Acids Occurring in Fruits. GUNNER JÖRGENSEN (*Zeitsch. Nahr. Genussm.*, 1909, 17, 396—412).—The author has submitted the process described previously (Abstr., 1907, ii, 312) to further examination, and has introduced certain modifications in the manipulation. The separation of the citric and malic acids from one another is best carried out by taking advantage of the different solubilities of their barium salts in 26% alcohol; barium malate is fairly soluble in alcohol of this strength, whilst barium citrate is but slightly soluble. Results of estimations of organic acids in wines are given, the figures agreeing, on the whole, with those published previously. Citric acid does not appear to be a natural constituent of pure grape wines. The flesh of the common

sloe (*Prunus communis*) was found to contain considerable quantities of malic acid, but tartaric and citric acids were absent. A small quantity of another acid, possibly succinic, was also present.

W. P. S.

Estimation of Calcium Citrate and of Lemon Juice. L. GADAIS and J. GADAIS (*Bull. Soc. chim.*, 1909, [iv], 5, 287—289).—Calcium citrate can be estimated by almost neutralising its solution in dilute hydrochloric acid with *N*-potassium hydroxide, adding a c.c. of saturated calcium chloride, and precipitating the calcium citrate by boiling; the precipitate is washed free from chloride, and the combined filtrate and washings are evaporated to about 15 c.c., whereby a second precipitate of calcium citrate is obtained. If necessary, the filtrate and washings are again concentrated and treated with alcohol to precipitate the last traces of calcium citrate. The combined precipitates are dried at 105° and ignited to the carbonate, which is dissolved in 30 c.c. of *N*-hydrochloric acid. After boiling to expel carbon dioxide, the excess of hydrochloric acid is titrated by *N*-potassium hydroxide.

Citric acid in lemon juice is estimated by diluting 120 c.c. to 1 litre; 25 c.c. are neutralised by *N*-potassium hydroxide, and 20 c.c. of saturated calcium chloride solution are added. The precipitation and estimation of the calcium citrate are then performed as above.

C. S.

Estimation of Uric Acid in Urine. A. VERDA (*Chem. Zentr.*, 1909, i, 794; from *Schweiz. Woch. Chem. Pharm.*, 1909, 47, 6—9).—A slight modification of the iodine process recommended by Ruhemann (*Abstr.*, 1902, ii, 435). In order to redissolve any uric acid which may have deposited, 50 c.c. of the sample are heated with addition of 1 gram of dry sodium acetate until a clear liquid has been obtained.

L. DE K.

Estimation of the Relative Amounts of the Organic Acids Occurring in Tobacco before and after Fermentation. JULIUS TÓTH (*Chem. Zeit.*, 1909, 33, 338—339).—A reply to Kissling's criticism (*ibid.*, 1908, 32, 717). The author upholds the accuracy of his process (*Abstr.*, 1908, ii, 238, 330). An exhaustive table is given showing the effect of fermentation on the amount of dry matter and the volatile and non-volatile organic acids present in tobacco. They are represented respectively as oxalic and acetic acids.

L. DE K.

Estimation of Soil Acidity. ROBERT ALBERT (*Zeitsch. angew. Chem.*, 1909, 22, 533—537).—The soil (20—50 grams) is boiled with a known amount of magnesia, lime, or baryta, and an excess of an ammonium salt (200 c.c. of 5% ammonium sulphate), and the ammonia liberated absorbed by *N*/10-acid and estimated, using sodium alizarin-sulphonate as indicator. The difference in the amounts of ammonia liberated by the alkaline earth alone and with the soil represents the acidity of the soil.

Determinations of acidity in several soils by the new method and by Tacke's method (*Süchting, Abstr.*, 1908, ii, 231) showed in most cases concordant results. In one case, however, a very much higher result

was obtained than by Tacke's method. This was with a soil which is supposed to contain inorganic acid compounds (acid silicates : compare Kozai, this vol., ii, 87).

With regard to quantitative tests for soil acidity, Baumann and Gully (*Naturwiss. Zeitsch. Forst.-Landw.*, 1908, 1) have shown that Schütze's ammonia test is uncertain, as although absence of colour indicates absence of acid, a brown coloration does not necessarily indicate that acid is present.

Acidity may be detected and the amount approximately ascertained by adding lithium phosphate to a little soil (3 grams) suspended in water in a test-tube. The mixture is frequently shaken, and then left for some days until the colour ceases to become darker. The method of Baumann and Gully (*loc. cit.*) is also recommended. In this method the soil (3 grams) is added to a solution of potassium iodide (2 grams) and iodate (0.1 gram) in 100 c.c. of water. After being repeatedly shaken during fifteen minutes, the solution is filtered, and approximately equal amounts added to dilute starch solution. The two methods gave quite similar indications, according with the estimations by the process described above.

N. H. J. M.

Modification of Halphen's Reaction. LÉON GARNIER (*J. Pharm. Chim.*, 1909, [vi], 29, 273—274).—In applying Halphen's reaction for the detection of cotton seed oil in edible oils, the author uses carbon disulphide containing 2% of powdered sulphur in place of 1%, as generally recommended, and the liquid is employed with any undissolved sulphur in suspension. For quantitative purposes, comparison of the depth of colour obtained in any one case is made with a set of standard colours given by oils containing known quantities of cotton seed oil.

T. A. H.

Colour Reaction of Fats. ERNEST SCHLUMBERGER (*Bull. Soc. ind. Mulhouse*, 1909, 79, 32—36).—When a concentrated aqueous solution of dextrose is added to a cooled mixture of equal parts of olive oil and sulphuric acid, and the preparation is then warmed to about 55° and stirred continuously, it becomes cherry-red in colour, then purple, and finally deep plum violet, or almost black, in thick layers. The coloration appears to be due to the action on oleic acid of furfuraldehyde formed by the action of sulphuric acid on the dextrose, and can be obtained by the direct action of furfuraldehyde on oleic acid in presence of sulphuric acid. Oils, such as castor oil, containing ricinoleic acid give a similar, but not identical, colour reaction.

T. A. H.

Saponifying Constituents of the Kola Nut. WILLEM P. H. VAN DEN DRIESSEN MAREEUW (*Pharm. Weekblad*, 1909, 46, 346—356).—Chiefly a review of the work of Mastbaum, the results of which are higher than those obtained by the author. This is attributed to a difference in the mode of drying the kola nut.

A. J. W.

Detection of Acetone in Urine by Lieben's Test. W. WEITBRECHT (*Chem. Zentr.*, 1909, i, 794; from *Schweiz. Woch. Chem. Pharm.*, 1909, 47, 23—24).—A modification of Lieben's test (con-

version into iodoform). The precipitate formed in the distillate is extracted with ether, and the latter is introduced into a flat dish in which is placed a strip of filter paper, which protrudes about 1 cm. over the sides of the dish and the ends of which have been torn, but not cut. When the ether has evaporated at the ordinary temperature, the iodoform remains on the paper, and may be identified with the aid of a magnifying glass, and also by its odour. L. DE K.

Theory of the Colour Reactions of Dihydroxyacetone in Sulphuric Acid. GEORGES DENIGÈS (*Compt. rend.*, 1909, 148, 422—424. Compare this vol., ii, 272, 273).—The colour reactions previously studied in connexion with dihydroxyacetone have now been obtained with the oxidation products of polyhydric alcohols containing more carbon atoms than glycerol. The same reactions are readily given by methylglyoxal; hence the conclusion is drawn that the mechanism is analogous to that of Pettenkofer's reaction, an alcohol of the type $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$ undergoing dehydration by the sulphuric acid. The resulting aldehyde of the type $\text{CH}_3\cdot\text{CO}\cdot\text{CHO}$ then condenses with the phenol or alkaloid (compare Ville and Derrien, *Compt. rend. Soc. Biol.*, 1909, 66, 175). W. O. W.

Detection of "Saccharin" in Beer. GUNNER JÖRGENSEN (*Ann. Falsif.*, 1909, 2, 58—59).—Five hundred c.c. of the sample are evaporated on the water-bath to syrupy consistence, and the residue is repeatedly extracted with strong alcohol. After recovering the bulk of the alcohol, the residue is diluted with water and heated on the water-bath until the alcohol has completely disappeared. When cold, the solution is acidified with dilute sulphuric acid, filtered if necessary, and repeatedly agitated with ether. The united ethereal extracts are concentrated to a small volume, and the residue is diluted with water, acidified with dilute sulphuric acid, and treated with a very slight excess of potassium permanganate, which is then again removed by cautious addition of oxalic acid. The "saccharin," now free from any salicylic acid, is recovered by shaking the filtrate with a mixture of ether and light petroleum, which is then evaporated to dryness. The residue is submitted to the well-known tests (conversion into salicylic acid, etc.). L. DE K.

Detection of Glycine. EMIL ABDERHALDEN and MARKUS GUGGENHEIM (*Zeitsch. physiol. Chem.*, 1909, 59, 29—31).—Hirschstein (*Arch. exp. Path. Pharm.*, 1908, 59, 401) states that treatment with potassium hydroxide (1 to 5%) destroys or alters glycine in such a way that it no longer can be detected with β -naphthalenesulphonyl chloride. The correctness of this statement is entirely denied.

W. D. H.

Estimation of Urea in Urine. CHARLES G. L. WOLF and EMIL OSTERBERG (*J. Amer. Chem. Soc.*, 1909, 31, 421—428).—Benedict and Gephart's method (this vol., ii, 103) for estimating urea in urine gives higher results than that of Folin (*Abstr.*, 1901, ii, 630; 1903, ii, 116, 518). It has now been shown that in the former method, not only

does the urea undergo quantitative decomposition, but also that ammonia is simultaneously produced from the uric acid and creatinine, thus giving rise to the high results. The method is therefore inaccurate. E. G.

Estimation of Ammonia and Urea in Urine. PAUL E. HOWE and PHILIP B. HAWK (*J. Biol. Chem.*, 1909, 5, 477—484).—Both Spiro's and Folin's methods for estimating urea and ammonia give good results with solutions of urea and of urea and ammonium chloride. But in urine, Spiro's method gives results which are higher by 6 to 10% than Folin's. This is because the nitrogen of the creatinine and hippuric acid and a portion of the uric acid nitrogen will be reckoned as urea nitrogen by Spiro's method. W. D. H.

Exact Gasometric Estimation of Urea and Urinary Ammonia. ALBERT FLORENCE (*Compt. rend.*, 1909, 148, 943—946).—Analysis of samples of commercial urea shows that although the usual hypobromite method indicates only 92% of the theoretical amount, yet this corresponds with 97.5% when calculated on the actual amount of urea as indicated by the Kjeldahl method.

The ordinary gasometric method for estimating urea in urine has the disadvantage that the hypobromite attacks uric acid, creatinine, and ammonium salts with liberation of nitrogen. The following method, which avoids this source of error, is based on the observation that basic lead acetate removes uric acid and creatinine, and that, on heating, it decomposes the ammonium salts before attacking the urea. Ten c.c. of urine mixed with 5 c.c. officinal basic lead acetate solution are allowed to remain twenty to thirty minutes, and then filtered. The filtrate and washings are heated on the water-bath for about seventy minutes. The volume is made up to 100 c.c., and 19 c.c. withdrawn and treated in the ureometer with 12 c.c. of Moreigne's hypobromite solution. The ammonia is estimated by difference, by estimating the urea in a portion of the urine which has been defecated, but not heated with lead acetate.

A comparison is made, in a table, between results obtained in this way with results obtained by the Moerner process and the Moerner-Joquist method as modified by Braunstein. W. O. W.

Estimation of Thiocyanates with Permanganate. HERMANN GROSSMANN and LOTHAR HÜLTER (*Chem. Zeit.*, 1909, 33, 348).—Thiocyanates cannot be estimated satisfactorily by titration with permanganate in acid solutions. Attempts to estimate the sulphate formed in the reaction both in acid and ammoniacal solution proved unsuccessful.

Bromine added to a solution of ammonium thiocyanate causes, however, a complete oxidation of the sulphur. L. DE K.

Estimation of Caffeine in Coffee. K. LENDRICH and E. NOTTBOHM (*Zeitsch. Nahr. Genussm.*, 1909, 17, 241—265).—The following method is proposed as the result of a considerable amount of experimental work, each part of the process having been submitted to

a separate investigation. Twenty grams of the ground raw or roasted coffee are mixed with 10 c.c. of water and stirred occasionally for from one to two hours; the moist mass is then transferred to a cartridge or extraction thimble, and extracted for three hours with carbon tetrachloride. One gram of solid paraffin is added to the carbon tetrachloride solution, the solvent is distilled off, and the residue is extracted with four successive quantities of boiling water, using 50 c.c. the first time, and 25 c.c. for each of the following extractions. The aqueous solution is cooled, filtered through a moistened filter, and the residue is washed with hot water. The filtrate is treated, when cold, with from 10 to 30 c.c. of 1% potassium permanganate solution, and, after the lapse of fifteen minutes, the excess of permanganate is decomposed by the addition, drop by drop, of 3% hydrogen peroxide solution containing 1% of acetic acid. The whole is heated on a boiling water-bath for fifteen minutes, then filtered, and the residue washed with hot water. The filtrate and washings are evaporated to dryness, the residue is heated for fifteen minutes at a temperature of 100°, and extracted with chloroform. The chloroform solution is filtered, evaporated, and the residue of caffeine dried at 100° and weighed. The caffeine may be extracted directly with chloroform from the filtrate after the treatment with permanganate if this procedure is preferred.

W. P. S.

Reaction to Differentiate α - from β -Eucaine. G. CANDUSSIO (*Boll. chim. farm.*, 1909, 48, 95—96).— α -Eucaine is said to be distinguishable from the β -compound by the action of mercuric chloride solution, with which it gives a white precipitate. The author points out, however, that when the mercuric chloride is first added, the turbidity obtained disappears and is only permanent when excess of the reagent is present. The two compounds may be distinguished as follows. On adding to about 2 c.c. of a 1% solution of β -eucaine two drops of a solution of 1 gram of potassium iodide, 0.5 gram of iodine, and 10 c.c. of water, an intense reddish-brown coloration is formed immediately, and after one to two hours a slight, dark brown precipitate is deposited, the liquid itself becoming clear. Under similar treatment, a solution of α -eucaine gives at first an abundant reddish-brown precipitate, which in one to two hours becomes orange-coloured, the liquid having then a lemon-yellow colour owing to the presence of suspended precipitate.

T. H. P.

Nicotine Silicotungstate and on the Estimation of Nicotine. GABRIEL BERTRAND and MAURICE JAVILLIER (*Bull. Soc. chim.*, 1909, [iv], 5, 241—248).—Since Schloesing's method for the estimation of nicotine, depending on the extraction of the alkaloid with ammoniacal ether and subsequent spontaneous evaporation of the solvent and titration of the residue with standard acid, gives untrustworthy results, due (1) to slight loss of alkaloid during evaporation of the solvent, (2) uncertain end titration point, and (3) simultaneous extraction of certain basic products along with the nicotine, the authors have devised a method of using silicotungstic acid, already suggested as an alkaloid reagent (*Abstr.*, 1899, ii, 456), for the estimation of nicotine.

Nicotine silicotungstate, $12\text{WO}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2 + 5\text{H}_2\text{O}$, obtained by adding potassium silicotungstate to nicotine tartrate dissolved in water slightly acidified with hydrochloric acid, is a pinkish-white salt, which becomes anhydrous at 120° , and is decomposed by alkalis or by magnesia. A precipitate of the salt is formed when a solution of potassium silicotungstate is added to one containing 1 part of nicotine in 300,000 of water acidified with 1 part of hydrochloric acid per 1000.

In estimating nicotine in tobacco, about 10 grams of leaf are ground and extracted successively four times with ten times its weight of 5% hydrochloric acid, each digestion occupying fifteen to twenty minutes on the water-bath. To the united liquors, potassium silicotungstate solution (10 to 20%) is added, the precipitate collected, washed, and placed in a distilling flask with water and magnesia. The nicotine thus liberated is distilled off, preferably in a current of steam, collected in water, and titrated with standard sulphuric acid. A number of results quoted in the original indicate that the process gives good results, and is more suitable for purely scientific work than that of Schloesing.

T. A. H.

Colour Reactions of Indole Derivatives with Sugars. JULIUS GNEZDA (*Compt. rend.*, 1909, 148, 485—487).—Ten c.c. of a concentrated aqueous solution of glucose are boiled briskly and treated with two drops of sodium hydroxide solution and 6—10 mg. of 2-methylindole. When no more oily drops remain, the solution is allowed to remain for two minutes and then rapidly cooled. Two drops of fuming hydrogen chloride (D 1.19)* are added, and when the solution has become pale, 3 c.c. or a little more of the acid. The green precipitate obtained under these conditions consists of a mixture of two substances which have not yet been completely separated. No precipitate is obtained with sucrose, raffinose, inositol, or amygdalin.

The precipitate is in some cases of a different colour when the hydrogen chloride is added to a hot solution. Rhamnose, dextrose, galactose, lævulose, and lactose give green precipitates, both in hot and cold solutions. Xylose, arabinose, and ganbose give green precipitates in the cold and red precipitates in the hot solution.

Glucosoxime gives a red precipitate in each case. Mannose and maltose form green precipitates in the cold, but in hot solution the precipitates are brown and violet-grey respectively.

Under the same conditions, 1-methylindole gives an azure-blue precipitate with glucose in hot solution, and 3-methylindole, a brown coloration.

W. O. W.

Detection of Albumin and Mercury in Urine. CARL BOENING (*Chem. Zeit.*, 1909, 33, 376—377).—The author has arrived at the following conclusions. When testing urine for mercury, the urine should not be filtered as the mercury may be contained in the deposit. If the usual tests for albumin fail, but if the deposit shows the presence of kidney cells, it is quite possible that the albumin has precipitated as an insoluble mercury compound. Hence, when testing

* Misprinted as D 1.12 in original.—AUTHOR.

the urine of a patient undergoing mercurial treatment for albumin, the microscopical examination of the deposit should not be omitted.

L. DE K.

Detection of Protein in Urine. G. HASWELL WILSON (*J. Path. Bact.*, 1909, 13, 484—499).—The biological test (deviation of the complement) is from ten to one hundred times more sensitive than any chemical test for albuminous substances in urine; it cannot be obtained with normal urine; this property when present in disease is destroyed by boiling and unaffected by dialysis; it apparently resides in the albumin and globulin, and a mixture of these proteins obtained from the urine by salting out has a deviating power equal to that of the original urine.

W. D. H.

The Biuret and Nitric Acid Tests for Protein. KARL H. VAN NORMAN (*Bio.-Chem. J.*, 1909, 4, 127—135).—The delicacy of these reactions was studied especially from the point of view of detecting protein in the urine. The limit of delicacy of the nitric acid test is six parts of albumin in 10,000,000 parts of distilled water, or in 3,000,000 of urine. The limit of delicacy in the biuret reaction is four parts of albumin in 1,000,000 parts of water, or in 2000 of urine. Uric acid, urates, and creatinine interfere with the reaction. The intensity of the biuret reaction is increased by boiling.

W. D. H.

Abrastol. ERCOLE COVELLI (*Boll. chim. farm.*, 1909, 48, 53—56).—The dark coloration obtained after precipitating a solution of abrastol with basic lead acetate, and boiling the filtrate with mercurous nitrate (Vitali, *Abstr.*, 1908, ii, 642), is due to the reduction of a part of the mercury to the metallic state.

Abrastol is a sensitive reagent for the detection of nitrous acid, and conversely. When a drop of dilute nitrous acid is added to a solution of abrastol, and concentrated sulphuric acid then poured down the inclined wall of the test-tube, a ruby-red ring is produced. When *p*-phenylenediamine is added to a concentrated solution of abrastol, and then ferric chloride, a blue coloration, changing to red, is produced. In dilute solution, the red coloration only is obtained. A 1:150,000 solution of abrastol gives the coloration in five minutes.

An alkaline diazotised solution of atoxyl gives a red coloration with abrastol, the solution becoming fluorescent, owing to the action of the alkali.

C. H. D. 4

General and Physical Chemistry.

The Dispersion of Light in Gases. II. Ethylene and Ethane. STANISLAS LORIA (*Bull. Acad. Sci. Cracow*, 1909, 195—207.* Compare this vol., ii, 279).—Some small modifications have been made in the method previously employed. Ethylene, purified by fractional distillation at the temperature of liquid air, gives the values $a = 0.0006303$ and $b = 1.477 \times 10^{-10}$ for the constants in the equation $n - 1 = a(1 + b/\lambda^2)$.

Ethane, prepared by the Grignard reaction, gives the values $a = 0.0007365$ and $b = 9.308 \times 10^{-11}$. The results hitherto obtained for gaseous hydrocarbons are not in agreement with the requirements of the valency-electron theory. C. H. D.

Wave-length Tables of the Spectra of the Elements. Sir HENRY E. ROSCOE, MARSHALL WATTS, Sir W. NORMAN LOCKYER, Sir JAMES DEWAR, GEORGE D. LIVEING, ARTHUR SCHUSTER, W. NOEL HARTLEY, WOLCOTT GIBBS, Sir WILLIAM DE W. ABNEY, and WALTER E. ADENEY (*Brit. Assoc. Report*, 1908, 119—201).—Wave-length tables of the arc and spark spectra of tantalum, zirconium, and lanthanum.

T. H. P.

Wave-lengths of Lines in the Secondary Spectrum of Hydrogen. HERBERT E. WATSON (*Proc. Roy. Soc.*, 1909, 82, A, 189—204).—Accurate measurements of the wave-lengths of lines in the secondary spectrum of hydrogen have been made, three primary hydrogen lines and the yellow and green mercury lines being used as standards. No lines could be detected on the less refrangible side of the C-line, but, on the other hand, a considerable number were measured the wave-lengths of which were less than $\lambda = 3646$, which is the theoretical limit of the primary spectrum according to Balmer's formula. Some of these very refrangible lines may, however, be due to the presence of water vapour.

H. M. D.

Radiation and Temperature of the Flame of the Bunsen Burner. EDMOND BAUER (*Compt. rend.*, 1909, 148, 908—910).—By a method depending on the reversal of the D-ray, the mean temperature of the radiation from a Bunsen burner has been determined; the value obtained is 1750 — 1760° , in exact agreement with the result obtained by the emission method already described (this vol., ii, 106). By the same method, the temperature of different regions of the flame has been determined; the curve representing the results corresponds with those obtained by Schmidt, who measured with an optical pyrometer the temperature of a platinum wire immersed in the flame (*Inaug. Diss. Berlin*, 1909), except that the values of the latter observer are 50° lower throughout. The agreement of the two methods

* and *Ann. Physik*, 1909, [iv], 29, 605—622.

indicates that the temperature is the essential factor in the emission of line spectra by flames.

Neither the absorptive and emissive power of a flame for the residual rays of fluor spar, nor its temperature is sensibly affected by rendering it luminous and a conductor of electricity. G. S.

Absorption of Ultra-violet Light by Dilute Solutions. F. B. PIDDUCK (*Phil. Mag.*, 1909, [vi], 17, 710—715).—The observation that the electrical action of ultra-violet light is diminished very much more by passing through tap-water than through distilled water has led the author to examine the absorptive power of dilute solutions. The dependence of the absorption on the concentration of the solution was investigated in the case of sodium chloride and potassium bromide. The latter salt is much more active than the former; the galvanometer deflexion after passing through 15 mm. of a 5×10^{-6} *N*-solution was only 0.91 of that obtained after passing through 15 mm. of distilled water. Observations on supply water and artificial water containing the same chief constituents are also recorded. H. M. D.

New Type of Magnetic Decomposition of Absorption Bands of Crystals. Simultaneous Production of Systems Circularly Polarised in Opposite Senses. JEAN BECQUEREL (*Compt. rend.*, 1909, 148, 913—915).—Further examination of the plates representing the absorption spectra of crystals of tysonite at -253° (compare Becquerel and Onnes, *Abstr.*, 1908, ii, 338) show that under the conditions in question one of the lines gives a quadruplet formed by two doublets polarised in opposite senses. Further observations at -193° with varying magnetic fields confirm these conclusions. Dufour (*Le Radium*, 1908, 5, 295), who has made somewhat similar observations on the emission spectra of certain chlorides and fluorides, ascribed them to incomplete polarisation of the light, but it is now shown that polarisation is complete. The observations are best interpreted on the assumption of the existence of positive electrons (compare *Abstr.*, 1908, ii, 751). G. S.

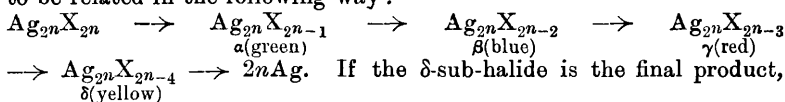
Triboluminescence. MAX TRAUTZ (*Physikal. Zeitsch.*, 1909, 10, 255—258).—A claim for priority in respect of certain observations recorded by Gernez (this vol., ii, 108). Many of the discrepancies between the two series of observations are shown to be readily explainable. H. M. D.

Electro-chemistry of Light. VI. WILDER D. BANCROFT (*J. Physical Chem.*, 1909, 13, 269—331. Compare this vol., ii, 362).—The author gives a third set of excerpts from papers dealing with solarisation. A lengthy summary of the conclusions which have been drawn by the various authors under review deals mainly with the nature of the latent photographic image and its reversal. R. J. C.

Calculations in Photochemical Processes. ALFRED BYK (*Ber.*, 1909, 42, 1145—1149. Compare *Abstr.*, 1908, ii, 338).—It is claimed that Weigert's treatment of the subject (this vol., ii, 219) is practically identical with that developed previously by the author. J. J. S.

Photochemistry of Silver (Sub-)halides. A. P. H. TRIVELLI (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 11, 730—748. Compare Abstr., 1908, ii, 1036).—The author is of the opinion that a series of sub-halides containing gradually decreasing proportions of halogen are formed in the photochemical decomposition of the silver halides. From observations of the colour changes which take place under different conditions, the colour sequence of the successive sub-halides has been found to be: green, bluish-green, blue, violet, red, orange, yellow. Since the order is the same for different halogens, the sub-halides of analogous composition appear to have analogous absorption spectra.

In the simplest case, the colours which appear may be referred to four corresponding with four sub-halides, which are supposed to be related in the following way:



If the δ -sub-halide is the final product, and corresponds with Ag_{2n}X_n , then n is equal to 4, and the formulæ of the four sub-halides may be written Ag_8X_7 , Ag_8X_6 , Ag_8X_5 , and Ag_8X_4 .
H. M. D.

Stability of the Colours of Minerals Produced by Radium. CORNELIO DOELTER (*Centr. Min.*, 1909, 232—234. Compare this vol., ii, 363).—The colours produced by subjecting various minerals to the action of radium rays are in many cases (sapphire, quartz, fluor spar) destroyed by heating the mineral at about 300°. Generally, the colour resulting from the action of radium is destroyed by ultra-violet light, more especially with fluor spar, rock salt, topaz, and sapphire. The colours produced by acting on natural rubies and emeralds with radium are very stable, but are nevertheless destroyed by ultra-violet light. Artificial rubies, likewise coloured diamonds, are not appreciably altered either by radium rays or ultra-violet light.

The periods of exposure necessary to produce the various colour changes differ largely with the various minerals. Fluor spar is extremely sensitive, whilst the several varieties of quartz change very slowly.
W. H. G.

Expulsion of Radioactive Matter in the Radium Transformations. SIDNEY RUSS and WALTER MAKOWER (*Proc. Roy. Soc.*, 1909, 82, A, 205—224 *).—Experiments are described in which the authors have investigated the radiation effects which result from the recoil of the atomic residues when α - and β -particles are emitted from radium emanation and its products of disintegration. When the emanation is condensed at the bottom of an exhausted tube immersed in liquid air, active deposit particles are radiated up the tube. From the rate of decay of the activity which collects on a surface exposed to the radiation from the condensed emanation, it appears that both radium-A and -B are radiated. In air and hydrogen, the amount of the radiation which reaches a surface at a fixed distance from the condensed emanation is an exponential function of the gas pressure.

* and *Physikal. Zeitsch.*, 1909, 10, 361—372.

A surface which has been rendered active by exposure to emanation is found to radiate both radium-*B* and radium-*C* through an exhausted tube. Since it is probable that the transformation of radium-*B* gives rise only to β -particles, the radiation of radium-*C* must be due to the recoil of the atoms resulting from the emission of electrons.

H. M. D.

Volatility of Radium-*A* and Radium-*C*. WALTER MAKOWER (*Mem. Manchester Phil. Soc.*, 1908-9, 53, (2), 1-8).—A nickel rod was exposed to a known quantity of radium emanation for ten minutes at a series of gradually increasing temperatures, the α -ray activity of the rod being examined after each exposure. At 885° the initial rapid fall in the α -ray activity was found to have nearly disappeared, and at 925° there was practically no evidence of the initial fall.

The observations indicate that radium-*A* begins to have an appreciable vapour pressure at 800°, and that at 900° it is completely volatilised.

In the investigation of the volatility of radium-*C*, the active deposit from radium was collected on plates of various materials by exposing them to emanation for several hours. After the lapse of sufficient time for the radium-*A* to have almost completely disappeared, the plates were heated for five minutes at various temperatures in a platinum-strip furnace, and the loss of activity determined. Experiments with platinum, nickel, and quartz plates indicate that the volatilisation of the radium-*C* is influenced by the nature of the material on which it is deposited. In all cases volatilisation begins between 700° and 800°, but whereas it is complete at 1200° when deposited on platinum or nickel, it is still incomplete at 1300° when deposited on quartz.

An experiment is described which shows that radium-*C* is not electrically charged when formed from radium-*B*.

H. M. D.

Condensation of the Radium Emanation. ERNEST RUTHERFORD (*Phil. Mag.*, 1909, [vi], 17, 723-729. Compare this vol., ii, 202).—The temperatures at which radium emanation condenses under different pressures have been determined. The following results are recorded :

Temperature	-127°	-101°	-78°	-65°
Vapour pressure.....	0.9	5.0	25	76 cm. mercury

At the temperature of liquid air the volume of the liquid emanation corresponding with 100 mg. of radium was found to be not greater than 1.2×10^{-4} cubic mm. Assuming that the emanation is a monatomic gas of atomic weight 222, it is calculated from this that the density of liquid emanation is not less than 5.

H. M. D.

Differences in the Decay of the Radium Emanation. ERNEST RUTHERFORD and Y. TUOMIKOSKI (*Mem. Manchester Phil. Soc.*, 1909, 53, (2) xii).—Measurements of the rate of decay of radium emanation have shown that this is often irregular, and depends to some extent on the treatment to which the emanation has been subjected. A sample,

purified by condensation with liquid air, was found to decay for the first five days with an average period of 3.58 days; between five and twenty days the average period was 3.75 days, whilst between twenty and forty days the decay was nearly exponential with a period of 3.85 days. A second preparation was found to decay exponentially from the commencement with a period of 4.4 days. The samples of emanation which decay most rapidly are more easily absorbed by water and are more easily condensed by liquid air than the more slowly decaying fractions. The products of transformation of the emanation which decays slowly could not be distinguished from those of the rapidly decaying emanation. It appears probable that the physical and chemical properties of the emanation vary to some extent with the life of the emanation, and that the atoms undergo a progressive change in properties before disintegration.

H. M. D.

Direct Evidence of the Charge of the α -Rays. HEINRICH GREINACHER (*Ber. Deut. physikal. Ges.*, 1909, 11, 179—184).—The experimental demonstration of the positive charge of the α -rays is rendered difficult by the fact that slowly-moving electrons are simultaneously emitted by radioactive substances. The method of demonstration described is similar to that which has been used to show the negative charge of the β -rays; the α -rays are allowed to fall on a thin, metal plate, which acts as receiver, and in order to prevent the escape of the charge, this plate is combined with a plate of solid, insulating material.

H. M. D.

Leakage of Helium from Radioactive Minerals. Hon. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1909, 82, A, 166—169).—The fact that helium is not always present in larger quantity in geologically older minerals than in more recent formations of equal activity has been attributed to the escape of the gas. In connexion with this hypothesis, experiments have been made on the rate of leakage of helium from monazite and thorianite, which show that helium is given off at a rate which far exceeds the rate of production by radioactive change. The accumulation of the gas must be due to the fact that the conditions of existence of the minerals in nature are much more favourable to the retention of helium.

H. M. D.

Absorption of Röntgen Rays. CHARLES G. BARKLA and C. A. SADLER (*Phil. Mag.*, 1909, [vi], 17, 739—760).—The authors have investigated the absorption of X-rays by various elements, using homogeneous beams of varying penetrating power. For soft rays the absorption coefficients of different elements remain in the same ratio when the penetrating power of the rays changes considerably. As the primary radiation is made more penetrating, a point is reached at which the absorbing element begins to emit homogeneous secondary rays which are characteristic of the element; at this point the absorption increases very rapidly to a maximum which corresponds with an absorption many times greater than that experienced by a somewhat less penetrating radiation; further increase in the hardness of the

primary rays leads to a diminution in the absorption, and corresponding with this the secondary radiation decreases at the same rate as the ionisation produced by the primary radiation in a thin film of air. Of the various elements examined, chromium, iron, nickel, copper, zinc, platinum, gold, and arsenic were found to emit these characteristic homogeneous rays. No such radiation was observed in the case of carbon, magnesium, and aluminium. It is pointed out that the behaviour of nickel in all emission and absorption experiments corresponds with that of an element of atomic weight about 61.3.

H. M. D.

Conversion of Diamond into Coke in High Vacuum by Cathode Rays. A. A. CAMPBELL SWINTON (*Proc. Roy. Soc.*, 1909, 82, A, 176. Compare Abstr., 1908, ii, 275).—Spectrum tubes connected with a cathode-ray tube containing diamond, on which the cathode rays were focussed, were sealed off before and after the conversion of the diamond into coke. No difference could be detected in the two spectra except in regard to the relative brightness of certain lines. If gas is set free, it can therefore only be one or more of the comparatively common gases usually found as residuals in cathode-ray tubes exhausted from air in the ordinary way.

H. M. D.

Radiation of Potassium Salts. E. HENRIOT (*Compt. rend.*, 1909, 148, 910—912. Compare Campbell and Wood, Abstr., 1907, ii, 217; McLennan and Kennedy, Abstr., 1908, ii, 750).—It is shown by absorption experiments with tin-foil that, contrary to the statements of previous observers, the radiation from potassium salts is fairly homogeneous; the absorption follows the formula $I = I_0 e^{-\lambda d}$, where I is the intensity of the radiation which has traversed a thickness, d , of the absorbing substance, and I_0 is the initial intensity. The ratio λ/ρ , where λ is the coefficient of absorption and ρ the density of the tin, is 16, which is regarded as supporting the view that the radiation consists of β -rays.

The form of the radiation renders it improbable that the radioactivity of salts of potassium is due to a known active element.

G. S.

Distribution of Thorium in the Earth's Surface Materials. JOHN JOLY (*Phil. Mag.*, 1909, [vi], 17, 760—765).—A method for the detection of thorium in minerals is described. The material to be examined is brought into solution by the use of thorium-free reagents. The solution is boiled in a flask provided with a reflux condenser for twenty to thirty minutes in order to expel any accumulated radium emanation, and then a slow current of air is drawn through the flask in order to transfer the emanation to the electroscope. Arrangements are described for drying the air and reproducing the same velocity of air-flow in successive experiments. With three exceptions, all the rocks examined by the author were found to contain thorium. The results obtained with Vesuvian lavas accord well with Blanc's observations on the abundance of thorium emanation in the atmosphere at Rome. The quantities of thorium observed in some of these materials

are about three times as large as the average uranium content of rocks.

H. M. D.

Thermal and Ionising Action of Thorium in Rocks. GIAN A. BLANC (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 289—294).—The author has found previously (Abstr., 1908, ii, 248, 452; 1909, ii, 366) that a sample of soil in Rome contains at least 1.45×10^{-5} gram of thorium per gram, whilst 5 samples of granitic rock contained from 2.07 to 8.28×10^{-5} gram per gram. He now proceeds to consider the two following effects due to the presence of thorium: (1) the heat effect, produced principally by the transformation of kinetic energy accompanying the absorption of the α -particles in the interior of the rock and soil, and (2) the ionising action of the air, owing to the radiation directly emitted by the various products in the soil.

The above figures, together with Pegram and Webb's results (this vol., ii, 111), give the quantities of heat generated per hour in 1 gram of the soil and rocks examined, owing to the thorium present, as varying from 3.45 to 19.70×10^{-10} cals., the mean being 1.01×10^{-9} cals. This amount of heat is about double that produced by the uranium-radium-radium-*F* group in the igneous rocks examined by Strutt.

The mean proportion of thorium existing in the materials examined by the author being 4.25×10^{-5} gram per gram, and that of radium in the igneous rocks examined by Strutt being 3.35×10^{-12} gram per gram, the intensity of the γ -radiation emitted by the thorium in the former case will be 5.7 times as great as that of the γ -radiation due to the radium in the latter.

The method employed by Eve (Abstr., 1906, ii, 593) for deducing the quantity of radium contained in 1 c.c. of the soil at Montrea from the intensity of the penetrating radiation emitted by the soil, is inaccurate, since the observed effects are due to all the radioactive substances present emitting γ -rays. To this is probably due the discrepancy between the results obtained by Eve (*loc. cit.*) and those given by Eve and McIntosh (Abstr., 1907, ii, 729).

T. H. P.

Product and Rays of Uranium-X. FREDERICK SODDY (*Nature*, 1909, 79, 366—367; *Le Radium*, 1909, 6, 53).—The difference between the atomic weights indicates the expulsion of three α -particles in the change of uranium into radium, of which only two are known. Uranium-X preparations, after the decay of the β -activity, were found to possess a feeble residual α -radioactivity, which remains constant over a term of years. The constancy is attained before the β -radiation has decayed, so that if the α -ray substance is a true product of uranium-X, it must be the direct product. Some of the β -rays of uranium-X are very difficult to deviate by a magnetic field, and possess values for $H\rho$ as high as 6500, whilst with radium some rays with values as high as 9000 to 11,000 are present. The velocity of these rays must be more than 99% of that of light, and their mass from four to six times the normal mass. These

facts have prevented so far the attempt to detect the growth of the feeble α -radiation during the decay of the β -radiation, to be expected if the α -ray substance is a product of uranium-X.

F. S.

Rays of Uranium-X. FREDERICK SODDY (*Nature*, 1909, 80, 37—38. Compare preceding abstract).—A second series of experiments has indicated the growth of the feeble α -radiation before referred to during the decay of the β -radiation of uranium-X. Fifty kilos. of uranyl nitrate were employed. The uranium-X immediately after preparation, when examined in a magnetic field such that no β -rays with value for $H\rho$ below 8640 could enter the electroscope, gave no α -rays. The leak in the electroscope was due, one-fourth to γ -rays, and three-fourths to still undeviated β -rays. In a few hours a feeble α -radiation made its appearance, and grew to a maximum in 2.5 days. It has since remained constant. The results are not yet capable of a complete interpretation, but indicate the existence of a new substance, presumably in the uranium-radium series, with a period of the order of one day, the product of which gives α -rays and has a very long period of life.

F. S.

γ -Rays of Uranium. FREDERICK SODDY and ALEXANDER S. RUSSELL (*Physikal. Zeitsch.*, 1909, 10, 249—251).—The authors have separated uranium-X from fifty kilograms of uranyl nitrate, and examined the γ -rays which it emits. The whole of the γ -radiation of uranium is emitted by uranium-X. The activity of this, as measured by the γ -rays, falls to half value in twenty-two days, which is identical with the half-decay period obtained by examination of the β -rays.

The absorption of the γ -rays by different substances was examined. The absorption in lead for thicknesses ranging from 1 to 5 cm. takes place according to an exponential equation, the value of the absorption-coefficient (λ) being 0.62. In general, the value of λ/d is equal to 0.055, whereas the corresponding ratio for the γ -rays of radium is 0.021. This means that the γ -rays of uranium are absorbed about two and a-half times as quickly as those of radium. Although 0.055 is the mean value of λ/d , the separate values vary from 0.045 (iron) to 0.068 (paraffin), and the exactness of the density law is questioned.

For greater thicknesses of absorbing material than correspond with 5 cm. of lead, the value of the absorption-coefficient diminishes, and there is some evidence of the existence of rays which are still more penetrating than the γ -rays.

H. M. D.

Conduction of Electricity in Electro-negative Vapours and A_1 -Rays. OTTO REICHENHEIM (*Ber. Deut. physikal. Ges.*, 1909, 11, 168—178).—Experiments on the discharge of electricity through exhausted tubes containing halogens and other metalloidal elements are described. The abnormally large fall of potential at the anode which characterises the discharge through such tubes is supposed to

be due to the facility with which electrons are absorbed by the electro-negative vapours. In support of this view it is found that the potential drop at the anode is greatly diminished when electrons are generated in the discharge tube by means of a Wehnelt cathode.

When discharge takes place through a tube containing phosphorus vapour, the degree of exhaustion gradually increases, and this is found to be due to the deposition of the vapour in the form of red phosphorus on the walls of the tube. An experiment is described which indicates that the phosphorus vapour is negatively charged. The discharge through iodine vapour also leads to a gradual exhaustion of the tube; the degree of exhaustion diminishes if the tube is left for some hours. An explanation of this phenomenon has not been obtained.

A new type of radiation (A_1 -rays) emitted by the anode is described. These are similar to the K_1 -rays which Goldstein has found to be given off from the cathode. The A_1 -rays are positively charged, and it is supposed that the rays are formed from negatively charged gaseous ions by the loss of two electrons.

H. M. D.

Electrical Conductivities of very Dilute Solutions in Anhydrous Sulphur Dioxide. PAUL DUTOIT and ERNST GYR (*J. Chim. Phys.*, 1909, 7, 189—203).—Walden and Centnerszwer (Abstr., 1902, ii, 245) have found that the laws which hold for the conductivity of aqueous solutions are not applicable to solutions in liquid sulphur dioxide. The majority of organic solvents were formerly considered to behave similarly to sulphur dioxide, but Dutoit and his co-workers have shown that with very dilute solutions the same laws hold as for aqueous solutions, the only difference being in the dissociating power of the solvents. The authors have consequently further investigated the behaviour of liquid sulphur dioxide as a solvent.

A special apparatus was devised in which the solutions could be made and diluted to any strength without once coming into direct contact with the external atmosphere, all traces of moisture being rigorously excluded. The first experiments were made in red light in order to prevent any photochemical action which would result in the formation of sulphur trioxide, but it was found that white light had no effect on perfectly anhydrous sulphur dioxide. Moreover, under the same conditions, oxygen has no oxidising effect, even in the presence of the platinum electrodes. The specific conductivity of anhydrous sulphur dioxide at -15° was found to be 0.85×10^{-7} , which is the lowest value the authors have obtained for any solvent. The electrolytes used were tetramethylammonium iodide and bromide, and the iodides and bromides of ammonium, potassium, and rubidium; the dilutions varied from 125 to 64,000 litres. The results show that the molecular conductivity tends towards a maximum as the dilution increases, although this maximum is not attained at 64,000 litres. Graphic extrapolation and calculation by Ostwald's formula gave approximately the same numbers for the conductivity at infinite dilution; these numbers conform to Kohlrausch's law of the independent migration velocities of the ions. In the stronger solutions the salts of tetramethylammonium are much more strongly dissociated than those of the alkali metals, and the iodides more than the

bromides. For dilutions of 8000 litres, Ostwald's dilution law holds approximately, the salts of rubidium giving the worst results.

T. S. P.

Temperature-coefficient of the Electrical Conductivity of Certain Acids and Bases in Aqueous Solution. A. WÖRMANN (*Ann. Physik*, 1909, [iv], 29, 194—200, 623—624).—The author has measured the conductivity of $1N$, $\frac{1}{2}N$, $\frac{1}{4}N$, $\frac{3}{8}N$, and $\frac{1}{10}N$ solutions of hydrochloric and nitric acids and of potassium and sodium hydroxides at 0° , 18° , and 32° . From the data, the values of the constants c and c' in the equation $K_t = K_0(1 + ct + c't^2)$ are calculated and compared with the coefficients given by other observers.

H. M. D.

Behaviour of Ethyl Ether on the Passage of an Electrical Current. JOHANNES SCHRÖDER (*Ann. Physik*, 1909, [iv], 29, 125—152).—The electrical conductivity of ethyl ether has been examined in detail with the object of throwing light on certain discrepancies which are exhibited by other feebly conducting liquids. The observed conductivity depends very largely on the previous treatment of the platinum electrodes. If the electrodes are charged with gases, the current increases with the applied *E.M.F.* more rapidly than corresponds with Ohm's law. The application of higher potential differences appears to favour the liberation of substances from the electrodes, which give rise to ions in the ethyl ether. With electrodes which have been heated to redness to remove volatile impurities, this effect is not observed, but the existence of a saturation current is indicated. When the current is passed in the same direction through the ethyl ether for a considerable time, the conductivity diminishes and approximates asymptotically to a lower limiting value.

H. M. D.

Oxidation Potentials in Non-aqueous Solvents. RICHARD ABEGB and J. NEUSTADT (*Zeitsch. Elektrochem.*, 1909, 15, 264—266).—Nernst believes that oxidising and reducing agents react with the solvent-water, forming oxygen and hydrogen, which change the electrodes into gas electrodes of definite potential. The authors test this view by measuring the potentials of a platinum electrode in solutions of cuprous and cupric chlorides, and of ferrous and ferric chlorides, in pure dry pyridine; the potentials are measured against a silver electrode in a solution of silver nitrate in pyridine. The results show that the potentials in the pyridine solutions are nearly the same as those in aqueous solutions, from which the authors draw the conclusion that the potential of the electrode is due to the exchange of charges between the ions of different valency at its surface, the intervention of water being unessential.

T. E.

Electrolytic Potentials of Silver and Thallium. FRANCIS J. BRISLEE (*Trans. Faraday Soc.*, 1909, 4, 159—165).—The potential of silver electrodes, freshly-silvered and measured against a $N/10$ calomel electrode, has the value $+1.076$ volt in silver nitrate and $+1.074$ volts in silver acetate solutions, the ionic concentration being calculated from the conductivity of the electrolyte. Thallium in thallous nitrate gives

-0.042 volt, and in thallous chloride, -0.042 volt. The values in thallous hydroxide increase with the dilution of the electrolyte, so an indirect method has been used, a thallium electrode in thallous nitrate being used for comparison, and the liquid potential difference being calculated by Planck's formula. This gives -0.044 volt. C. H. D.

Part Played by Contact Electrification in the Permeability of Membranes to Electrolytes. PIERRE GIRARD (*Compt. rend.*, 1909, 148, 1047—1050).—It was shown (Abstr., 1908, ii, 456) that a membrane interposed in a liquid concentration couple lowers the voltage if the liquid in question is acidic or basic, but not if neutral. The membrane is considered as a bundle of capillary tubes, at the surfaces of which contact electrification takes place in the manner suggested by Perrin (Abstr., 1908, ii, 754). A difference of osmotic pressure on the two sides will establish a flow through the membrane, leaving an excess of positive and negative charges on either side. This is the same as a filtration *E.M.F.*, so that its value can be calculated with the aid of Helmholtz's theory. The agreement between calculated and experimental values is not very striking, however.

Acids and bases which diffuse in water more rapidly than neutral salts traverse a membrane more slowly, since, it is supposed, they electrify the membrane by contact. If a salt solution diffusing through a membrane into water is rendered slightly acidic or alkaline, the membrane becomes polarised, and diffusion is promoted or hindered, according to the direction of the *E.M.F.* set up. Thus the amount of magnesium chloride passing in thirty minutes from a normal solution into water across a film of gelatin was found to be 0.0012 gram; if the solution was acidified with a little *N*/100 HCl, only 0.00035 gram passed, but in presence of a trace of soda the amount passing was almost 0.0024 gram. This effect might be reversed in the case of another salt, hence a membrane electrified by contact might exhibit selective permeability to salts. The protoplasmic interior of a living cell is never neutral, and polarisation must be set up at the membrane constituting the cell wall. The author claims that it may legitimately be supposed that this polarisation is the origin of selective permeability in living membranes. R. J. C.

Oxide Theory of the Oxygen Electrode. III. RICHARD LORENZ and E. LAUBER (*Zeitsch. Elektrochem.*, 1909, 15, 206—212. Compare this vol., ii, 15, 371).—The arrests in the discharge curve of a polarised cadmium anode in normal potassium hydroxide are at about 1.7, 1.1, 0.64, 0.35, 0.17, 0.07, and 0.03 volt.

In the experiments with platinum, the cathode was a platinised platinum sheet kept in a current of hydrogen; the electrolyte was sulphuric acid of maximum conductivity. The anode was comparatively easily formed. A platinised anode gives discharge curves with indistinct rounded arrests, whilst a smooth anode gives curves with sharp arrests. If the cathode is too small, the discharge curves are parallel to each other, their relative height depending on the time and strength of current used in charging. By using suitable current densities in charging, certain arrests can be developed and others suppressed. The

arrests observed are at 1.95, 1.65, 1.3, 1.05, 0.97, 0.94, 0.74, 0.64, 0.57, 0.43, 0.27, 0.12, 0.05, and 0.008 volt. Many of these can be identified with the potentials of known oxides or hydroxides of platinum.

T. E.

Action of Continuous Current on Symmetrical Chains of Aqueous Solutions of Electrolytes which have no Common Ion. M. CHANOT (*Compt. rend.*, 1909, 148, 986—988. Compare this vol., ii, 292).—The potential differences set up at the liquid interfaces when a current is passed through a series of solutions of electrolytes, $MR \mid MR' \mid MR$, are due, not only to local differences in concentration of MR' , but also to the formation of new salts MR' and $M'R$ at the respective surfaces. The potential differences are not necessarily of opposite sign, as would be the case if concentration alone were concerned, for the effect of the new salts produced may be the main factor, and the potential differences may even change in sign with prolonged passage of the current.

By employing coloured salts, such as cupric sulphate or potassium permanganate, the changes in concentration induced by a current may be observed. The formation of the new salts MR' and $M'R$ may also be observed if these are insoluble substances, such as $AgCl$ or $Cu(OH)_2$.

R. J. C.

Electrolysis of Acids and Bases. UMBERTO CIALDEA (*Nuovo Cim.*, 1909, [v], 17, 66—68).—The increase of concentration of dilute sulphuric acid at the anode and the diminution at the cathode after a current has been passed can be readily shown by means of the following apparatus. Two platinum wires, passing nearly to the bottom of the two limbs of a U-tube containing the acid, are connected through a galvanometer, sensitive to 0.001 ampere, to a continuous current generator having P.D. 50—100 volts. When the circuit is closed, the current remains constant for some time, but later falls gradually to zero. It will now be found that the cathode liquid does not give an acid reaction. Addition of a drop of acid to the anode limb of the U-tube now causes no change, but, if added to the cathode limb, the current will speedily begin to pass again. Similar results are obtained with sodium or potassium hydroxide solution, the anode liquid becoming free from the base. Complete separation of the anodic from the cathodic liquid may be effected by placing one of the electrodes in a tube closed at the bottom by means of a porous diaphragm, the tube being filled with the solution and immersed in a beaker filled with the same solution, into which the other electrode dips. When the current drops to zero, the tube is removed.

T. H. P.

Apparatus to Demonstrate the Different Velocities of Displacement of Electrolytic Ions. UMBERTO CIALDEA (*Nuovo Cim.*, 1909, [v], 17, 69—70).—This apparatus resembles that devised by Loeb and Nernst for the determination of Hittorf's transport numbers, but has no tap in either of the side-tubes. A solution of, for example, zinc chloride is electrolysed so that the Zn-ions arriving at the cathode find there chlorine with which to re-form zinc chloride, whilst the Cl-

ions similarly find zinc at the anode. This is effected by using a spiral of zinc wire as anode and a spiral of silver wire coated with fused silver chloride as cathode. As the velocities of the zinc and chlorine ions differ considerably, about ten to twenty minutes after closing the circuit a concentration cell is formed, as may be seen by connecting two auxiliary electrodes (of platinum wire, the end of which is covered with a thin layer of zinc or of zinc amalgam), one in each limb, through a galvanometer or electrometer sensitive to 0.001 volt. From the sense of the *E.M.F.*, it is seen that the greater concentration of zinc chloride is at the anode. Diffusion in the electrolyte may be avoided by suspending the apparatus in a thermostat, and by using very small currents of 10–50 milliamperes. T. H. P.

Electrical Charge of Colloidal Silver. WILLIAM C. McC. LEWIS (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 209–211).—The author doubts the validity of Burton's method (*Abstr.*, 1906, ii, 841) of deducing the charge on the particles of colloidal metals. Whereas Burton assumed that the whole of the added electrolyte takes part directly in the neutralisation of the charge on the colloidal particles, the author considers that an equilibrium condition is set up which is determined by the concentration of the adsorbed ions and of the ions in the aqueous solution. H. M. D.

Specific Heats of Air and Carbon Dioxide at Atmospheric Pressure by the Continuous Electrical Method at 20° and 100°. W. F. G. SWANN (*Proc. Roy. Soc.*, 1909, 82, A, 147–149).—A steady stream of the gas was passed through a jacketed tube, in which it was heated by a current of electricity passing through a platinum coil, the rise in temperature being measured by means of two platinum resistance thermometers used differentially. By means of a second experiment, in which the rate of flow of the gas was about half that in the first experiment, and in which the current was adjusted so that the rise in temperature was the same as before, the loss of heat due to radiation and other causes could be eliminated.

The specific heat of air was found to be 0.24173 at 20° and 0.24301 at 100°, and that of carbon dioxide, 0.20202 at 20° and 0.22121 at 100°. The separate determinations agreed in each case to about 1.5 parts in 1000, and it is estimated that the mean results are probably correct to 1 part in 1000. H. M. D.

Specific Heats of Non-metals: Sulphur. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 311–312).—The author has re-determined the specific heat of rhombic sulphur by means of the bomb-calorimeter, pieces of sulphur 1.5–2 mm. in diameter being employed in order to avoid a too retarded transference of heat to the calorimeter; the highest temperature employed was below that at which rhombic sulphur changes into the monoclinic form. The mean specific heat between 23° and 92° was found to be 0.1759, the greatest variation from this value being 5%. This low degree of accuracy is caused by the necessity of (1) using a short range of temperature, and

(2) placing the sulphur in water which has a high specific heat, every other substance dissolving sulphur to some extent.

There is no doubt but that the atomic heats of sulphur and phosphorus (*ibid.*, 1907, 39, 1181) at corresponding temperatures are lower than those of the metals, and the conclusion is drawn that the molecules of these two non-metals in the crystalline state are more complex than those of metals.

T. H. P.

Slowness of the Spontaneous Transformation of the Unstable Variety of Certain Dimorphous Substances at Low Temperatures. DÉSIRÉ GERNEZ (*Compt. rend.*, 1909, 148, 1015—1019 *).—Both dimorphous forms of sulphur (transition point, 97.6°) can exist in the metastable state. Orthorhombic sulphur may be heated above 97.6° , and monoclinic sulphur, if cooled to a point much below this, persists for a very long time. The same peculiarity is particularly noticeable in mercuric iodide and thallous iodide.

Mercuric iodide sublimed in a vacuum on to a water-cooled tube always appears in the yellow form, although the red variety is stable at the temperature employed. The yellow sublimate alters but very slowly, each red crystal serving as a nucleus for the propagation of the change. The stability of the yellow form depends largely on the care exercised in excluding red particles from the sublimate. Even after ten years, isolated patches of yellow crystals could be seen. Thallous iodide (transition point, 168°) exhibits the same property, the unstable red variety having persisted at the ordinary temperature for nine years.

Yellow mercuric iodide, obtained by rapid evaporation of its solutions, may be kept unchanged for a very long time if dust is excluded.

R. J. C.

Freezing-point and Boiling-point Curves in a Binary System. W. P. A. JONKER (*Zeitsch. physikal. Chem.*, 1909, 66, 300—306).—Bakhius Roozeboom (*Heterogene Gleichgewichte II*, 328) has deduced the changes occurring in the freezing-point and boiling-point curves of a binary system when one or both components is volatile. The author has obtained the same results by a simple graphic method, depending on the relative displacement of the chief points on the diagram.

G. S.

Determination of the Density of Small Quantities of Liquids. H. VON WARTENBERG (*Ber.*, 1909, 42, 1126—1131).—The density of a liquid, of which only a small quantity is available, can be determined by sucking the liquid into a minute pipette, of a few tenths cm. capacity, which is suspended horizontally from the arm of Nernst's micro-balance (*Abstr.*, 1903, ii, 571), by which the weight is ascertained.

C. S.

Physico-chemical Constants of Some Gases. PHILIPPE A. GUYE (*Bull. Soc. chim.*, 1909, [iv], 5, 339—340).—A brief summary of the values obtained by the author and his colleagues for the densities, critical constants, and coefficients of compressibility of certain gases

* and *Ann. Chim. Phys.*, 1909, [viii], 17, 290—296.

compare Abstr., 1904, ii, 612, 812; 1905, ii, 506; 1906, ii, 20; 1907, ii, 80; 1908, ii, 372, 940); the following constants have not been recorded previously:

Weight of a litre of gas under reduced pressure at 0°.

Gas.	Pressure.	Density.	Gas.	Pressure.	Density.
SO ₂	570.0 mm.	2.1789	OMe ₂ ...	501.37 mm.	1.3790
	518.2 "	1.9802		379.40 "	1.0391
	380.0 "	1.4456	MeCl ...	547.40 "	1.6495
	311.3 "	1.1820		341.45 "	1.0228

Critical Constants.

Gas.	Critical temperature.	Critical pressure.
NH ₃	+132.3°	109.6 atmos.
SO ₂	157.2	78.0 "
HCl	51.8	83.6 "
PH ₃	51.3	64.5 "
OMe ₂	127.1	53.0 "
MeCl.....	143.2	65.85 "

Coefficients of Compressibility at 0°.

Coefficient of compressibility measured directly under

Gas.	40—80 cm. Hg.	20—40 cm. Hg.	0—1 atmos.
H ₂	-0.0000069	—	-0.00052
He	-0.0000079	—	-0.00060
O ₂	+0.0000127	—	+0.00097
NO	+0.0000154	—	+0.00117
NH ₃	+0.0002008	+0.0001997	+0.01521
SO ₂	+0.0003137	+0.0003105	+0.02379

The following coefficients of compressibility calculated from densities under 7—1 atmos.: SO₂, +0.02381; OMe₂, +0.02656; MeCl, +0.02215.

M. A. W.

Cohesive and Electrical Forces. Contact Electricity. ISIDOR TRAUBE (*Ber.*, 1909, 42, 1594—1602).—In continuation of the relations shown to hold between the internal pressure of the metals, deduced from a modified van der Waals' equation, and their physical properties, it is now shown that the order of the coefficients of thermal expansion, 3β , and of the heats of volatilisation, a/v , which are inversely proportional to them, is approximately parallel with the electrical potential series. There is, however, an exact correspondence between the latter and the order of the magnitude, $a/v^{2/3}$. Since a/v = the surface energy $\gamma v^{2/3}$, $a/v^{2/3} = \gamma v$, that is, a magnitude which may be regarded as the attraction which a sq. cm. of surface experiences from the inner side. The potential difference of two metals in contact is then proportional to their difference of surface tension. This is confirmed by the effect of small quantities of impurities on the metals, internal pressure and electrolytic potential being similarly affected. The effect of mechanical hardening on potential is also in accordance with this relation. The effect of the surface-tension of the electrolyte is also discussed.

The behaviour of an electrode is determined by the equality or inequality of a/v and Q , the heat of formation. If $a/v > Q$, as for the noble metals, there is no positive solution pressure, and the metal tends to fall out from solution. With most metals, $a/v < Q$.

C. H. D.

Dissociation of Water Vapour. ALFRED HOLT, jun. (*Phil. Mag.*, 1909, [vi], 17, 715—723).—The discrepancy between the values obtained for the degree of dissociation of water vapour at temperatures above 1300° by the author (Abstr., 1907, ii, 450) and those obtained by Nernst and Wartenberg (Abstr., 1906, ii, 729) and by Langmuir (*ibid.*, ii, 848) has been traced to the fact that the estimated temperatures used in the author's experiments were much higher than the true temperatures. When the corrected temperature values are used, the author's data agree satisfactorily with those of the other experimenters.

New measurements are recorded with a somewhat improved form of apparatus for temperatures ranging from 1233° to 1637°. From these data, the value of the equilibrium constant K in the thermodynamic equation of Nernst and Wartenberg is found to be 3.806. When the data of other investigators are taken into consideration, the most probable mean value obtained for the constant is 3.80.

H. M. D.

The Dissociation of Sulphuric Acid and of Nitrogen Dioxide. MAX BODENSTEIN and MASSAO KATAYAMA (*Zeitsch. Elektrochem.*, 1909, 15, 244—249).—Sulphuric acid (85 to 100% of H_2SO_4) or nitrogen peroxide are weighed into a vacuous quartz-glass bulb to which a quartz-glass manometer, constructed on the principle of the Bourdon gauge, is sealed. The whole is heated in an electric furnace, and the degree of dissociation calculated from the pressure. The quartz glass manometer begins to undergo permanent deformation at temperatures above 600°, but if it is enclosed in a vessel in which the pressure is kept equal to that in the inside of the spiral, so that the pointer remains at the zero of the scale, it may be used for temperatures above 700°. The values of the dissociation constants for sulphuric acid, $\log K = \log[SO_3][H_2O]/[H_2SO_4]$, are calculated by means of Nernst's thermodynamic theorem. The simplified form gives $\log K = -Q/4.571T + 0.75 \log T + 4.086$ (concentrations taken in gram-molecules per litre). The temperature of half dissociation at atmospheric pressure calculated from this equation is 599° absolute, whilst the experiments give 623°; by adding cT to the equation to allow for the difference of specific heat of the substance formed and destroyed in the change, the equation becomes

$\log K = -22850/4.571T + 0.75 \log T - 0.00057T' + 4.086$,
and this reproduces the experimental results very exactly.

The dissociation constants for nitrogen dioxide between 200° and 700°, $\log K = \log[NO]^2[O_2]/[NO_2]^2$, are represented very well indeed by the simple expression $\log K = -Q/4.571T + 0.75T' + 4.086$, where $Q = +27,400$ cals., which is the value found by direct calorimetric experiments.

T. E.

Adsorption of Sugars by Animal Charcoal. REGINALD O. HERZOG and J. ADLER (*Zeitsch. physiol. Chem.*, 1909, 60, 79—84. Compare Rona and Michaelis (this vol., ii, 384).—The adsorption of dextrose by animal charcoal has reached its maximum at the end of thirty minutes, and in the presence of air is not accompanied by any appreciable oxidation.

Experiments made with different sugars, and using 100 c.c. of solutions of varying concentrations and 5 grams of charcoal, show that $C = KB^n$, where C represents the sugar adsorbed by the charcoal, B the amount left in solution, and K and n are constants which vary with the different sugars:

	n .	K .
Dextrose	0.474	0.766
Lævulose	0.539	0.338
Galactose	0.694	1.016
Sucrose.....	0.127	0.106
Maltose	0.133	1.142
Milk sugar	0.135	1.138

Experiments were also made by varying the amount of charcoal.

J. J. S.

Adsorption with Special Reference to the Ascent of Salt Solutions in Filter Paper. RUDOLF KRULLA (*Zeitsch. physikal. Chem.*, 1909, 66, 307—348).—The method of experiment was as follows: A beaker 13 cm. high and 6 cm. in diameter contained 50 c.c. of a salt solution, and was covered by a piece of paste board in which were three slits, each 1 cm. long. Through these slits pass strips of filter paper which dip in the solution, and the height to which the different salts rise for the same height of water is determined. In order to investigate the distribution of the salt in the strips of paper, the latter are removed from the solution, rapidly dried, dipped in the solution of a substance which reacts with the salt (colour reaction), and again rapidly dried. In some cases investigations were made with the same time of immersion, instead of comparing equal heights of ascent of water.

On the basis of experiments, chiefly with solutions of lead nitrate and of copper sulphate, the following comparative formula for adsorption under the conditions of the experiment is deduced: $eahp'H'/e'a'h'pH = 0.835 p'/p + 0.167$, where h and h' represent the respective heights of the salts, H and H' those of the water in the two cases, p and p' the percentage strengths of the solutions, e and e' are expressions for the relative absorptive powers of the papers, and a and a' are the limiting values for the adsorption of the salts at zero concentration. For the same paper and the same height of water (the usual experimental conditions) the formula becomes simplified in an obvious way.

When all the factors but one are known, the formula can be used for various purposes, for example, to find the relative degree of adsorption of filter paper for salts ($a : a'$), or to determine the strength of a solution (p' when a' is known). The values of a' , compared with lead nitrate as unity, are given in tabular form for a number of salts; the values are in all cases less than unity.

Some experiments on adsorption from mixed salt solutions are described. When the salts have a common ion, the degree of adsorption for the components separately is smaller than when the salts are present alone in the same proportion, but if the ions are different there is no reciprocal influence. Highly ionised salts are often adsorbed to a much smaller extent than those only slightly ionised. In explanation of this observation, it is assumed that at the surface of contact water-amorphous substance the adsorbed salt is completely ionised, and the greater the concentration of the dissociation products in the solution the more of the salt is adsorbed. The fact that solutions of neutral salts often become acid or alkaline in the presence of an absorber is due to the different affinity of the latter for the two ions.

The application of the method to qualitative and quantitative analysis is briefly considered. A bibliography of the subject is given.
G. S.

Capillary Constants and Molecular Weights. PAUL DUTOIT and PIERRE MOJOIU (*J. Chim. Phys.*, 1909, 7, 169—188).—Although the method of Ramsay and Shields is generally considered to be the best for determining the molecular weight of a liquid, the work which has been carried out by Guye has shown that the temperature-coefficient (K) of the molecular surface energy often possesses values greater than 2.12; in the case of liquids which have a large molecular volume and a high boiling point, K may even attain the value 3. If Ramsay and Shields' method is considered an exact one, it would be necessary to make the improbable assumption that such liquids are dissociated. The authors put forward a formula connecting the molecular weight (M), vapour pressure (p), and specific cohesion (a^2) which may be used to determine molecular weights, and show that it gives more satisfactory results than Ramsay and Shields' formula.

From a consideration of the relations between the latent heat of evaporation (L), density, thickness of the superficial layer, and specific cohesion of a non-associated liquid, it is shown that L is proportional to a^2 . The values obtained for L/a^2 at the boiling point under a pressure of one atmosphere for eleven different liquids are found to be approximately constant, varying only from 0.0173 to 0.0188, whereas for the same liquids the values of $ML/\gamma(Mv)^{\frac{2}{3}}$ vary from 0.0163 to 0.0205. This same relation may be deduced by a combination of the rules of Trouton ($ML/T = \text{const.}$) and Kistiakowsky ($Ma^2/T = \text{const.}$).

The empirical relation $M = \frac{0.6 T(4.8 - \log p)}{a^2}$, where T is the absolute boiling point under a pressure p , is found to give remarkably good results for pressures up to 1500 mm. Using the results for T , p , and a^2 obtained by other observers, the molecular weights for chlorobenzene, dimethylaniline, ethylene dibromide, benzene, carbon tetrachloride, and quinoline were found to be within 2% of the theoretical.

The authors then describe a simple apparatus by means of which the values of p and a^2 at any particular temperature up to 200° can be readily and simultaneously determined, and give results which they have obtained for twenty-two non-associated liquids. Liquids such as anisole, dimethylaniline, etc., which are dissociated according to

Ramsay and Shields, gave normal results, whilst, on the other hand, pyridine, nitrobenzene, aniline, and benzonitrile were found to be slightly associated at the ordinary temperature, whereas according to Ramsay and Shields they are normal, or else slightly dissociated. Experiments on the associated liquids, water and ethyl alcohol, gave association factors which lie between those found by Ramsay and Shields and Ramsay and Rose-Innes.

In an appendix it is claimed that this research is independent of that of Walden (Abstr., 1909, ii, 119, 122), and, moreover, that it is simpler and gives better results.

T. S. P.

Rate of Evolution and Absorption of Carbon Dioxide by Water. JULIUS MEYER (*Zeitsch. Elektrochem.*, 1909, 15, 249—252).—The surface of a gas bubble in a solution is bounded by a liquid capillary film, in which the concentration of the dissolved substance is different from that in the main bulk of the solution. It is quite analogous to the liquid film which adheres to the surface of a solid immersed in a liquid. Reactions between a gas and a liquid may therefore be treated in the same way as reactions between solids and liquids. The simple case of a series of air bubbles passing through an aqueous solution of carbon dioxide gives the rate of loss of carbon dioxide: $dx/dt = k(c - x)$, an expression which agrees well with Knox's experiments (*Ann. Phys. Chem.*, 1889, [ii], 54, 44). A similar expression applies to the absorption of carbon dioxide, but the experimental results do not agree very well with it.

T. E.

Method of Demonstrating the Phenomenon of Dialysis in a Very Short Time. UMBERTO CIALDEA (*Nuovo Cim.*, 1909, [v], 17, 71—72).—This method makes use of a dialyser containing distilled water in both the inner and outer vessels, into each of which dip two electrodes, consisting of glass tubes with pieces of platinum sealed into the ends and containing a little mercury. The inner and outer liquids are arranged in two different circuits, each of which contains a telephone, and both of which are served by the same induction coil or town mains. When the dialyser contains only water, the telephones show no current, and the same is the case when a colloid, such as ferric hydroxide, is introduced into the inner vessel. But when a few drops of saturated sodium or lithium chloride solution are added, the telephone of the inner vessel circuit sounds immediately, and the other in a few minutes time. It can be shown subsequently that the sodium or lithium chloride has diffused into the outer vessel, but that the colloid remains in the inner one.

T. H. P.

Mathematical Investigation of the Relationships Occurring in the Equilibrium of Binary Mixtures in Solution and in Vapour. WILLY BEIN (*Zeitsch. physikal. Chem.*, 1909, 66, 257—274).—The three binary systems, benzene-ethylene chloride, benzene-carbon tetrachloride, and acetone-chloroform, are dealt with in greater mathematical detail on the lines of Dolezalek's recent paper (this vol., ii, 22), and the conclusions arrived at are in substantial agreement with those already given. For the last two systems, different expressions

are obtained for the respective equilibrium constants in terms of n , $\rho = p/p_0$, and $\sigma = \pi/\pi_0$ (Dolezalek, *loc. cit.*), and corrections are applied which bring into agreement the values of the respective constants obtained by the different expressions. From the values of the corrections, the equilibria in the solutions can then be calculated. In the system acetone-chloroform, the compound present in the liquid phase also exists to some extent in the vapour. G. S.

Three-phase Equilibrium (with a Pressure Minimum) of a Dissociating Compound of Two Components. II. GERARD H. LEOPOLD (*Zeitsch. physikal. Chem.*, 1909, 66, 357—380. Compare this vol., ii, 218).—The complete equilibrium between chloral alcoholate and its components has been investigated. The compound was prepared by mixing chloral and ethyl alcohol in equivalent proportions; it was crystallised from light petroleum, and the last traces of the latter removed by sublimation under reduced pressure.

The true melting point of the compound (the temperature at which crystals of the alcoholate are stable in contact with the fused mass) is 46.6° , but on heating rapidly it only melts at about 55° , owing to the slow attainment of equilibrium. The curve falls steeply on both sides from the melting point, showing that the compound is only slightly dissociated. The eutectic point on the chloral side lies very near 100% of the latter.

The boiling point of the compound is $116.8^\circ/771$ mm.; the mixture of maximum boiling point contains 50.5 mol. % of chloral.

The vapour pressure of the alcoholate itself, as well as those of its saturated solutions in alcohol and chloral, have been determined at different temperatures by a tensimeter. The maximum sublimation point coincides with the melting point, 46.6° , within the limits of experimental error, the pressure at this point being 17.5 mm.; the compound, therefore, behaves like a non-dissociated substance. As the fused compound can readily be supercooled, it was found possible to determine a part of the metastable curve liquid-gas, which is throughout above the sublimation curve, in accordance with theory.

The curve of vapour pressure of saturated solutions of the alcoholate in chloral shows a maximum at 41° , the pressure being 19.8 mm.; but the existence of a minimum could not be determined experimentally, as it lies so near the melting point. The vapour-pressure curve of saturated solutions of the alcoholate in alcohol has a maximum at 38° , the pressure being 22.1 mm. It is shown that certain anomalies in the results obtained by Ramsay and Young (*Trans.*, 1886, 49, 685) for this system are due to the fact that their alcoholate was contaminated with alcohol, so that they measured a section of a three-phase curve instead of a sublimation curve. G. S.

Critical Solution Phenomena and Saturation Curves of the System: Water, Pyridine, and Sodium Carbonate. H. LIMBOSCH (*Bull. Soc. chim. Belg.*, 1909, 23, 179—200).—The author has examined in detail the influence of varying quantities of sodium carbonate on the miscibility of pyridine and water. The observations, which extend from -65° to about 200° , are diagrammatically

presented so as to show the relationship between the various saturation curves.

H. M. D.

The Nature of Liquid ("Flüssige" and "Fliessende") Crystals. GEORG WULFF (*Zeitsch. Kryst. Min.*, 1909, 46, 261—265).—From observations of drops and thin layers under the microscope, the author concludes that the liquid (flüssige) crystals of *p*-azoxyphenetole have a cellular, frothy structure, consisting of a solid skin of birefringent material filled with an isotropic liquid. On the other hand, the "fliessende" crystals of ethyl *p*-azoxybenzoate consist of minute platy crystals with like orientation in a liquid envelope.

L. J. S.

Colloid Chemistry. HENRY R. PROCTER (*Brit. Assoc. Report*, 1908, 201—221).—A résumé of our knowledge of the chemistry of colloids.

T. H. P.

Physico-chemical Properties of the Colloidal Particles or Granules. G. MALFITANO (*Compt. rend.*, 1909, 148, 1045—1047. Compare Abstr., 1906, ii, 647).—The author combats generally the theoretical views put forward by Duclaux (this vol., ii, 303). Freshly prepared ferric chloride solutions pass completely through collodion filters, but hydrolysis occurs when kept, and a certain proportion of the iron and chlorine enter into the colloidal state. The ratio Fe:Cl in the colloid is not an integral atomic one, but varies with the proportions of the two ions in the crystalloid liquid between the particles. If the colloidal particles are separated by the filter and suspended in water, a redistribution of the chlorine occurs, whereby the ratio of iron to chlorine in the colloid is increased. Since the colloid is a variable system, it cannot be said to be purer after washing with water, as Duclaux supposed (Abstr., 1906, ii, 677).

The conductivity of a colloid solution may be more or less than the conductivity of its filtered intergranular liquid, and although colloid particles doubtless have some conducting power when suspended in an electrolyte, the phenomena are too complicated to lead to a value of their separate conductivity. Colloidal particles are supposed to be double compounds, each insoluble molecule being associated with one molecule of an electrolyte, forming complex ions.

The author suggests that the osmotic pressure of colloidal particles is too small to be detected, and attributes the pressures measured by Duclaux to contained electrolytes, such as HCl.

Cryoscopic data are similarly treated.

R. J. C.

The Behaviour of Suspended Matter in Crystalloid and Colloidal Conditions. PAUL ROHLAND (*Physikal. chem. Centr.*, 1908, 6. Reprint).—The sedimentation of suspended particles is only accelerated by the addition of electrolytes when the former are of colloidal nature. The action is ascribed to the destruction of the colloidal envelope of the particles by the electrolytes.

S. B. S.

Theory of Coagulation. NICOLA PAPPADÀ (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 214—216).—The author recalls certain general

deductions which he has already made from observations on the properties of colloidal solutions, and points out that his views are in agreement with ultra-microscopic observations, with the electrical conducting properties, and with the phenomena of coagulation by the action of radium salts.

H. M. D.

Influence of the Colloidal State on Dyeing. LÉO VIGNON (*Compt. rend.*, 1909, 148, 1195—1197. Compare Abstr., 1898, i, 136).—The affinity of roccellin, magenta, and Congo-red for colloidal gelatin and starch has been examined by observing the extent to which the colouring matter diffuses from the dyed jellies when these are immersed in water. It is found that starch resembles cotton, whilst gelatin resembles silk and wool, in its behaviour towards these dyes.

W. O. W.

Decomposition of Substances Allied to Colloids. PAUL ROHLAND (*Zeitsch. angew. Chem.*, 1909, 22, 931. Compare Funk, *ibid.*, 145).—The accelerating effect of the addition of calcium chloride and other salts on the sedimentation of felspar suspensions is attributed to two causes: (1) The electrostatic attractions between the suspended particles, which are surrounded by a colloidal shell, and the electrical charges of the ions; (2) the removal of the colloid water. It is found that substances which are the most hygroscopic have the greatest effects.

Finely-divided particles of talc, alumina, ultramarine, and cement can also remain in suspension for several hours. Suspensions of talc are precipitated by the addition of ammonium carbonate, calcium chloride, or calcium sulphate solutions, and those of alumina by strongly-alkaline liquids. Ultramarine suspensions are caused to deposit by alkalis and various metallic chloride and sulphate solutions.

Finely-divided particles of calcium carbonate, calcium sulphate, and barium sulphate can only remain in suspension for a relatively short time, and the addition of electrolytes has no effect. The conclusion is drawn that the latter type of suspension is of crystalloid nature, whereas the former type is of colloidal nature, that is, the particles are capable of forming in contact with water colloidal substances of the type of silicic acid, aluminium hydroxide, etc. The larger the amount of colloid formed, the greater is the tendency to form permanent suspensions.

J. J. S.

Size and Electric Charge of the Oil Particles in Oil-Water Emulsions. WILLIAM C. MCC. LEWIS (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 211—212).—The emulsion obtained by violently agitating water with a mineral oil (D 0.9) for about forty-eight hours is stable for many weeks, and contains oil particles, the average diameter of which is 4×10^{-5} cm. The emulsions obtained: (1) by boiling water in contact with a small quantity of oil for about thirty hours in a vessel provided with a reflux condenser, (2) by dissolving the oil in alcohol and pouring the solution into water, (3) by the distillation of aniline in steam, all contain oil particles of the same order of magnitude, which is, moreover, the size of the particles in colloidal solutions of metals.

The oil particles are negatively charged, and move with a velocity of 4.3×10^{-4} cm. per second when the potential fall is 1 volt per cm. The difference of potential between the oil particles and the water is 0.05 volt, and the charge on the particles is 4.4×10^{-7} electrostatic units, this being approximately the same as the charge on colloidal metal particles.

H. M. D.

Conception of the Element. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 304—310. Compare Mieli, Abstr., 1908, ii, 478).—The author discusses the various conceptions of the element which have been held from time to time, including those introduced by Boyle, Lavoisier, Ostwald, Mendeléeff, Mieli, etc., and gives the following definitions. An atom is an object such that division thereof by external forces does not yield two or more objects of the same category. Atoms of the elements are complexes of atoms of a lower category which on decomposition yield in the free state electrons or groups of electrons, and the properties of which give them a place in the periodic system. Chemical elements are complexes of properties connected one with the other and passing from one substance to another, the magnitudes of the properties allowing them to be placed in the periodic system.

T. H. P.

True Atomic Weights According to Stas's Determinations.

III. LOUIS DUBREUIL (*Bull. Soc. chim.*, 1909, [iv], 5, 341—348).—By a similar method to that employed in the case of silver (compare Abstr., 1908, ii, 936, 1035; this vol., ii, 140), the author has recalculated the true atomic weights of lead, oxygen, sulphur, and nitrogen from the values obtained by Stas for the analytical ratios $\text{Pb}(\text{NO}_3)_2/\text{Pb}_2$ and PbSO_4/Pb with the following results:

	$\text{Pb}(\text{NO}_3)_2/\text{Pb}$.			PbSO_4/Pb .
Pb	206.9984	206.9983	206.9985	206.9971
O	16.0162	16.0172	16.0150	16.0250
N	14.0054	14.0057	14.0050	—
S	—	—	—	32.0062

M. A. W.

Exact Determination of Water of Crystallisation as Applied to Researches on Atomic Weights. PHILIPPE A. GUYE and DEMETRIUS E. TSAKALOTOS (*J. Chim. Phys.*, 1909, 7, 214—231).—During the last century a great number of atomic-weight determinations have been made which depend on the ratio between an anhydrous salt and the water of crystallisation of the hydrated salt. The method is very convenient, but the preparation of the dry hydrated salt has generally been effected in a purely empirical manner, and the determination of the water of crystallisation has not been exact.

After a discussion, from a physico-chemical standpoint, of the various principles involved, the authors describe special apparatus which they have designed for (a) drying the hydrated salt, (b) dehydrating the salt, (c) weighing the anhydrous salt. A number of experiments have been carried out on barium chloride. The results

show that the ratio $\text{BaCl}_2 \cdot 2\text{H}_2\text{O} / \text{BaCl}_2$ can be determined with great accuracy, the values obtained agreeing with each other to within one part in 10,000—20,000. They cannot be used, however, for the calculation of the atomic weight of barium, since the barium chloride was not quite pure, having been recrystallised in glass vessels, and, moreover, the crystallised salt is probably not a chemical individual but a solid solution of hydrated and anhydrous salt.

T. S. P.

Inorganic Chemistry.

Molecular Condition of Chlorine Exposed to Light. GOTTFRIED KÜMMELL and F. WOBIG (*Zeitsch. Elektrochem.*, 1909, 15, 252—254).—The density of pure chlorine is determined by weighing it in glass bulbs filled (*a*) in the dark, (*b*) when exposed to the light of two arc lamps. The mean of the first set is 2.453, that of the second, 2.476. If bulbs filled in the light are kept in the dark for five or ten minutes before sealing them, the high density is still found. The authors consider that no dissociation occurs, but that possibly the glass takes up chlorine under the influence of light. T. E.

Activity of the Halogens, Chlorine, Bromine, and Iodine in Relation to Salts in General. M. C. SCHUYTEN (*Chem. Zeit.*, 1909, 33, 480. Compare Abstr., 1908, ii, 683).—Experiments showing that several sulphates and nitrates take up traces of halogen, probably by a substitution process. The annexed table shows the results: + positive, - negative, ? uncertain, * precipitate.

H ₂ SO ₄	Pb	Ag	Hg'	Hg''	Cu	Bi	Cd	Al	Cr	Zn	Mn	Fe''	Fe'''	Co	Ni	Ba	Si	Ca	Mg	K	Na	NH ₄
Cl	+		-*	-*	+		+	+	-	-*	+	+	+	+	+	-	-	+	+	?	+	+
Br	+		-*	-*	+		+	+	+	+	+	+	+	+	+	-	-	+	+	+	+	+
I	+		-*	-*	+		+	+	+	+	+	+	+	+	+	-	-	+	+	+	+	+
HNO ₃																						
Cl	+	+	+	+	-	+	-	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Br	+	+	+	+	-	+	-	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
I	+	+	+	+	-	+	-	+	+	+	+	+	+	+	+	+	+	-	+	?	+	+

Salts with acids weaker than the halogen hydrides exhibit this property in a still higher degree, for instance, sodium dihydrogen phosphate. L. DE K.

Hybrid Elements. MAX LE BLANC and D. REICHNSTEIN (*Zeitsch. Elektrochem.*, 1909, 15, 261—264).—The behaviour of iodine, arsenic, antimony, and phosphorus is studied by the method previously applied to tellurium and other elements (Abstr., 1906, ii, 742). An iodine anode dissolves quantitatively in 2*N*-sulphuric acid (when the current density is small) with the valency 5. The same valency is found in solutions of sodium chloride and carbonate and of iodic acid. The iodine therefore dissolves as IO₃'. When used as cathode, the iodine

dissolves with valency 1 in the form of iodion, I' . The potential difference between arsenic and sulphuric acid is almost the same whether the arsenic is anode or cathode, and the same is true when a solution of sodium hydroxide is used as electrolyte. Arsenic dissolves with the valency 3 both as anode and cathode. Antimony behaves in much the same way as arsenic. Its cathodic valency in sodium hydroxide solution could not be determined, because the antimony hydride (or possibly sodium antimonide) formed appeared to decompose at once. Phosphorus exhibited no electromotive activity. T. E.

Preparation of Pure Iodic Anhydride. MARCEL GUICHARD (*Compt. rend.*, 1909, 148, 923—925).—Iodic acid is practically insoluble in nitric acid of $D=1.4$, and the impure acid, prepared by the action of sulphuric acid on barium iodate, can easily be purified by adding the aqueous solution to an equal volume of nitric acid, $D=1.33$, and concentrating until the iodic acid separates. The process is repeated several times if necessary. When iodic acid is prepared by the action of fuming nitric acid on iodine, the yield is only about 4%, but a yield of 40% is obtained by the action of the vapour of nitric anhydride on iodine. The iodine, wetted with fuming nitric acid, is spread out in a tube 80 cm. long and 2.5 cm. wide, which is connected to a tubulated retort, in which the nitric anhydride is prepared by gently heating a mixture of fuming nitric acid and phosphoric oxide. G. S.

Influence of the Silent Electric Discharge on Certain Mixtures of Gases and Vapours. EZIO COMANDUCCI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], 15, 15—17).—When a mixture of oxygen and an oxidisable substance is subjected to the action of the silent discharge, for instance, by being passed through an ozoniser, the substance undergoes more or less oxidation, no more ozone being formed (compare Losanitsch and Jovitschitsch, *Abstr.*, 1897, i, 179; 1908, i, 866, ii, 32; Löb, *Abstr.*, 1908, i, 117).

Thus water is formed from oxygen and hydrogen when these are in almost equal proportions, or when the latter predominates, but if the oxygen is in excess, water and ozone are formed, and not hydrogen peroxide. Chlorine or hydrochloric acid and oxygen yield hypochlorous anhydride or acid, the amount of the latter being, in one instance, 6.59% of that of the hydrogen chloride taken. Mixed with oxygen, methyl and ethyl alcohols give the corresponding aldehydes; ethyl ether, acetaldehyde and paraldehyde give acetic acid, and formaldehyde, formic acid.

The hydrogenating power of hydrogen is increased by the dark discharge; thus a good yield of hydrogen chloride is obtained from hydrogen and chlorine, whilst acetaldehyde and hydrogen give ethyl alcohol.

Carbon disulphide and acetone are not oxidised by this method; ammonia yields traces of hydroxylamine, but no hydrazine or nitrous acid; carbon monoxide and chlorine do not react. T. H. P.

Hydrogen Persulphides. GIUSEPPE BRUNI and ALESSANDRO BORGIO (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 355—361).—The authors have

investigated the persulphides, H_2S_2 and H_2S_3 (compare Bloch and Höhn, Abstr., 1908, ii, 579), by the methods previously employed by them (Abstr., 1908, ii, 102).

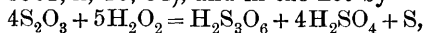
Attempts to prepare higher sulphides by leaving hydrogen disulphide or trisulphide in contact with sulphur for forty-eight hours at the ordinary temperature, either alone or dissolved in bromoform, were unsuccessful. The successive decomposition of the various hydrogen polysulphides, $\text{H}_2\text{S}_7 \rightarrow \text{H}_2\text{S}_6 \rightarrow \text{H}_2\text{S}_5 \rightarrow \text{H}_2\text{S}_4 \rightarrow \text{H}_2\text{S}_3 \rightarrow \text{H}_2\text{S}_2 \rightarrow \text{H}_2\text{S}$, is hence not a reversible reaction.

The authors reply to Paternò's criticisms (this vol., ii, 118) on their former work (*loc. cit.*) (compare also Borgo and Amadori, this vol., ii, 309; Schenck and Falcke, Abstr., 1908, ii, 762). T. H. P.

Action of Hydrogen Peroxide on Thiosulphates in Presence of Metallic Salts. NAZARENO TARUGI and G. VITALI (*Gazzetta*, 1909, 39, i, 418—425).—Phenolphthalein, which was employed by Willstätter (Abstr., 1903, ii, 543) for measuring the alkalinity developed in the interaction of hydrogen peroxide and a thiosulphate, is useless for this purpose, since, when the hydrogen peroxide is perfectly neutral, a solution alkaline to this indicator is never obtained.

With methyl-orange, however, the alkalinity produced corresponds with the equation: $2\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}_2 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaOH}$. After an hour, the alkalinity towards methyl-orange diminishes, and the liquid ultimately assumes a degree of acidity equal to that obtained when phenolphthalein is employed. Estimation of the SO_4 ion as barium sulphate shows that the whole of the thiosulphate exists finally as sulphate.

When the reaction takes place in presence of a salt the corresponding hydroxide of which is insoluble, such as a zinc, nickel, or cobalt salt, there is immediate precipitation of the hydroxide, and the solution remains perfectly neutral; in this manner any possible action of the hydroxyl ions on the ions derived from the dissociation of the thiosulphate is avoided. Calculation of the alkalinity developed from the amount of metallic hydroxide precipitated shows that this alkalinity is exactly double that indicated by methyl-orange, so that the whole of the sodium thiosulphate is transformed into sodium hydroxide according to the equation: $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}_2 = 2\text{NaOH} + \text{S}_2\text{O}_3$. There is then a further action, represented in the cold probably by $4\text{S}_2\text{O}_3 + 5\text{H}_2\text{O}_2 = \text{H}_2\text{S}_4\text{O}_6 + 4\text{H}_2\text{SO}_4$, which is in accord with Nabl's results (Abstr., 1901, ii, 16, 94), and in the hot by



which agrees with Willstätter's results (*loc. cit.*).

Hence, hydrogen peroxide is capable, under the conditions employed by the authors, of causing complete dissociation of sodium thiosulphate into 2Na^+ and $\text{S}_2\text{O}_3^{2-}$, the formation of tetrathionate being due to a secondary action of the S_2O_3 anion with excess of the peroxide, whilst trithionate is formed as the result of decomposition of the tetrathionate by heat.

T. H. P.

Synthesis of Ammonia from its Elements. JAKOB LIPSKI (*Zeitsch. Elektrochem.*, 1909, 15, 189—206).—The dissociation pressure

of cerium nitride is measured. The material used was made either by heating a mixture of cerium dioxide and magnesium in an atmosphere of nitrogen, or from the pure metal and nitrogen. Since the first method yields a mixture of cerium and magnesium nitrides, the dissociation pressure of magnesium nitride was also studied. Equilibrium is attained very slowly; at 320° no measureable pressure was observed, and at 460° the dissociation pressure lies between 6 and 13 cm. of mercury. The experiments with cerium nitride gave somewhat inconclusive results, owing to the very slow change of pressure. The author thinks that equilibrium is probably established quickly on the surface, and that the nitride then dissolves in the metal, further change being then dependent on diffusion in the solid. The pure nitride gave the following pressures: 610° , 34 cm.; 675° , 37 cm.; 715° , 38 cm.; 762° , 40 cm., but the figures are only roughly approximate. Admixture of cerous chloride, or of alkali or earth alkali chlorides, did not accelerate the absorption or evolution of nitrogen.

The author's intention was to try the action of hydrogen and nitrogen on cerium hydride and nitride under pressure at moderately high temperatures; he observed, however, that cerium hydride smells of ammonia when exposed to the air, which led him to work at atmospheric pressure and low temperatures.

When perfectly pure, dry nitrogen is passed over the freshly prepared hydride in the cold, ammonia is formed rapidly (about one half the possible quantity in three and a-half hours); the reaction, however, soon becomes slower, probably owing to superficial formation of nitride. The reaction is $\text{CeH}_3 + \text{N}_2 = \text{CeN} + \text{NH}_3$. Raising the temperature to 200° increases the rate of reaction very little.

No ammonia is formed by the action of hydrogen on cerium nitride in the cold, but the reaction $\text{CeN} + 3\text{H}_2 = \text{CeH}_3 + \text{NH}_3$ takes place at temperatures between 100° and 400° , the best temperature being about 200° ; the rate of formation falls off less rapidly than is the case with the hydride.

By allowing a mixture of hydrogen and nitrogen to act on cerium nitride at 250° , 25.1 c.c. of gas disappeared, and ammonia equivalent to 26.9 c.c. was formed, but the reaction stopped completely in twenty-four hours; the action is, therefore, purely catalytic; traces of oxygen and moisture in the gas possibly account for its cessation.

Experiments made with nitride and hydride, prepared from commercial cerium carbonate by converting this into the dioxide and heating it with magnesium in a current of hydrogen or nitrogen, showed them to be equal to the purer substances.

A number of experiments were made in order to find the best conditions for a continuous production of ammonia. The reaction soon stops if a mixture of nitrogen and hydrogen is used, but it goes on continuously (although slowly) when nitrogen and hydrogen are passed alternately at short intervals. A mixture of hydride and nitride gives the best results, and the rate of production is very much increased by spreading the material out over a large surface

of asbestos, glass wool, or copper gauze. When the contact material is allowed to cool off and remain unused for some hours, its activity increases. The quantity of ammonia produced is proportional to the quantity of contact material used, and independent, within fairly wide limits, of the rate of passage of the gas. The highest concentration of ammonia reached by the author was 6.4% by volume in the gas passed over cerium nitride, and 1.4% over the hydride.

T. E.

Phosphates, their Isomerism and the Transformations they Undergo in Soil. ANTONIO QUARTAROLI (*Staz. sper. agrar. Ital.*, 1909, 42, 121—160).—The author has investigated various phosphates in order to obtain an explanation of the contradictory views concerning their efficacy as manures and the changes they undergo in the soil.

Two forms of dicalcium phosphate exist: (1) the amorphous variety, which undergoes complete solution on addition of a quantity of phosphoric acid sufficient to transform it into the monocalcium salt, and is converted into tricalcium phosphate by means of calcium hydroxide; (2) the crystalline variety, which dissolves with difficulty in citric acid, and is not converted into the tricalcium salt by calcium hydroxide, or into the monocalcium salt by a strong acid.

Further, the amorphous form is markedly decomposed by water, whilst the crystalline form is not. Also, tricalcium phosphate exists in two modifications, one of which is convertible into the dibasic phosphate and is hydrolysed by water, whilst the other cannot be changed into the dibasic salt and is not decomposed by water.

These observations are explained by the author as due to the existence of an asymmetric phosphoric acid, $\overset{+}{\text{H}} \mid \text{H}_2\text{PO}_4$, and a symmetrical one, $\overset{++}{\text{H}_2} \mid \text{PO}_4$, and thus of asymmetric and symmetrical salts, $\text{ca} \mid \text{caHPO}_4$ and $\overset{\text{ca}}{\text{ca}} \mid \text{HPO}_4$, only the former of which is capable of yielding monocalcium phosphate. Similarly, with the tricalcium salt, there should be an asymmetric form, $\text{ca} \mid \text{ca} \mid \text{ca} \mid \text{PO}_4$, two partially symmetrical forms, $\overset{\text{ca}}{\text{ca}} \mid \text{ca} \mid \text{PO}_4$ and $\text{ca} \mid \overset{\text{ca}}{\text{ca}} \mid \text{PO}_4$, and a symmetrical form, $\overset{\text{ca}}{\text{ca}} \mid \text{PO}_4$. Of these, the first is capable of yielding di- and mono-calcium salts and free phosphoric acid when treated with acid, the second giving symmetrical dicalcium phosphate and phosphoric acid, the third, monocalcium phosphate and phosphoric acid, and the fourth, only phosphoric acid.

T. H. P.

Formation of Graphite by the Interaction of Magnesium Powder and Carbonates. H. RUSSELL ELLIS (*Trans. Faraday Soc.*, 1909, 4, 172—174).—In the reduction of barium, strontium, or calcium carbonate by magnesium, the carbon obtained is partly in the

form of graphite. Small quantities of graphite are found in the carbon obtained by passing carbon dioxide over heated magnesium.

C. H. D.

Thiocarbonates. NAZARENO TARUGI and A. MAGRI (*Gazzetta*, 1909, 39, i, 405—418).—When an aqueous solution of potassium thiocarbonate is boiled out of contact with air and in an atmosphere of nitrogen, the first phase of the decomposition occurring is represented by the equation $K_2CS_3 = K_2S + C_2S$. The potassium sulphide thus formed subsequently undergoes hydrolysis, giving potassium hydroxide and hydrogen sulphide: $K_2S + 2H_2O = 2KOH + H_2S$. In presence of air or oxygen, the decomposition of the thiocarbonate effected by boiling its solution is represented by the equation: $2K_2CS_3 + 2H_2O + 4O = K_2S_2O_3 + K_2CO_3 + CS_2 + 2H_2S$. Finally, in an atmosphere of carbon dioxide, decomposition occurs according to the equation $K_2CS_3 + CO_2 + H_2O = K_2CO_3 + CS_2 + H_2S$. The equation $K_2CS_3 + 3H_2O = K_2CO_3 + 3H_2S$, usually given in the literature as representing the decomposition of alkali thiocarbonates in solution, is hence in direct contradiction to the truth.

Under the action of sunlight and in presence of air, solutions of thiocarbonates undergo, at the ordinary temperature and with an increased velocity, the same transformation as takes place on boiling in absence of sunlight. In vessels evacuated and then exposed to sunlight, thiocarbonates remain unaltered for a long time, the equilibrium $K_2CS_3 \rightleftharpoons K_2S + CS_2$ not being disturbed by the removal of one of the products of the decomposition.

Towards organic compounds, thiocarbonates behave in such a way as to confirm the fact that they decompose into a sulphide and carbon disulphide. Thus, with aniline, potassium thiocarbonate yields the condensation product of thioformanilide (compare Nicol, *Abstr.*, 1882, 958).

Under other conditions, thiocarbonates behave like simple sulphides; thus benzoyl chloride and a thiocarbonate in equimolecular proportions yield benzoyl disulphide, which is also formed by the interaction of benzoyl chloride and potassium hydrogen sulphide. T. H. P.

Action of some Oxidising Agents on Silicochloroform. ADOLPHE BESSON and L. FOURNIER (*Compt. rend.*, 1909, 148, 1192—1194. Compare this vol., ii, 398, 399).—In sunlight, dry oxygen slowly attacks silicochloroform at -80° , forming the compound Si_2OCl_6 with other oxychlorides. Ozone has a similar action, but forms, in addition, a small quantity of silica, with oxychlorides of high molecular weight. An explosion occurs when nitrogen peroxide is mixed with silicochloroform at -20° ; when the materials are diluted with carbon tetrachloride, however, a reaction occurs, represented by the equation: $SiHCl_3 + 2NO_2 = SiO_2 + 2NOCl + HCl$.

Silicochloroform reacts with sulphur trioxide at 100° , forming sulphur dioxide, pyrosulphuryl chloride, $S_2O_5Cl_2$, and probably chlorosulphonic acid, together with viscous oxychlorides of silicon. Under certain conditions, a blue compound, probably the oxide, Si_2O_3 , is obtained.

Silicochloroform and chromium trioxide react at the ordinary

temperature, forming oxychlorides of silicon and a compound, Cr_3OCl_7 . This is an unstable, brown powder soluble in water with decomposition.
W. O. W.

Stas's Investigation of the Solubility of Silver Chloride. KARL DRUCKER (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 216—219).—Experimental observations made by Stas in an investigation on the haloid salts of silver (*Oeuvr. compl.*, 1, 87) are reviewed from the colloido-chemical standpoint. The facts indicate the existence of a whole series of reproducible forms of silver chloride ranging from the true gel to the crystalline form. Each of these has a definite solubility, which increases as the colloidal character of the chloride increases. A comparison is made between the influence of the form of the substance on its solubility and that of temperature on the miscibility of two liquids.
H. M. D.

Crystals of Calcium Hydroxide in Roman Cement. SERGEI F. GLINKA (*Zeitsch. Kryst. Min.*, 1909, 46, 303—304; from *Cement*, 1904, 37—43, 217—225).—Small tabular crystals of calcium hydroxide were observed in a hydraulic cement and also in a Roman cement. They are hexagonal, with a perfect basal cleavage, $a:c = 1:1.20$; $D\ 2.254$; $H\ 2-3$; refractive indices, $\omega = 1.644$, $\epsilon = 1.446$. These crystals are not isomorphous with the mineral brucite ($\text{MgO}, \text{H}_2\text{O}$).
L. J. S.

Colloidal Barium Sulphate. ERNEST FEILMANN (*Trans. Faraday Soc.*, 1909, 4, 175—178).—When barium chloride is added to a mixture of sodium sulphate and alkaline casein solution, a creamy liquid is obtained, from which acetic acid precipitates a curd-like mass. After washing and adding sodium hydroxide solution, a milky liquid is obtained, yielding a translucent solid on evaporation. This solid yields a stable colloidal solution. The particles of barium sulphate are probably surrounded by a protective layer of casein.
C. H. D.

Electrical Properties (Thermoelectricity and Resistivity) of Copper-aluminium Alloys. HECTOR PÉCHEUX (*Compt. rend.*, 1909, 148, 1041—1042. Compare this vol., ii, 294).—The author has measured the thermoelectric properties and specific resistance of six commercial copper-aluminium alloys containing 3, 5, 6, $7\frac{1}{2}$, 10, and 94% of aluminium respectively. The *E.M.F.* of a thermojunction of each alloy with electrolytic copper was determined at a series of temperatures up to 820° . The variation of *E.M.F.* with temperature (dE/dt) is in all cases very approximately equal to $(A+Bt)$, where *A* and *B* are constants for each alloy, that is, the *E.M.F.* obeys a parabolic law.

As the percentage of aluminium increases from 3 to 10, the *E.M.F.* of the couple falls, but beyond this increases, so that the *E.M.F.* of the 94% alloy approaches that given by pure aluminium. The order of the alloys in this property, which is not the same as their order in composition, is often modified by temperature changes.

A small proportion of aluminium greatly increases the resistivity of copper, but addition of 6% of copper to aluminium does not increase the resistance of the latter. The alloy $7\frac{1}{2}\%$ aluminium, $92\frac{1}{2}\%$ copper exhibits a maximum of resistivity.
R. J. C.

Cuprous Hydroxide and Cuprous Oxide. HORACE W. GILLET (J. *Physical Chem.*, 1909, 13, 332—335).—It is known that yellow cuprous hydroxide or red cuprous oxide, or a mixture of the two, is obtained by electrolysis of sodium chloride solution between copper poles according as the temperature is below 60° , above 95° , or intermediate. The author has endeavoured to obtain precipitates of the red cuprous oxide at the ordinary temperature.

Addition of extremely concentrated sodium hydroxide to cuprous chloride dissolved in sodium chloride gives a precipitate of red oxide, but elevation of temperature is much more effective than increase of concentration, although cuprous hydroxide, once formed, cannot be dehydrated by eighty hours' boiling.

The electrolysis of sodium chloride proceeds normally in presence of acid. On the other hand, when only 0.5% of sodium hydroxide is present, oxygen is evolved at the anode, and no oxidation of the copper occurs. With less alkali, in addition to cuprous hydroxide, some indication of oxide is observed. In no case is the amount of oxide formed on the anode more than 1% of the whole precipitate.

When a thick paper diaphragm is interposed between the electrodes, yellow cuprous hydroxide appears on both sides, but unmistakably scarlet oxide is deposited in the paper itself. No explanation of this is offered.
R. J. C.

Isomorphism and Polymorphism of the Mercury Haloids. W. J. LUCIZKY (*Zeitsch. Kryst. Min.*, 1909, 46, 297—298; from *Bull. Ges. Naturf. Kiev.*, 1906, 20, 191—207).—Crystals of mercury iodide, bromide, and chloride, and mixed crystals of the iodide and bromide and of the chloride and bromide (but not of the iodide and chloride) were obtained from solutions in ethyl and methyl alcohols. The several modifications are tabulated as follows:

	HgI ₂ .	HgBr ₂ .	HgCl ₂ .
First modification	Tetragonal	—	—
Second „	Rhombic	Rhombic α	Rhombic β
Thrd „	—	Rhombic β	Rhombic α

Rhombic crystals, probably representing a double salt, $\text{HgCl}_2 \cdot \text{HgBr}_2$, were also obtained.
L. J. S.

Preparation of Pure Cerium Salts and the Colour of Cerium Oxide. ARTHUR C. NEISH (J. *Amer. Chem. Soc.*, 1909, 31, 517—523).—A study has been made of the methods of preparing pure cerium salts, and special attention has been devoted to cerium oxide, CeO_2 , the colour of which has been the subject of much controversy. The following method is recommended for preparing pure cerium salts from the crude oxalate.

The oxalate is first heated with dilute hydrochloric acid in order to

remove iron, calcium, etc., and the residue is treated with hot ammonium oxalate solution. The purified oxalate is then heated with a solution of potassium hydroxide in order to free it from aluminium, etc. The hydroxide thus obtained is dissolved in sulphuric acid, and the solution is treated with potassium sulphate, yttrium, ytterbium, erbium, and samarium being thus eliminated. The crystalline double sulphate produced is dissolved in dilute hydrochloric acid, potassium hydroxide is added, and the mixture is heated until all the cerium has been re-precipitated as hydroxide. The hydroxide is treated with dilute potassium hydroxide, and chlorine is slowly bubbled through the mixture. This treatment is repeated until the oxide is free from lanthanum and didymium. The hydroxide is now boiled with dilute hydrochloric acid, and hydrogen peroxide is added to effect complete solution and reduce the ceric chloride to the cerous condition. After adding concentrated hydrochloric acid and heating the solution nearly to boiling, a solution of oxalic acid is added, and, on cooling, crystals of cerium oxalate separate. By heating this oxalate in hydrogen and afterwards in pure oxygen, pure ceric oxide is obtained. This oxide has a pale yellow colour, resembling that of chamois leather.

The occurrence of a red or pink colour indicates the presence of coloured oxides, whilst if the preparation is very pale or almost white, it contains white oxides as impurities. The colour of the pure oxide is not due to the presence of nitrogen from the air, since the colour is the same whether ignition is carried out in dry air, free from carbon dioxide, or in pure oxygen. E. G.

Heats of Combustion of Aluminium, Calcium, and Magnesium. FRANK E. WESTON and H. RUSSELL ELLIS (*Trans. Faraday Soc.*, 1909, 4, 166—171. Compare this vol., ii, 46).—In further experiments on the thermite reaction, aluminium is found to reduce lime only when heat is supplied; magnesia is not reduced. Heating calcium with magnesia results chiefly in the formation of nitride.

C. H. D.

Peroxides. SEBASTIAN TANATAR (*Ber.*, 1909, 42, 1516—1517).—According to Pellini and Meneghini (this vol., ii, 50), nickel peroxide does not reduce permanganate, contrary to the statement of the author (*Abstr.*, 1900, ii, 211). It is now shown that the peroxide prepared by means of sodium hypobromite reduces permanganate, and that hydrogen peroxide may be prepared from it in quantity by the action of hydrogen cyanide and potassium cyanide. Hydrogen peroxide could not be obtained in this way from cobalt or lead peroxides, or from silver peroxynitrate (*Abstr.*, 1902, ii, 73). The "true nickel peroxide" of Pellini and Meneghini is probably a molecular compound of nickel hydroxide and hydrogen peroxide (compare Willstätter, *Abstr.*, 1903, ii, 537).

C. H. D.

Signification of Colloidal Solutions of Manganese Oxide in Biochemical Oxidations. BOUWE SJOLLEMA (*Chem. Weekblad.*, 1909, 6, 287—294).—The influence of manganese compounds on biochemical oxidations has been investigated. A colloidal solution of an oxide of

manganese higher than manganous oxide was obtained by treating manganese sulphate or acetate with potassium sodium tartrate, and then with hydrogen peroxide and dilute sodium hydroxide. When protected from light, the solution thus obtained remains unaltered for some weeks, retaining its dark brown colour. Its colloidal nature was proved by dialysis. It gives characteristic reactions with oxydase reagents, irrespective of whether it has been dialysed or not. It at once imparts a blue colour to an alcoholic solution of guaiacum resin, and to a solution of *p*-phenylenediamine hydrochloride. In presence of light, it oxidises quinol rapidly, yielding crystals of quinhydrone. Aniline sulphate is at once coloured violet or blue. Pyrogallol is oxidised, yielding a dark-coloured precipitate. It acts as a catalyst, decomposing hydrogen peroxide. It does not oxidise hydriodic acid in neutral, alkaline, or acid solution. It does not oxidise tyrosine in acid or alkaline solution, in this respect resembling the ordinary oxydases.

The oxidation of quinol, pyrogallol, and hydrogen peroxide has been studied qualitatively, the results indicating that a colloidal solution of higher oxides of manganese behaves in many respects like an oxydase. The author considers that the part played by manganese in biochemical oxidations is often important, and probably also in oxidations in the soil.

A. J. W.

Preparation, Composition, and Thermal Properties of Electrolytic Iron. ARTHUR MÜLLER (*Metallurgie*, 1909, 6, 145—160).—For the preparation of electrolytic iron from ferrous ammonium sulphate, anodes of pure iron should be used, enclosed in porous cells, and the anode mud frequently removed. Low current density and temperature should be employed. The cathode deposit still contains some sulphur, and to obtain a pure product the electrolysis should be repeated, using ferrous chloride as the electrolyte. The final product contains only 0.03% total impurities, of which 0.02% is carbon. Hydrogen and nitrogen are also present to the extent of 0.02—0.08% and 0.02—0.03% respectively.

The thermal behaviour has been investigated, using a vacuum furnace with carbon spiral resistance, the construction being a modification of that adopted by Oberhoffer (*Abstr.*, 1907, ii, 736). In this furnace, 70 grams of iron may be raised to above 1700° in twenty minutes.

After melting in a magnesia crucible, the iron contains 0.017% C, 0.089% Si, 0.028% P, 0.025% Mn, and 0.037% S. The values found for the critical points are Ar_3 894°, Ac_3 917°, Ar_2 763°, Ac_2 770°. A critical point between 1000° and 1500° could not be observed. The iron, after melting, is silver-white with crystalline fracture. It is perfectly malleable, and so soft as to be cut with a knife. C. H. D.

The Electrolytic Theory of the Corrosion of Iron. WILLIAM H. WALKER (*J. Iron and Steel. Inst.*, 1909, i. Compare Walker, Cederholm, and Bent, *Abstr.*, 1907, ii, 875; Friend, *Abstr.*, 1908, ii, 698).—The electrolytic corrosion of iron begins even in the absence of an acid. Ferrous ions pass into the water, hydrogen being deposited

in a film and hydroxyl ions being left in solution. Friend's analytical methods were insufficiently delicate to detect these minute quantities, but both ions may be made evident by the use of gelatin containing potassium ferricyanide and phenolphthalein, called the ferroxyl reagent. In the absence of an acid, the polarising film of hydrogen prevents further action.

C. H. D.

Influence of the Treatment on the Solubility of Iron and Steel in Sulphuric Acid. E. HEYN and O. BAUER (*J. Iron and Steel Inst.*, 1909, i. Compare Abstr., 1908, ii, 849).—The effect of quenching and tempering on the solubility in acid of steel containing 1% of carbon has been studied. The hardened steel (martensite) becomes more soluble in 10% sulphuric acid if reheated until 400° is reached, after which the solubility again diminishes. The steel of maximum solubility is called by the authors "osmondite"; it passes through troostite into martensite, on the one hand, and through sorbite into pearlite, on the other. The troostites leave their whole carbon content in the form of carbon free from iron, whilst pearlite contains only carbide carbon, which is evolved in the form of hydrocarbons in the action of acid.

In the tempering of martensite, the greatest development of heat is below the osmondite point.

Steel containing only 0.07% C also shows a maximum solubility when tempered at 400°, indicating that the allotropy of the iron has an influence on solubility.

The solubility of soft steel is increased by cold-working, but again diminished by reheating, heating even to 100° having a marked effect. A permanent strain of only 2% in length may be detected in this way. On the other hand, cold-worked aluminium is less soluble than annealed metal. The same holds good of copper, but in this case the changes are very small.

C. H. D.

The Decarburisation of Iron-Carbon Alloys. WILLIAM H. HATFIELD (*J. Iron and Steel Inst.*, 1909, i. Compare Wüst, Abstr., 1908, ii, 286).—Experiments with iron containing 1.64% of carbon in the form of cementite show that temper carbon is not formed in the decarburising process, and that practically the whole of the carbon may be removed by oxidation. This disproves Wüst's theory that the carbon is only oxidised after intermediate formation of temper carbon. The results are confirmed by the behaviour of white iron. The reaction between the carbide and the oxidising medium begins at 750°.

C. H. D.

Formation of True Peroxides of Iron. GIOVANNI PELLINI and D. MENEGHINI (*Gazzetta*, 1909, 39, i, 381—398; *Zeitsch. anorg. Chem.*, 1909, 62, 203—217. Compare this vol., ii, 50).—The action of hydrogen peroxide on ferrous or ferric chloride, ferrous hydroxide, or ferric oxide gives rise to a very unstable, pale red substance, which has a less colloidal appearance than ferric hydroxide and all the characters of the true peroxides. The composition of this substance cannot be established with certainty, owing to its instability, to admixture of varying proportions of ferric oxide, and to the presence

of alkali chloride in the precipitates obtained by the action of alkali on ferrous and ferric chlorides. In the peroxides obtained by the authors, the ratio Fe:O never exceeds 2, and, as the results of Manchot and Wilhelms (Abstr., 1901, ii, 658; 1903, ii, 152) and of Just (Abstr., 1907, ii, 852) indicate that the ratio Fe:O cannot be less than 1:3 or more than 1:2, the authors' peroxides correspond with a mixture of ferric oxide and peroxide. The constitution of the peroxide is $\text{Fe} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ or $\text{O}:\text{Fe}\cdot\text{O}\cdot\text{O}\cdot\text{Fe}:\text{O}$.

An alcoholic solution of ferrous chloride exhibits a yellowish-green coloration, the intensity of which is only slightly diminished by intense cold; with ferric chloride, the solution has a yellowish-brown colour, which fades appreciably on cooling. The solution of the ferrous salt reacts energetically with hydrogen peroxide, developing a considerable amount of heat and an intense brown coloration, which is not sensibly lightened by cooling; the solution of the ferric salt reacts at most feebly with hydrogen peroxide, the liquid obtained not differing appreciably from the original solution, and losing its colour in the same way on cooling. This behaviour indicates that some sort of chemical combination takes place between the ferrous salt and hydrogen peroxide, whilst with ferric chloride such combination takes place either not at all or only extremely slowly.

T. H. P.

Chemical and Magnetic Study of Complex Compounds. P. PASCAL (*Ann. Chim. Phys.*, 1909, [viii], 16, 359—402, 520—574). —A résumé of work already published (compare Abstr., 1908, ii, 193, 500, 756, 757, 927, 1013). The ferropyrrophosphates reduce organic compounds at least as readily as do ferrous oxalate or ferrous hydroxide; picric acid, on reduction with ferrophosphates in the cold, yields picramic acid, whilst at 60° the reduction proceeds further, with the formation of nitrodiaminophenol; similarly, trinitroresorcinol yields dinitroaminoresorcinol. Nitrobenzene is not appreciably reduced by ferrophosphates even on prolonged heating at 60°. *p*-Nitrophenol is slowly reduced to *p*-aminophenol, whilst *m*-nitrophenol is readily reduced even in the cold to the corresponding aminophenol and azo-compound.

M. A. W

Revision of the Atomic Weight of Chromium. I. Analysis of Silver Chromate. GREGORY P. BAXTER, EDWARD MUELLER, and MURRAY ARNOLD HINES (*J. Amer. Chem. Soc.*, 1909, 31, 529—541*). —The results of determinations of the atomic weight of chromium hitherto recorded show considerable discrepancy, and a re-determination has therefore appeared desirable. Careful analyses of silver chromate have been carried out, this substance being chosen since it can be obtained of definite composition, and can be completely dried without decomposition. The chromate of silver is also very suitable for the purpose on account of the ease with which its silver can be estimated. In order to determine the ratio of the atomic weight of chromium to that of silver or oxygen, the exact ratio of the atomic weights of silver and oxygen should be known. Although this knowledge is at present

* and *Zeitsch. anorg. Chem.*, 1909, 62, 313—330.

lacking, the data obtained by the analysis of silver chromate will be subsequently available for the calculation of the atomic weight of chromium. The methods employed in preparing pure silver chromate and effecting its analysis are described in detail.

In some experiments, the silver was precipitated as chloride, and in others as bromide. From the average of three experiments with two different samples of the chromate, the ratio $2\text{AgCl}:\text{Ag}_2\text{CrO}_4$ was found to be 0.864094 [$\text{Ag}:\text{AgCl}=0.752632$ (Richards and Wells, *Abstr.*, 1905, ii, 451)], and the percentage of silver in the chromate, 65.0345. From the average of eleven experiments with four different samples of the chromate, the ratio $2\text{AgBr}:\text{Ag}_2\text{CrO}_4$ was found to be 1.13207 [$\text{Ag}:\text{AgBr}=0.574453$ (Baxter, *Abstr.*, 1906, ii, 740)], and the percentage of silver in the chromate, 65.0321. The average result of all the analyses gives $\text{Ag}=65.0333\%$. Assuming certain values for the atomic weight of silver referred to oxygen as 16.000, the atomic weight of chromium is found to have the following values: $\text{Cr}=52.06$ [$\text{Ag}=107.93$]; $\text{Cr}=52.01$ [$\text{Ag}=107.88$]; $\text{Cr}=51.98$ [$\text{Ag}=107.85$].

Pure, unfused silver chromate has D_4^{25} 5.625.

E. G.

Revision of the Atomic Weight of Chromium. II. Analysis of Silver Dichromate. GREGORY P. BAXTER and RICHARD HENRY JESSE, jun. (*J. Amer. Chem. Soc.*, 1909, 31, 541—549*).—Baxter, Mueller, and Hines (preceding abstract) have prepared and analysed pure silver chromate with a view to throwing light on the atomic weight of chromium. A similar investigation has been carried out with silver dichromate, which has the advantages of containing a much larger proportion of chromium than silver chromate and of being readily crystallised from nitric acid, and thus freed from impurities carried down with it during precipitation. The pure salt was carefully prepared and analysed by methods which are described. Silver dichromate cannot be completely dried without decomposition, and, when crystallised from nitric acid, retains traces of the acid. Since, however, the silver and chromium are present in equivalent proportions, the inclusion of mother liquor can do no harm. Estimations were made of moisture and nitric acid in specimens of the salt crystallised from nitric acid of different concentrations.

From the average of nine analyses of three different samples of the dichromate, the ratio $2\text{AgBr}:\text{Ag}_2\text{Cr}_2\text{O}_7$ was found to be 0.869856 [$\text{Ag}:\text{AgBr}=0.574453$ (Baxter, *Abstr.*, 1906, ii, 740)], and the percentage of silver in the salt, 49.9692. Assuming certain values for the atomic weight of silver referred to oxygen as 16.000, the atomic weight of chromium is found to have the following values: $\text{Cr}=52.06$ [$\text{Ag}=107.93$]; $\text{Cr}=52.01$ [$\text{Ag}=107.88$]; $\text{Cr}=51.98$ [$\text{Ag}=107.85$]. These values are identical with those obtained by Baxter, Mueller, and Hines (*loc. cit.*).

Silver dichromate has D_4^{25} 4.770.

E. G.

Solubility of Ammonium Metavanadate. JULIUS MEYER (*Zeitsch. Elektrochem.*, 1909, 15, 266—268).—The solubility of ammonium metavanadate in water is (in gram-molecules per litre): 18° , 0.0372;

* and *Zeitsch. anorg. Chem.*, 1909, 62, 331—343.

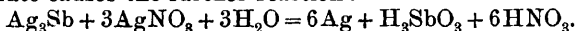
25°, 0.0519; 35°, 0.0898; 45°, 0.1341; 55°, 0.1704; 70°, 0.2599. In 0.05*N*-ammonium chloride solution, the solubilities are: 18°, 0.0142; 25°, 0.0225; 35°, 0.0445; 45°, 0.0757; 55°, 0.0954. In 0.1*N*-ammonium chloride they are: 18°, 0.00356; 25°, 0.00995; 35°, 0.0235; 45°, 0.0451; 55°, 0.0631. Each of these sets of results shows a change of direction in the solubility curve between 39° and 41°, indicating a change in the solid salt at this temperature. The solubility in 0.05*N*- and 0.1*N*-ammonium nitrate solutions are also measured, and found to be very slightly greater than those in the corresponding ammonium chloride solutions. The salt is very much more soluble in ammonia than it is in pure water. In 0.0677*N*-ammonia, the solubilities at 18° are 0.0476, at 25° 0.0603; in 0.2452*N*-ammonia it is at 18°, 0.0680, and at 25° 0.073; in 0.5872*N*-ammonia at 18°, 0.1029, and at 25°, 0.108.

T. E.

Action of Antimony Hydride on Dilute Silver Solutions.

HANS RECKLEBEN (*Ber.*, 1909, 42, 1458—1464).—The black precipitate produced by antimony hydride in silver nitrate solutions has been assumed to have the composition Ag_3Sb (Lassaigne, *J. Chim. Méd.*, 1840, 17, 443), but secondary reactions are known to occur. The precipitate contains oxygen, but not in the form of antimonious acid, which is not produced when dilute nitric acid acts on antimony hydroxide; it has therefore been described as a mixture of metallic silver and antimony hydroxide (Vitali, *Abstr.*, 1893, ii, 206).

Owing to secondary reactions, the method adopted in the case of arsenic hydride (Reckleben, Lockemann, and Eckardt, *Abstr.*, 1908, ii, 36) is not applicable. The black precipitate is decolorised by oxidising agents, of which iodine is the most convenient. Iodine in presence of tartaric acid readily converts metallic antimony into antimonious acid: $\text{Sb} + 5\text{I} + 4\text{H}_2\text{O} = \text{H}_3\text{SbO}_4 + 5\text{HI}$, and the free antimony may be estimated in this way. The result of the analyses shows that the first reaction of antimony hydride with silver nitrate is that described by Lassaigne: $\text{SbH}_3 + 3\text{AgNO}_3 = \text{Ag}_3\text{Sb} + 3\text{HNO}_3$, but that the excess of silver nitrate causes the further reaction:



The final precipitate therefore consists of silver and antimony hydroxide with a little metallic antimony, some antimony at the same time passing into solution.

C. H. D.

Influence of High Potential Discharge on Amorphous Gold.

BAYARD G. COBB (*Chem. News*, 1909, 99, 209—210).—When amorphous gold, precipitated from auric chloride by ferrous sulphate, washed thoroughly many times with nitric acid, and finally with distilled water, is submitted to the influence of the high potential discharge of a ten-inch Rhumkorf coil between platinum electrodes, it becomes active towards a photographic plate, and appears to develop traces of copper. This experiment has been repeated four times with similar results, and, in addition, pure amorphous gold placed between pure platinum electrodes in a partly evacuated glass tube and subjected in a like manner to the high potential discharge for three-quarters of an hour, when subsequently dissolved and analysed, gave even more distinct indications of copper.

J. V. E.

The Supposed Hydrolytic Action of Platinum-black. W. E. GROVE and ARTHUR S. LOEVENHART (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxviii—xxix ; *J. Biol. Chem.*, 6).—After a month no hydrolysis of starch occurred on the addition of platinum-black. The effect observed by others who used large quantities is due to oxidation by the platinum oxides contained in platinum-black, but there is no evidence of catalytic action. W. D. H.

Mineralogical Chemistry.

Paraffin Content of Mineral Oils as Criterion for Judging their Relative Geological Age. MICHAEL RAKUSIN (*Ber.*, 1909, 42, 1211—1215. Compare this vol., ii, 153, 246).—It is found as the result of the investigation of samples of mineral oils from the same district that the percentage of paraffin hydrocarbons present in the natural petroleum decreases with an increase in the geological age of the oil.

It is possible that in nature, fractionation of the mineral oil takes place in a manner similar to that observed by Gilpin and Cram (this vol., i, 1), as a result of which the paraffin hydrocarbons are found nearer the surface than the denser, unsaturated hydrocarbons.

W. H. G.

Gases Occluded in the Lavas of the Last Eruptions of the Mounts St. Pelée and Vesuvius. GROSSMANN (*Compt. rend.*, 1909, 148, 991—992).—Two lavas from each volcano were examined by heating in a vacuum, the gases being absorbed by the usual reagents. Nitrogen was finally absorbed by lithium at a very dull red heat, and the residues were examined spectroscopically. The lava from Vesuvius (1906) contained much more gas than that from St. Pelée (1902). Carbon dioxide, carbon monoxide, hydrogen, and nitrogen were present in all, oxygen and methane only in Vesuvian lavas. Helium was found in one St. Pelée sample, and argon in one from Vesuvius. Ethylene, acetylene, propylene, and benzene were absent. R. J. C.

Composition of Bauxite. H. ARSANDAUX (*Compt. rend.*, 1909, 148, 936—938).—Fifteen specimens of bauxite have been analysed by heating each with concentrated hydrochloric acid for an hour on the water-bath, which extracts all the iron and very little aluminium; the residue containing practically all the aluminium, and also titanium and silicon, is then treated with concentrated sulphuric acid, and the analysis completed in the usual way. By determining the proportion of water in the part insoluble in hydrochloric acid, an approximate value is obtained for the degree of hydration of the alumina. The results show that the proportion of water associated with the aluminium is independent of the proportion of iron in the mineral,

and (in all cases but one) corresponds approximately with the formula $\text{Al}_2\text{O}_3, \text{H}_2\text{O}$. The oxide of iron is practically anhydrous. Titanium is present in very small proportion, and probably exists as metatitanic acid. The proportion of silicon varies considerably. G. S.

Three New Manganese Minerals: Vredenburgite, Sitaparite, and Juddite. L. LEIGH FERMOR (*Rec. Geol. Surv. India*, 1908, 37, 199—212. Compare Abstr., 1907, ii, 700; 1909, ii, 153).—*Vredenburgite* is found as crystalline masses in the manganese deposits at Beldongri in the Nágpur district, Central Provinces, India (anal. I), and at Garividi in the Vizagapatam district, Madras (anal. II). It is dull steel-grey with metallic lustre, and in strong sunlight shows a bronzy colour; the streak is dark brownish-black. There are well-marked octahedral cleavages, indicating that the mineral is either cubic or tetragonal; $H = 6\frac{1}{2}$. A striking feature is the very strong magnetism, equal to that of magnetite, which is often polar in character. The simplest formula is $3\text{Mn}_3\text{O}_4, 2\text{Fe}_2\text{O}_3$. The magnetic character suggests, however, that the iron may be present as Fe_3O_4 , in which case the two analyses give the formulæ $2\text{Mn}_2\text{O}_3, 3(\text{Mn}, \text{Fe})_3\text{O}_4$ and $7\text{Mn}_2\text{O}_3, 8(\text{Mn}, \text{Fe})_3\text{O}_4$ respectively.

	MnO_2	MnO	Fe_2O_3	Al_2O_3	BaO	CaO	MgO	SiO_2	H_2O (at 100°)	H_2O (comb.)	Total	Sp. gr.
I.	23·67	38·24	28·85	1·32	1·30	1·53	0·99	1·77*	0·18	1·32	—	—
II.	24·94	38·53	31·29	2·10	0·03	0·90	1·20	0·20	0·20	0·30	—	—
III.	36·79	26·89	27·60	1·02	0·10	6·14	1·02	1·17	0·09	—	100·82	4·93

	K_2O	Na_2O	S.	P_2O_5	As_2O_5	CoO	CuO	TiO_2	CO_2	Total	Sp. gr.
I.	—	—	—	1·07	0·01	—	—	—	0·09	100·34	4·74
II.	0·06	0·14	0·03	0·03	nil	0·05	0·03	0·14	nil	100·17	4·84

* Combined silica, 0·91; free silica, 0·86%.

Sitaparite is found, together with hollandite and other manganese minerals, at Sitapár in the Chhindwára district, Central Provinces. In its dark bronze-grey colour it closely resembles *vredenburgite*, but it is distinguished from this by being only feebly magnetic. It is brittle with perfect cleavages; $H = 7$; D 4·93—5·09. Analysis III gives the formula $10\text{MnO}_2, 9\text{MnO}, 4\text{Fe}_2\text{O}_3, 3(\text{Ca}, \text{Mg}, \text{Ba})\text{O}$, or more simply, $9\text{Mn}_2\text{O}_3, 4\text{Fe}_2\text{O}_3, \text{MnO}_2, 3\text{CaO}$.

Juddite is a manganiferous amphibole occurring in association with the manganiferous pyroxene *blanfordite* (Abstr., 1907, ii, 701) at Kácharwáhi in the Nágpur district. It is distinguished by its very strong pleochroism—carmine, blue or green, and orange. L. J. S.

Stanniferous Rutile from Vaux (Rhône). GEORGES FRIEDEL and GRANDJEAN (*Bull. Soc. franç. Min.*, 1909, 32, 52—54).—Small crystals, forming an accessory constituent of a very fine-grained biotite-schist, have D 4·238, and contain 1·75% SnO_2 and (approximately) 98·9% TiO_2 . The amount of tin present in the rock itself is 0·0095%, corresponding with 0·54% of stanniferous rutile. L. J. S.

Crystalline Form of Conichalcite. LÉOPOLD MICHEL (*Bull. Soc. franç. Min.*, 1909, 32, 50—51).—Crystals of this rare mineral have

not previously been found. Material from the veins of copper ore (copper-pyrites, malachite, etc.) at Maya-Tass in province Akmolinsk, western Siberia, presents a crystalline structure, and cavities are lined with minute, indistinct crystals. The optical characters point to orthorhombic symmetry. Analysis gave:

As ₂ O ₅ .	P ₂ O ₅ .	CuO.	CaO.	Fe ₂ O ₃ .	MgO.	H ₂ O.	Total.	Sp. gr.
36.40	1.30	31.55	23.10	0.40	1.90	5.15	99.80	4.15

L. J. S.

Artificial and Natural Hydrated Calcium Carbonates.

PETER N. TSCHIRWINSKY (*Zeitsch. Kryst. Min.*, 1909, 46, 302—303; from *Ann. Géol. min. Russie*, 1906, 8, 238—244; *deutsch. Rés.*, 245—249).—The paper of L. L. Iwanoff (*tom. cit.*, 23—25) on the occurrence of hydrocalcite in the neighbourhood of Novo-Alexandria is criticised, and a review is given of the knowledge of the hydrated forms of calcium carbonate. Only three of these, namely, CaCO₃.3H₂O, CaCO₃.5H₂O, and CaCO₃.6H₂O, are regarded as being definitely established, and of these only the first two, distinguished respectively as trihydrocalcite and pentahydrocalcite, are known as minerals. One of the forms described by Iwanoff appears to be a monoclinic or triclinic form of anhydrous calcium carbonate with D 2.626.

L. J. S.

Pyromorphite from Rhenish Prussia. RHEINHARD BRAUNS

(*Centr. Min.*, 1909, 257—264).—A description is given of material from several mines in the neighbourhood of Rheinbreitbach. Dark brown crystals ($a : c = 1 : 0.72926$) from Ägidienberg gave on analysis : PbO, 81.88; P₂O₅, 15.80; Cl, 2.53 = 100.21.

L. J. S.

Phenacite from Brazil. EUGEN HUSSAK (*Centr. Min.*, 1909,

268—270).—Considerable numbers of perfectly colourless and transparent crystals of phenacite have recently been found in a gold mine at San Miguel de Piracicaba, in Minas Geraes; they measure up to 6 cm. across, and are of a flat, rhombohedral habit with numerous bright faces; D 2.97. They occur in a pegmatite-vein together with amazon-stone, quartz, mica, tourmaline, columbite, monazite, xenotime, etc. The xenotime has the form of cubes, being bounded by the tetragonal prism and the basal plane; analysis by G. Florence gave:

P ₂ O ₅ .	Y ₂ O ₃ , etc.	Al ₂ O ₃ + Gl ₂ O ₃ .	SiO ₂ .	Total.	Sp. gr.
33.21	62.62	3.05	1.41	100.29	4.4

L. J. S.

Sardinian Minerals: Mimetite from the Cupriferous Strata of Bena (d) e Padru (Ozieri). AURELIO SERRA (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 361—363).—In these strata, the author finds two varieties of mimetite: one yellow and more frequent, and the other, colourless or white, which occurs rarely. The yellow variety has the composition:

PbCl ₂ .	PbO.	As ₂ O ₅ .	P ₂ O ₅ .	Total.
9.02	67.83	22.89	0.29	100.03

which corresponds with the formula $3[\text{Pb}_3(\text{AsO}_4)_2]\cdot\text{PbCl}_2$, and the axial ratio of the crystals is $a:c=1:0.72840$. The angle $(10\bar{1}1):(0001)$ varies in magnitude with the chlorine-content of the mineral, its value being (1) $40^\circ 4'$ for the yellow variety, which contains 2.30% Cl, and (2) $39^\circ 52'$ for the white variety, containing 2.44% Cl.

T. H. P.

Weathering Processes. KONSTANTIN D. GLINKA (*Zeitsch. Kryst. Min.*, 1909, 46, 283—287; from *Trav. Soc. Nat. St. Pétersbourg*, 1906, 34, 1—175; *deutsch Rés.*, 175—178).—A detailed study was made of the action of weathering processes on silicates, more especially of aluminosilicates, not only in the surface soil, but also in the sub-soil where humus is absent. Numerous analyses are given of various rock-forming minerals and zeolites and of their weathering products. Experiments were also made to determine the action of water, carbonated water, dilute acid solutions, and humus acid solutions on these minerals. It is shown that one and the same mineral may give rise to different products according to the conditions of weathering to which it has been subjected, the presence or absence of humus acid being of importance in this direction.

L. J. S.

Allophane from Abbey Wood, Kent. R. H. CHANDLER (*Geol. Mag.*, 1909, [v], 6, 222—223).—A considerable amount of allophane was found in a denehole at Abbey Wood near Woolwich; it forms a seam between the Thanet Sand and the Chalk, and along a fault fissure extends downwards into the Chalk. The material is cream or buff-coloured and friable. Analysis by J. L. Foucar gave:

SiO_2	Al_2O_3	CaO	Fe	H_2O Loss on ignition (at 100°). ($\text{H}_2\text{O} + \text{CO}_2$).	Total.
28.80	23.52	2.45	trace	23.19 20.77	98.73

L. J. S.

Studies of Garnet. MAX [PAUL WILHELM] SEEBACH (*Zeitsch. Kryst. Min.*, 1909, 46, 312—315; from *Inaug. Diss., Heidelberg*, 1906, 1—64).—The following varieties of garnet were examined with a view to determining how far the material, after fusion, is decomposed by hydrochloric acid. For the complete analyses the material was decomposed by fusion with boron trioxide. Determinations were also made of the sp. gr. and the refractive indices of the material both before and after fusion. Melanite from Frascati (anal. I—IV), after fusion, is not completely decomposed by hydrochloric acid. Demantoid from Polewskoi Zawod, Urals (V and VI); also not completely decomposed. Pyrope from Meronitz, Bohemia (VII and VIII); over 16% is insoluble in hydrochloric acid; the fused material in this case was not an isotropic glass, but contained octahedra, probably of chromite, set in a birefringent ground-mass. Pyrope from Colorado River, Arizona (IX and X). Almandine from Ceylon (XI and XII) fuses to a black, strongly magnetic glass, of which about 28% is not decomposed by acid; the isotropic glass contains skeletal crystals, probably of magnetite. Almandine from Jeypur, India (XIII and XIV); 26% insoluble.

Andradite from Dognaczka, Hungary (XV and XVI); the crystals show a zonal structure with isotropic and birefringent bands; the fused glass is practically all decomposed by hydrochloric acid. Grossular from Xalostoc, Mexico (XVII and XVIII); completely decomposed.

	SiO ₂ .	TiO ₂	Al ₂ O ₃ .	Fe ₂ O ₃ .	Cr ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Total.	Sp. gr. after fusion.	Sp. gr.
I.	34.47	2.63	5.56	21.31	—	1.99	0.56	32.01	1.66	100.29	3.774	3.263
II.	34.98	1.47	5.29	22.36	—	1.99	0.56	32.83	1.49	100.97		
III.	34.21	2.04	5.74	21.90	—	1.99	0.60	32.93	0.98	100.39		
IV.	35.29	—	5.17	22.22	—	1.99	0.78	32.59	0.14	99.91*		
V.	35.44	—	1.63	28.80	1.36	0.52	0.29	32.18	0.16	100.38	3.801	3.335
VI.	35.30	—	1.45	28.98	1.29	0.52	0.38	32.34	0.25	100.51		
VII.	42.94	—	21.43	1.00	1.97	7.80	0.47	4.42	20.52	100.55		
VIII.	43.02	—	21.24	0.90	2.15	7.80	0.53	4.52	20.82	100.98	3.679	3.251
IX.	43.29	—	20.87	—	2.50	10.21	0.58	4.62	18.26	100.33		
X.	43.45	—	21.12	—	2.21	10.21	0.46	4.45	18.58	100.48	3.715	3.190
XI.	37.34	—	19.39	3.37	—	35.45	1.29	2.42	1.20	100.46†		
XII.	37.16	—	19.47	3.21	—	35.45	1.18	2.59	1.06	100.12	4.025	3.240
XIII.	38.11	—	19.56	2.13	—	31.58	1.40	5.11	2.80	100.69		
XIV.	38.03	—	19.70	2.19	—	31.58	1.31	4.95	2.73	100.49		
XV.	36.74	—	1.51	29.19	—	0.69	0.29	31.41	0.69	100.52	3.600	3.171
XVI.	36.84	—	1.27	29.41	—	0.69	0.23	31.38	0.85	100.67		
XVII.	40.75	—	21.62	0.21	—	0.43	1.18	35.52	0.30	100.42‡		
XVIII.	40.82	—	21.78	0.15	—	0.43	0.95	35.73	0.48	100.74	3.506 2.866	

* Including K₂O, 0.14.

† Na₂O, trace.

‡ Loss on ignition, 0.41.

|| Loss on ignition, 0.40.

The fusing of garnets is thus accompanied by a decrease in sp. gr. of 12.5—20%, and the refractive indices are also lowered by 4.2—6.6%.

L. J. S.

Basalts from the Plateau Round Tiesi, Northern Sardinia. AURELIO SERRA (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 399—405).—The author describes various samples of basalt from different points of the plateau surrounding Tiesi.

(1) From Monte Santo.—The fundamental mass consists of slender, felspathic strips, embedded in which are crystals of labradorite, olivine, delessite, augite, apatite, ilmenite, and magnetite. Its chemical composition is:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	TiO ₂ .	P ₂ O ₅ .	CaO.
53.15	24.47	1.40	3.60	0.32	0.60	0.56	6.83
MgO.	K ₂ O.	Na ₂ O.	H ₂ O (at 110°).	H ₂ O (at red heat).	Total.		
1.22	2.59	4.97	0.20	0.57	100.48		

These results correspond with 1.3RO, R₂O₃, 3.80SiO₂; R₂O:RO = 1:1.99.

(2) From Monte Pelao.—The stripy felspar exhibits inclusions of labradorite, olivine, augite, hypersthene, magnetite, apatite, and granules of oxidised iron formed by alteration of the olivine and magnetite. The composition is:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	TiO ₂ .	P ₂ O ₅ .	CaO.
53.36	23.17	1.92	3.34	0.48	0.59	0.60	7.34
MgO.	K ₂ O.	Na ₂ O.	H ₂ O (at 110°).	H ₂ O (at red heat).	Total.		
0.89	3.08	4.62	0.55	0.83	100.77		

These numbers lead to the formula : $1.6\text{RO}, \text{R}_2\text{O}_3, 3.94\text{SiO}_2$; $\text{R}_2\text{O} : \text{RO} = 1 : 2.3$.

(3) From Monte Giave.—The matrix consists of small microliths of felspar containing crystals of plagioclase, augite, and olivine, and small granules of magnetite. Analysis gives the following results :

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MnO .	TiO_2 .	P_2O_5 .	CaO .
52.14	21.89	1.74	3.50	0.40	0.51	0.77	9.16

MgO .	K_2O .	Na_2O .	H_2O (at 110°).	H_2O (at red heat).	Total.
2.81	2.34	4.15	0.32	0.93	100.66

the formula being $1.8\text{RO}, \text{R}_2\text{O}_3, 4.08\text{SiO}_2$.

These rocks are more acid, and contain more alkali, than the mean of 19 basalts examined by Loewinson-Lessing (*Studien über Eruptivgesteine*, Internat. Geol. Cong., St. Petersburg, 1899, 193—461), the mean formula being $2.64\text{RO}, \text{R}_2\text{O}_3, 4.63\text{SiO}_2$; $\text{R}_2\text{O} : \text{RO} = 1 : 7.85$. The rocks examined by the author are evidently intermediate to the andesites and basalts, and approximate the more nearly to the former class. They differ considerably from the more recent eruptive rocks of Northern Sardinia (compare this vol., ii, 156), the mean formula for which is : $1.9\text{RO}, \text{R}_2\text{O}_3, 4.09\text{SiO}_2$. T. H. P.

Chemical Composition of the Deposits from the Thermal Waters of Uriage (Isère). GUSTAVE MASSOL (*Bull. Soc. chim.*, 1909, [iv], 5, 404—405. Compare Abstr., 1908, ii, 1004).—The waters of the thermal spring of Uriage deposit on cooling a pale yellowish-grey solid, soft and oily to the touch, and consisting of sulphur, 56.4% ; mineral matter, 35.94% ; organic matter, 6.44%, and moisture, 1.22%. The sulphur is almost entirely soluble in carbon disulphide ; the organic matter contains nitrogen ; the mineral matter is composed chiefly of silicic acid, and, in addition to the elements calcium, magnesium, and arsenic found by Lefort, contains also zinc, manganese, lead, and copper.

M. A. W.

Physiological Chemistry.

Biological Oxidation. CARL ENGLER and REGINALD O. HERZOG (*Zeitsch. physiol. Chem.*, 1909, 59, 327—375).—A discussion mainly historical and theoretical of the knowledge of oxidation in the body. The organism takes in gaseous oxygen, and the first phase of its action is an auto-oxidation with the formation of additive compounds of the autoxidisable substances with a molecule of oxygen, for which the name *moloxides* is suggested; the action of peroxides on “acceptors” and the part played by oxydases are also considered. The oxydases are regarded as enzymes in the sense of catalytic agents. W. D. H.

The Partition of the Sugar in Blood. ADOLF HOLLINGER (*Biochem. Zeitsch.*, 1909, 17, 1—12).—In normal circumstances the fluid and corpuscular portions of the blood contain about the same amount of sugar. In the majority of cases of hyperglycemia, the amount in the corpuscles increases more than that in the plasma. It is therefore necessary in every case to make an estimation in the whole blood.
W. D. H.

Enzyme Concentration in Saliva. J. G. RYAN (*Amer. J. Physiol.*, 1909, 24, 234—243).—The rabbit's submaxillary saliva contains no diastase; the parotid saliva contains about the same concentration of ptyalin as human parotid saliva, but cases are found where the enzyme is absent both in the parotid saliva and serum of rabbits. Most ptyalin is obtained in saliva obtained by stimulating the cervical sympathetic nerve, or by lessening the blood supply of the gland. During prolonged secretion, the ptyalin concentration falls off and may reach zero. The same is probably true for enzyme concentration in other secretions.
W. D. H.

Enterokinase in Infancy. ARTHUR E. AUSTIN (*Proc. Amer. Soc. Biol. Chem.*, 1908, viii—ix; *J. Biol. Chem.*, 6).—Extracts of the pancreas of infants, from twenty-four days of age onwards, contained trypsin at least partly activated. The intestinal mucous membrane of the same children, irrespective of age or cause of death, contained enterokinase. No antikinase was discovered.
W. D. H.

Human Pancreatic Juice. HAROLD C. BRADLEY (*J. Biol. Chem.*, 1909, 6, 133—172).—Owing to an accident followed by an operation, the opportunity occurred of obtaining for some time a supply of human pancreatic juice. Its specific gravity was about 1.010; its alkalinity varied from a *N*/10 to a *N*/20 sodium hydrogen carbonate solution. No definite relation occurred between diet and enzyme content. The amount of enzymes varies a good deal, except amyllopsin, which was fairly constant from day to day. When excreted slowly, the juice is more concentrated in total solids, carbonates, and lipase. Rennin, invertase, and lactase were not found. Neither manganous sulphate nor bile accelerated its power to digest starch. Trypsin was found in about half the samples; the inactive samples became gradually active after a time, even in the presence of toluene or chloroform. Activation was rapidly brought about by enterokinase. Saponification, both of olive oil and of ethyl butyrate, varied in a parallel way in the different samples; probably a single enzyme is concerned in both cases. Bile exercises a two-fold influence on the digestion of olive oil: it assists emulsification, and protects the enzyme from the inhibitory action of the acid liberated. The effect on the digestion of ethyl butyrate is more complex; it inhibits or accelerates according to its concentration.

The hydrolysis of olive oil proceeds at first as an autocatalytic reaction. This may be due to soap formation and consequent emulsification. At certain stages there is a constant relation between the amount of acid liberated and the time of the reaction. Continuous shaking inhibits the reaction. This may be due to air bubbles diminishing the surface contact between zymolite and enzyme. Up to

30°, rise of temperature increases the reaction, and above that inhibition occurs by an increase in the inhibitory effect of the oleic acid; at 50°, the enzyme is weakened, and about 60°, it is destroyed.

W. D. H.

Activation of Pancreatic Juice. BARBARA AYRTON (*Quart. J. Exp. Physiol.*, 1909, 2, 201—217).—Pancreatic trypsinogen may be activated by enterokinase, and also by calcium salts, probably by chemical action. The spontaneous activation which occurs when the juice is kept free from the enterokinase is mainly due to the presence of calcium salts in the juice. But some other factor is present, for, after decalcification, addition of calcium salts does not produce activation. Excess of calcium salts inhibits activation. Spontaneous activation is accelerated by heat; the calcium reaction of the juice is not affected by changes of temperature under 40°; activation by enterokinase is retarded at 35°, as the enzyme is destroyed by that temperature in an alkaline medium; in a neutral medium, elevation of temperatures quickens activation.

W. D. H.

Action of Electrolytes on the Hydrolysis of Fats by the Pancreatic Secretion. ÉMILE F. TERROINE (*Compt. rend.*, 1909, 148, 1215—1218).—Experiments are described bearing on the influence exerted by the sodium halides, and by the chlorides of calcium, barium, and magnesium, on the pancreatic hydrolysis of fats. The experiments do not support the view that these salts accelerate digestion by facilitating the formation of fatty emulsions.

W. O. W.

Metabolism of a Breast-fed Infant. SAMUEL AMBERG and W. P. MORRILL (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxxv—xxxvi; *J. Biol. Chem.*, 6).—Details are given of the nitrogenous metabolism in an infant a month old, for two periods in which it received different amounts of milk. The retention of nitrogen decreased with advance in age. The ammonia coefficient is not so much dependent on the amounts of protein and fat in the food as on the ratio between them. In the first period the fat:protein ratio was 3.2:1, and the ammonia coefficient, 8.1%; in the second period, on a scantier diet, the F:P ratio was 5.1:1, and the ammonia coefficient, 18.3%.

W. D. H.

Influence of Salicylic Acid and its Isomerides on Metabolism. ELBERT W. ROCKWOOD (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxxv; *J. Biol. Chem.*, 6).—In a purine-free diet in man, the ortho-compound increases the output of uric acid, possibly because it inhibits the uricolytic enzyme. *m*- and *p*-Hydroxybenzoic acids have no such effect.

W. D. H.

The Transfer of Protein in Inanition. ALBERT WOELFEL (*J. Biol. Chem.*, 1909, 6, 189—201).—It is well known that in inanition certain organs, such as the brain and heart, are nourished at the expense of less important organs. This suggests that the same may occur even when food is taken, and the suggestion occurred that a

difference in the autolysis of some tissues might account for their lability and the transfer of protein to other tissues. A large number of autolysis experiments are recorded in detail which, although of interest in themselves, did not solve the problem, nor do they entirely exclude the suggestion mentioned. Among the points made is this : the blood-free tissues from fasting animals show no marked difference in autolytic properties from normal tissues, hence there is no evidence of increased autolysis, or diminution of anti-enzymes in starvation.

W. D. H.

The Physiological Protein Minimum. LOUIS MICHAUD (*Zeitsch. physiol. Chem.*, 1909, 59, 405—491).—A point hitherto neglected in considering the effect of giving to a starving animal the same amount of protein as it loses during inanition, is the kind of protein used. A mere nitrogen estimation in the food-protein is insufficient ; the proportion between the cleavage products is important. It is shown by experiments on dogs that a protein foreign to the body, such as edestin, will not produce equilibrium if given in quantity equal to the protein lost during inanition, but this can be accomplished if protein obtained from dog's muscle, blood, and other organs is administered ; horse flesh or casein are not so readily built into the dog's organism. By alternate periods of feeding and inanition, the protein minimum is reached in a staircase-like manner until it reaches 0.1 gram nitrogen per kilo. of body-weight.

W. D. H.

Fat Absorption. R. H. WHITEHEAD (*Amer. J. Physiol.*, 1909, 24, 294—296).—If cats are fed on fat coloured with Sudan-red III, the globules found after absorption in the villi are uncoloured. This is additional evidence in favour of the view now generally held that fat-splitting occurs before fat products are absorbed by the intestine.

W. D. H.

Absorption of Phenol from the Alimentary Canal. PAUL HANZLIK and TORALD SOLLMANN (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxxvii ; *J. Biol. Chem.*, 6).—If concentrated phenol is introduced into the stomach or intestine of cats and dogs in the dose of 1 gram per kilo. of body-weight, about 38% is absorbed within five minutes, and then absorption completely ceases ; the cause of the arrest is not clear, for it is stated not to be due to corrosion, or local injury, or low blood-pressure, or re-excretion, or to a greater solubility in the gastric contents.

W. D. H.

The Fats of Hens' Eggs. RAFFAELE PALADINO (*Biochem. Zeitsch.*, 1909, 17, 356—360).—The yolk of hens' eggs contains both liquid and solid fats, amongst the products of hydrolysis of which were oleic, palmitic, and stearic acids. Phosphoric acid, iron, and sulphur were also found. Formic acid was probably also present.

S. B. S.

Origin and Destiny of Cholesterol in Animals. III. **Absorption of Cholesterol.** CHARLES DORÉE and JOHN A. GARDNER. IV. **Cholesterol of Eggs and Chicks.** G. W. ELLIS and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1909, B, 81, 109—128, 129—132. Compare Abstr., 1908, 514).—Consideration of the

previous work of the authors and of others appears to show that some of the cholesterol of the bile is the débris of blood-corpuscles and other cells; this cholesterol is, however, re-absorbed and used in the making of new cells; the faeces of herbivora is free from cholesterol, and in carnivora, the faecal cholesterol is accounted for by that in the food, which may on certain diets be partly converted into coprosterol. There is, however, wastage of cholesterol through the skin, and the question arises how this is made good. Feeding experiments were therefore undertaken, and in rabbits considerable absorption of cholesterol added to the food occurs, and the percentage in the blood rises. In cats a difficulty arose in not at first being able to devise a diet free from cholesterol, and so the results are not so clear. This difficulty has now been overcome and further work promised. In the experiments on eggs and chicks, no synthesis of cholesterol was found to occur during embryonic development. W. D. H.

A Mono-aminodiphosphatide in Egg-Yolk. HUGH MACLEAN (*Bio-Chem. J.*, 1909, 4, 168—174).—The ethereal extract of egg-yolk contains ordinary lecithin, and also a mono-aminodiphosphatide which is somewhat different from the cuorin of heart-muscle. The difference probably depends on the presence of different fatty-acid radicles. The ethereal extract also contains pure tripalmitin. W. D. H.

Globulins of Egg-Yolk of Selachians. CARL L. ALSBERG (*Proc. Amer. Soc. Biol. Chem.*, 1908, xiii; *J. Biol. Chem.*, 6).—The ovarian eggs of the skate contain a characteristic vitellin, but in the eggs of the spiny dogfish none could be found. As the skate is oviparous and the dogfish viviparous, this may have a biological significance. W. D. H.

Chemical Analysis of Brain. WALDEMAR KOCH and SYDNEY A. MANN (*Arch. Neurol. and Psychiat. London County Council*, 1909, 4, 174—219).—The methods employed for the separation and estimation of the numerous constituents of nervous material are described with some fulness. As the brain grows, there is a decrease in the proportion of moisture, proteins, extractives, and ash, and an increase in the galactosides, lipoids, and cholesterol. There is an increase in lipid sulphur and phosphorus, but a decrease in neutral and inorganic sulphur and extractive phosphorus. A comparison of the human brain with that of other animals is deferred. In non-nervous disease the variations from the normal are unimportant. Examination of the brain in cases of dementia præcox confirm those previously published (*Abstr.*, 1908, ii, 52). In general paralysis, the destructive disease attacks the brain tissue as a whole, but the phosphatides appear to be the most readily destroyed constituents. The change in the neutral sulphur content which occurs in dementia præcox is not seen in general paralysis. W. D. H.

Influence of Age on the Quantity and Chemical Distribution of Phosphorus in Nerves. CHARLES DHÉRE and H. MAURICE (*Compt. rend.*, 1909, 148, 1124—1125).—Determinations have been made of the amount of phosphorus in the dried peripheral nerves of dogs

varying in age from four weeks to eight years. It is found that the total phosphorus diminishes as the age increases; the same is true of the lipid, nucleic, and inorganic phosphorus, although to a different extent in each case. When the amount of phosphorus in these states of combination is expressed as a fraction of the total phosphorus, it is found that whilst the proportion of inorganic phosphorus diminishes, the proportion of lipid and nucleic phosphorus increases with age.

W. O. W.

The Potassium in Cerebro-spinal Fluid. VICTOR C. MYERS (*J. Biol. Chem.*, 1909, 6, 115—131).—The cerebro-spinal fluid alters rapidly after death, probably owing to changes in the permeability of the cell wall in nervous structures; this especially leads to a rise in potassium, and occurs in health and disease. In degenerative nervous diseases, the amount of potassium in the fluid is not increased during life. There is a similar increase in the phosphates after death. Sulphates are present in the merest traces both during life and after death. The sugar in the fluid usually disappears after death. The proteins are increased in dementia paralytica during life. The occurrence of choline was not investigated.

W. D. H.

Effect of Salts on the Frog's Heart. F. C. COOK (*Amer. J. Physiol.*, 1909, 24, 263—268).—From a small number of experiments, the conclusions are drawn that nitrites in small doses slightly stimulate the heart, and that certain nitrates have a similar effect. The sulphates (except those of iron and hydrogen) increase the heart's rate, and chlorides produce the same result, except those of strontium and potassium.

W. D. H.

Retention of Alkali by the Kidney. LAWRENCE J. HENDERSON and H. M. ADLER (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxxviii—xxxix; *J. Biol. Chem.*, 6).—Urine is treated with potassium oxalate, filtered, diluted, and titrated with decinormal sodium hydroxide, using neutral-red as indicator. The end point is found by matching the colour with that given by a standard phosphate solution possessing the same reaction as blood. The result of the titration *plus* the urinary ammonia measures the alkali retention.

W. D. H.

The Action of Gases on Autolysis, with Special Reference to their Action on Metabolism. ERNST LAQUEUR (*Schrift. Physikal. ökonom. Ges. Königsberg*, 1909, 1; Reprint).—Under certain conditions in life, when an oxygen deficiency and excess of carbon dioxide occur in the organism, an increased nitrogen excretion as compared with the normal takes place. The author shows that oxygen inhibits autolysis, whereas carbon dioxide increases it. Carbonic acid, like all other acids, increases autolysis, but it appears to have a specifically powerful effect as compared with others.

S. B. S.

The Action of Arsenic on Autolysis. ERNST LAQUEUR (*Schrift. Physikal. ökonom. Ges. Königsberg*, 1907, 48; Reprint).—Kossel has shown that administration of arsenic and sodium arsenite to dogs

increases nitrogen excretion. Nevertheless, these substances inhibit autolysis of the liver.
S. B. S.

The Influence of Inorganic Colloids on Autolysis. VI. The Differences of Action of Various Hydrosols. M. ASCOLI and G. IZAR (*Biochem. Zeitsch.*, 1909, 17, 361—394. Compare Abstr., 1908, ii, 121, 713).—The rate of autolysis of ox-liver in presence of varying quantities of different colloids was investigated, and in each case the following determinations were made: total nitrogen, nitrogen of monoamino-acids, of purine bases, and of albumose. It was found that the formation of monoamino-acids in autolysis was influenced in the same way as the total autolysis. Scission of nucleins, however, was promoted by smaller quantities of a colloid than were necessary to markedly influence the total autolysis. The favouring action of the colloids on autolysis reaches an optimum with certain concentrations of the colloid, but above this concentration the colloid exerts an inhibitory influence. There are quantitative differences in the action of the various colloids, and in a few instances also qualitative differences, certain of the colloids having actions somewhat divergent from those above mentioned.
S. B. S.

Adsorption and Partial Purification of Catalase from the Liver. AMOS W. PETERS and H. W. STEWART (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxx—xxxi; *J. Biol. Chem.*, 6).—The aqueous extract of liver is treated with sodium phosphate and zinc sulphate. The precipitated zinc phosphate is heavily charged with catalase, which is removed with sodium phosphate and further purified by the same process of adsorption. The catalase so prepared gives a strong xanthoproteic reaction, but practically negative Millon's and biuret reactions. It is inactivated by boiling.
W. D. H.

Post-Mortem Glycogenolysis. JOHN J. R. MACLEOD (*Proc. Amer. Soc. Biol. Chem.*, 1908, xl—xli; *J. Biol. Chem.*, 6).—Glycogen in the dog's liver is unevenly distributed in the various lobes. If the liver is removed before death, the amount of glycogen is less than immediately after death, probably because in the former case the liver contains more blood. Glycogenolysis is quite slow immediately after death, and later is rapid. If the great splanchnic nerve is stimulated in the bloodless liver, the rate of glycogenolysis is more than doubled. The glycogenolytic fibres in this nerve are therefore independent of the vaso-motor fibres.
W. D. H.

Action of Phloridzin on the Liver. KARL GRUBE (*Pflüger's Archiv*, 1909, 128, 118—124).—By the simultaneous perfusion of dextrose and phloridzin through the liver, no increase of glycogen occurs in that organ such as takes place when dextrose alone is perfused. It may be that glycogen is formed, but this is masked by the energetic hydrolysis which follows its formation. Under the influence of phloridzin the glycogen already present in the liver decreases; this is not due to a simple washing out, for the lobe of the liver simultaneously perfused with Ringer's solution shows no such marked

decrease. The glycogen in the phloridzin lobe is from 21 to 54% less than in the other. That the glycogen is changed into sugar is regarded as probable, but the point was not specially investigated. Phloridzin acts directly on the liver cells.

W. D. H.

Chemico-physical Investigations on the Crystalline Lens.
VI. Imbibition of the Lens in Sodium Chloride Solutions of Various Concentrations. FILIPPO BOTTAZZI and NOÈ SCALINCI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 326—338, 379—384. Compare this vol., ii, 417).—Even in very dilute sodium chloride solutions (0.0008*N*) the imbibition of the crystalline lens is much less than in distilled water. This is the reverse of what occurs with gelatin or agar-agar, probably owing to the facts that the lens is impregnated to some extent with sodium chloride solution, and that the imbibition is accompanied by osmotic processes. The solution in equilibrium with the lens contains about 1.3% of sodium chloride.

In the more concentrated solutions (0.341—2.393*N*) of sodium chloride, the lens loses in the first hour 1.35—4.93% of its weight. With such solutions, there are three distinct periods, in which (1) the lens diminishes in weight continuously, reaching more or less rapidly a minimum; (2) the diminution in weight gradually disappears, the initial weight being attained, and (3) continuous increase in weight takes place. The more concentrated the solution the more rapidly do these periods succeed one another, the rapidity increasing more rapidly than the concentration.

The diminutions in weight which the lens undergoes in the concentrated solutions are small compared with the increases in weight in the dilute solutions in the same time, so that the lens is more inclined to take up water, increase in weight, and swell than it is to lose water, diminish in weight, and contract.

Prolonged immersion of two lenses in 0.834 and 1.709*N*-sodium chloride solutions shows that in the third period, after the lenses have first lost weight and then recovered it, increase in weight takes place only until a maximum is reached, the weight then oscillating about this maximum for some hours. There is thus an apparent tendency to arrive at an equilibrium between the force of imbibition of the body of the lens which tends to attract solution and the elastic tension of the capsule, the opposition of which to the entry of liquid increases with the volume of liquid penetrating it.

Immersion of lenses in water vapour of varying pressures at 38° shows that, no matter what the vapour pressure, disimbibition of the lens always takes place to about the same extent. When the capsule of the lens is removed, similar behaviour is observed, and, if the immersion is prolonged, the distillation of water from the lens to the liquid is continuous.

T. H. P.

Autolytic Formation of Lactic Acid in Muscles. R. S. FREW (*Zeitsch. physiol. Chem.*, 1909, 60, 15—19).—Fresh rabbit's muscle sometimes contains lactic acid (4 cases), sometimes not (3 cases). By short digestion in chloroform water, no formation of lactic acid occurred in 3 cases; in one case there was a positive result. By

prolonged digestion there is a decrease in the lactic acid, so there seems to be present an agent which destroys the acid, probably of the nature of an enzyme. The amount of water of crystallisation in the zinc salt shows that the acid is of the dextrorotatory variety, but on putrefaction there is generally a mixture. W. D. H.

Influence of Cold Storage on Flesh. A. D. EMMETT and HARRY S. GRINDLEY (*Proc. Amer. Soc. Biol. Chem.*, 1908, ix—x; *J. Biol. Chem.*, 6).—Three weeks cold storage causes no loss of water or protein in beef and chicken, an increase in soluble inorganic phosphates, and a decrease in non-protein nitrogen. Six weeks cold storage causes a slight loss of water, no further increase in phosphates, and an increase in extractives and soluble nitrogen. Cold storage meat loses less in cooking, and is juicier. W. D. H.

Diastatic Enzyme of Meat. AMOS W. PETERS and H. A. MATTILL (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxix—xxx; *J. Biol. Chem.*, 6).—During autolysis of muscle, the sugar obtained increases so long as the muscle remains edible; later the sugar diminishes, and finally vanishes. W. D. H.

Pharmacological Actions of the Placenta. S. HIGUCHI (*Biochem. Zeitsch.*, 1909, 17, 21—67).—The normal human placenta contains neither a toxin nor any substances of the nature of ergot, adrenaline, or saponin. It, however, contains enzymes which decompose hydrolytically many glucosides and esters, in some instances more powerfully than extracts of other animal organs. Any similar action on alkaloids is only exerted in small measure. W. D. H.

Physiology of Glands. XI. The Functions of the Spleen. LEON ASHER and HANS GROSSENBACHER (*Biochem. Zeitsch.*, 1909, 17, 78—119).—The amount of iron in the fæces has no relation to the total amount of fæces. The daily excretion of iron in dogs from which the spleen has been removed is much greater than in normal dogs (29.2 to 12.2 mg. a day). This is not due to lessened absorption, for the same is seen during inanition and in well-fed animals. The same phenomenon goes on five months after the operation. The spleen, therefore, plays a part in iron metabolism, enabling the body to retain and utilise it. W. D. H.

The Physiology of Glands. XII. The Function of the Spleen in Iron Metabolism. LEON ASHER and RICHARD ZIMMERMANN (*Biochem. Zeitsch.*, 1909, 17, 297—336. Compare this vol., ii, 163).—Dogs, even ten to eleven months after splenectomy, excrete more iron than normal animals. This difference between the excretion of iron in normal dogs and dogs without spleen is not much influenced by subcutaneous injection, and the spleen has but little significance on the utilisation of iron artificially introduced. After injection of acetylphenylhydrazine, which causes a destruction of blood-corpuscles, there is a slightly increased iron excretion in the splenectomised as compared with the normal dog. On the other hand, in starving dogs, where iron is derived from the breakdown of body proteins, the increased excretion in dogs without spleen is marked as compared

with that of normal animals. The experiments confirm Ascher's theory that the spleen is capable of causing the utilisation of iron derived from the breakdown of the tissue proteins. S. B. S.

The Iron of the Spleen. CESARE CAPEZZUOLI (*Zeitsch. physiol. Chem.*, 1909, 60, 10—14).—In ox spleen an iron-containing nucleo-protein is present; it contains 2.32—2.68% of phosphorus. It dissolves in boiling water with some difficulty; the percentage of iron in the nucleo-protein obtained by the first extraction with boiling water is 1.48—2.0, and by the second, 0.41—0.97. The filtrate still, however, contains a variable amount of iron, about 20—25% of the total.

W. D. H.

Neurine, a Constituent of the Suprarenal Gland. ALFRED LOHMANN (*Pflüger's Archiv*, 1909, 128, 142—144).—In addition to adrenaline, choline, and other bases previously separated from the suprarenal body, neurine is also present. It was separated as the aurichloride, and gave the chemical characters and physiological action of neurine.

W. D. H.

Determination of Iodine in Protein Combinations. LOUIS W. RIGGS. Absorption of Iodine by the Dog's Thyroid. ELEANOR VAN ALSTYNE and S. P. BEEBE. Iodine in Human Thyroids. LOUIS W. RIGGS and S. P. BEEBE (*Proc. Amer. Soc. Biol. Chem.*, 1908, xli, xli, xli—xlii; *J. Biol. Chem.*, 6).—Improvements in Baumann's process are suggested. In young dogs there is a maximum capacity for iodine absorption in the thyroid; this lessens with age, and in old animals it may reach zero. In the human thyroid the average quantity of iodine is 0.33 mg. per gram of fresh gland. Some cases gave higher numbers, but probably iodine had been given to these patients medicinally. In exophthalmic goitre, the average figure was much less (0.08). Other pathological thyroids gave very variable numbers.

W. D. H.

Phosphatides in Animal and Vegetable Materials. HANS VAGELER (*Biochem. Zeitsch.*, 1909, 17, 189—219).—From numerous analyses which are given, the phosphatides appear to be bound up with vital manifestations in plant life. The percentage present increases with development, and then decreases after maturity sets in. An analogous condition obtains in animal metabolism. They are characterised by their colloidal nature and readiness of oxidation, a process intimately associated with life. Methods for their sharp separation from one another are still largely lacking, and so it is impossible to state the relative importance of the different members of the group. Kyes' results on the part lecithin plays as an amboceptor are regarded as doubtful.

W. D. H.

Origin of Taurocholic Acid. ROBERT B. GIBSON (*Proc. Amer. Soc. Biol. Chem.*, 1908, xvi; *J. Biol. Chem.*, 6).—Experiments on cats are recorded which confirm the view of Bergmann and of Wohlgemuth that taurine originates from the cystine of protein. If

bromobenzene is administered, artificial cystinuria is produced, and the consequent fall in the taurine of the bile was observed.

W. D. H.

Analysis of Vernix caseosa. I. LEO RITTER VON ZUMBUSCH (*Zeitsch. physiol. Chem.*, 1909, 59, 506—519. Compare Ruppel, Abstr., 1896, ii, 199).—The amount of water and of substances insoluble in ether vary considerably. The insoluble material consists mainly of epidermal cells. The ash does not contain phosphates. The fat which was extracted by ether gave the following numbers: D 0.9003, m. p. 34°, f. p. 29.2°, acid number 8.11, hydrolytic value 128.9, Reichert-Meissl number 0.720, and iodine number 47.42. Sixty-three grams of the fat gave 19 grams of fatty acids and 38 grams of non-hydrolysable matter soluble in ether. Another portion (120 grams) gave 40 grams of non-volatile fatty acids, 71 grams of non-hydrolysable cholesterol derivatives, and small amount of volatile acids (formic). The fatty acids contained 41.2% of oleic acid. The solid fatty acids are odourless, comparatively hard, and have m. p. 56.5°, f. p. 48°, and iodine number 25.84.

J. J. S.

The Enzymes of Milk. FRÉD. BORDAS and F. TOUPLAIN (*Compt. rend.*, 1909, 148, 1057—1059).—Fresh milk is differentiated from boiled milk by the coloration it gives with tincture of guaiacol or *p*-phenylenediamine. The action is a catalytic oxidation of the indicator, and has been supposed to be due to an enzyme of the *oxydase* class, termed *lactanacrosyldase* by Dupuoy. By heating at 80°, the temperature at which enzymes are destroyed, the oxidising power of milk is lost. If, however, boiled milk is centrifugalised, both the cream and the solid residue give the colour, whilst casein extracted from fresh or boiled milk is found to give a very intense coloration. The authors reject the enzyme theory, and prefer to suppose that the reaction in question is brought about by casein or calcium caseinate. In boiled milk the casein proper is masked by a film of soluble casein deposited on the particles.

R. J. C.

The Ratio of Inorganic Bases to Acids in Normal Human Urine. STANISLAS KOZŁOWSKI (*Bull. Acad. Sci. Cracow*, 1909, 37—45).—Four series of experiments were made, two on a diet consisting chiefly of meat, one on a mixed diet, and one on a milk diet. On a meat diet, the inorganic bases considerably exceed the quantity required to saturate the inorganic acids, uric acid, and organic acids soluble in ether. The balance must be considered as combined with proteic acids. On a milk diet, on the other hand, the inorganic bases are insufficient even to saturate the inorganic acids, although uric, proteic, and ether-soluble organic acids are also present. The balance must be saturated by organic bases, of which creatinine can only form a small part. The mixed diet gives an intermediate result, the inorganic bases approximately saturating the inorganic, uric, and ether-soluble acids, but not the proteic acids.

The acidity of urine is only remotely related to the production of

acids in the organism. It is not due to an increased production of inorganic or uric acids, and it cannot be entirely due to acid phosphates.
C. H. D.

Composition of Dilute Urine. ARCHIBALD B. MACALLUM and C. C. BENSON (*J. Biol. Chem.*, 1909, 6, 87—104).—In dilute urine, obtained after drinking large amounts of distilled water, Δ ranges from -0.30 to -0.075 ; the proportion of potassium is usually greater than that in the more concentrated urine obtained before the experiment began, and is never the same as in blood-plasma. This is due to a "lag" in potassium secretion as compared with the chloride during the decrease in the concentration; the same "lag" is seen usually when the urine again begins to become more concentrated. The elimination of water and salts is due to activity of the renal epithelium, and is not a mere filtration.
W. D. H.

The Influence of Adrenaline on the Excretion of Carbon Dioxide and Urine. ST. WELECKI (*Bull. Acad. Sci. Cracow*, 1909, 119—124).—The injection of minute quantities of adrenaline into a vein causes an increase of blood-pressure in the main arterial system, but a decrease in the pulmonary arteries. Intraperitoneal injection causes an increase of pressure in both systems.

Experiments on dogs and rabbits show that intravenous injection of adrenaline causes an increase, and intraperitoneal injection a decrease, of the carbon dioxide excretion. In experiments on guinea-pigs, the quantity of urine was more than doubled after injections of adrenaline, the urine becoming more dilute, but the absolute quantity of dry substance and nitrogen being increased.
C. H. D.

Elimination of Barium. GUSTAVE M. MEYER (*Proc. Amer. Soc. Biol. Chem.*, 1908, xlvii; *J. Biol. Chem.*, 6).—Barium bromide was given to dogs by the mouth and subcutaneously; by the former method, only traces appear in the urine, and by the latter, none at all was found in that excretion.
W. D. H.

Estimation of Amino-acids in Urine. VALDEMAR HENRIQUES (*Zeitsch. physiol. Chem.*, 1909, 60, 1—9).—By means of Sørensen's method of titration with formaldehyde (Abstr., 1908, ii, 234), the amount of amino-acid nitrogen in urine can be estimated with great accuracy, and at the same time an estimation of ammonia nitrogen can be obtained. The amount of amino-acid nitrogen expressed in percentage terms of total nitrogen is in man on a mixed diet about 2; in the goat fed on hay about 0.7, and in the dog, numbers varying from 0.73 to 4.6 were obtained.
W. D. H.

Indole-producing Compounds of the Urine. CHARLES PORCHER (*Compt. rend.*, 1909, 148, 1210—1212).—A discussion of the decomposition of tryptophan in the digestive tract of the higher animals, and of the appearance of its breakdown-products in the urine. The relative proportion of indole-producing compounds (indolepropionic acid, indoleacetic, indole- β -carboxylic acid, etc.) to

indoxyl derivatives in the urine depends on the extent to which tryptophan has undergone proteolytic decomposition in the intestine.

W. O. W.

Metabolism in Dementia Præcox. GIACOMO PIGHINI (*Arch. Neurol. and Psychiat. London County Council*, 1909, 4, 220—243).—This is a metabolic study of twelve cases of dementia præcox, four in the acute and eight in the more advanced stage of the disease. In all cases modifications of normal metabolism are seen. In the acute stage (that of restlessness and violence) there is a negative balance of nitrogen (urea, uric acid, purine bases), of phosphorus and sulphur, indicating increased catabolism of protein, and phosphorised and sulphurised constituents. The body temperature is also raised.

In the advanced stage (that of dementia) there is a proportionate retention of nitrogen and phosphorus, also of sulphur proportionate to those elements, and an independent loss of calcium. In both phases the intake and excretion of water is diminished, especially by the skin; it is difficult to get the patients to take fluid, and most of the water excreted passes off by the kidneys. There is a relaxed (*sic*) excretion of chlorides.

W. D. H.

Intestinal Diabetes. EDUARD PFLÜGER (*Pflüger's Archiv*, 1909, 128, 125—135).—Resection or even injury of the small intestine, especially of its outer and peritoneal layers, produces glycosuria, which is held to be of nervous origin. It continues for some days. Injury to the pancreas was excluded.

W. D. H.

Destruction of Body-protein in Fever. PHILIP A. SHAFFER (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxvii; *J. Biol. Chem.*, 6).—In typhoid fever the loss of body-protein may be retarded, or even prevented, by diets of high calorific value containing a large amount of carbohydrate.

W. D. H.

The Large White or Soapy Kidney. OSKAR KLOTZ (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxxviii; *J. Biol. Chem.*, 6).—This pathological specimen contains less fat than the normal organ, but it contains excess of "myelins." By extraction with ether, and subsequent extraction of the ethereal extract with alcohol, the substance was obtained in solution and precipitated by chloroform. It proved to be a compound of two fatty acids (one of which is oleic), potassium, and sodium. The term soapy is therefore probably justified.

W. D. H.

Reaction of Blood-serum in Malignant Disease. W. N. WEST WATSON (*J. Path. Bact.*, 1909, 13, 429—436).—The alkalinity of the serum to dimethylaminoazobenzene in malignant disease is markedly increased, and this is most noticeable at an early stage of the disease, especially in carcinoma as compared with sarcoma. Removal of the growths produces no appreciable change in this condition, from which it appears that the alteration in the serum favours the growth of malignant tumours rather than results from their presence.

W. D. H.

Antagonistic Action of Ammonium and Calcium Salts.

CARL VOEGTLIN and I. KING (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxviii; *J. Biol. Chem.*, 6).—In acidosis the blood and urine contain excess of ammonia. The intravenous injection of ammonium lactate, chloride, and β -hydroxybutyrate produces symptoms of acid intoxication, whilst that of calcium salts antagonises the toxic action.

W. D. H.

Physiological Action of Allylthiocarbimide.

E. WACE CARLIER (*Bio-Chem. J.*, 1909, 4, 107—116).—Allylthiocarbimide (like allyl sulphide) acts as a poison, paralysing respiratory and vaso-motor centres, producing muscular spasms, affecting the heart-beat, and lowering body-temperature. The thiocarbimide is the more powerful of the two substances.

W. D. H.

Ureidoglucose [Carbamidodextrose].

PAUL MAYER (*Biochem. Zeitsch.*, 1909, 17, 145—155).—Schoorl has shown that a compound of urea and dextrose can be formed: $\text{CHO} \cdot [\text{CH} \cdot \text{OH}]_4 \cdot \text{CH}_2 \cdot \text{OH} + \text{CO}(\text{NH}_2)_2 = \text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH} \cdot [\text{CH} \cdot \text{OH}]_4 \cdot \text{CH}_2 \cdot \text{OH} + \text{H}_2\text{O}$, and the compound so formed (carbamidodextrose) can be resolved into its components by dilute mineral acids. Carbamidodextrose is lævorotatory; $[\alpha]_D - 23.3^\circ$. When given to rabbits by the mouth, about 7% is burnt in the body, and about 22% reappears unchanged in the urine, with a small quantity as carbamidoglycuronic acid. If given subcutaneously, 30 to 60%, and if given intravenously about 60%, reappears as such in the urine. Evidence was also obtained, although not absolutely conclusive, that the liver is in small degree able to resolve it into its constituents.

W. D. H.

Oxidation of Carbon Monoxide.

JOSEPH H. KASTLE (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxiii—xxiv; *J. Biol. Chem.*, 6).—Iodosobenzoic acid may be employed to oxidise carbon monoxide, but whether this oxidation can be accomplished when the gas is combined with hæmoglobin, for the relief of carbon monoxide poisoning, is not yet settled.

W. D. H.

Experimental Lead Poisoning.

KENNETH GOADBY (*J. Hygiene*, 1909, 9, 122—133).—Experiments on cats show that the inhalation of lead dust causes lead poisoning; the lead may therefore enter by the respiratory as well as by the gastro-intestinal tracts. That this also applies to men engaged in industrial processes was also shown by the fact that the laboratory workers suffered from the toxic effects until later during the work when precautions were taken to prevent inhalation of the dust.

W. D. H.

Mercurial Poisoning of Men in the Respiration Calorimeter.

Metabolism during Fever. THORNE M. CARPENTER and FRANCIS GANO BENEDICT (*Amer. J. Physiol.*, 1909, 24, 187—202, 203—233).—During the course of numerous observations on men in the calorimeter, toxic symptoms were observed in some cases which are attributed to the effect of mercurial vapour originating from the mercury used in the valves of the apparatus. Among the symptoms so produced, fever was

one, and an opportunity thus occurred of studying metabolism in the febrile state. The observations are fragmentary, seeing that they were not undertaken primarily for the study of fever. The data must be studied in the original papers. There is evidence that, at any rate during the height of the fever, there is increased heat production; conclusions regarding heat elimination are not so clear. W. D. H.

Protection to Acetonitrile Poisoning by Thyroid Feeding. S. P. BEEBE (*Proc. Amer. Soc. Biol. Chem.*, 1908, xiii; *J. Biol. Chem.*, 6).—In mice the protective action of thyroid feeding against acetonitrile poisoning is not so uniform as in Hunt's experiments. In about 40% of the mice there was no protective action. W. D. H.

The Mechanism of Atoxyl Action. A. BREINL and MAXIMILIAN NIERENSTEIN (*Zeitsch. Immunitätsforsch. exp. Therap.*, 1909, 1, 620—632; Reprint).—Atoxyl enters into combination with the proteins of serum. On treating this atoxyl combination under certain conditions with liver emulsion, oxidative ferments, or hydrogen peroxide, arsenic in an inorganic form is set free. Under these conditions, atoxyl will exert a trypanocidal action. The setting free of arsenic in this form can be accomplished *in vivo* either by organs of the body or by the trypanosomes themselves. At the same time a reduction process takes place, whereby arsenious acid and aniline are derived from atoxyl, and the aniline is excreted in the feces. The chief action of the atoxyl is due to the setting free of arsenic in inorganic form. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Efficiency of Berkefeld Filters. I. ANDREW WILSON. II. WILLIAM BULLOCH and J. ANDERSEN CRAW (*J. Hygiene*, 1909, 9, 33—34, 35—45).—In reply to Bulloch and Craw's statements as to Berkefeld filters (Abstr., 1908, ii, 314), Wilson points out that the filters are injured by sterilisation in the autoclave at 120°, and should be sterilised by boiling water. The former authors publish more experiments which support their previous statements, although they sterilised the filters in the way recommended by Wilson.

W. D. H.

Anti-putrescent Effects of Copper Salts. ALFRED SPRINGER, sen., and ALFRED SPRINGER, jun. (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxxii—xxxiii; *J. Biol. Chem.*, 6).—The non-putrescence of a certified milk excited suspicion of an added antiseptic; this was ultimately traced to copper from the boiler used for boiling cloths, pails, etc. Experiments showed that copper salts are selective in their action; they particularly inhibit the growth of putrefying bacteria, but the lactic acid organism among others is not much affected. W. D. H.

Differentiation of Lactose-fermenting Bacilli. ALFRED MACCONKEY (*J. Hygiene*, 1909, 9, 86—103).—The tests at present used are not adequate to differentiate lactose-fermenting bacilli. Other tests are suggested, the use of which it is hoped will put the bacteriological examination of water on a firmer basis. W. D. H.

Food-poisoning Bacilli and Efficiency of Rat Viruses. FRANCIS A. BAINBRIDGE (*J. Path. Bacteriol.*, 1909, 13, 443—466).—The viruses examined owe their potency to bacilli indistinguishable from *B. Aertryck* and *B. Gaertner*, but their destructive power on rats is inconstant, the death rate varying from 20 to 50%. Phosphorus paste is more efficient (61—67%). Probably some of the rats become immune. The entire innocence of the bacterial viruses for man is a statement which needs justifying. W. D. H.

Action of Bacteria and Yeasts in Rendering Soluble the Phosphoric Acid of Compounds Insoluble in Water. E. KRÖBER (*J. Landw.*, 1909, 57, 5—80).—The activity of bacteria and yeasts, by the production of acids, in liberating insoluble phosphoric acid may be of considerable importance. The chief agent is carbon dioxide; acetic, butyric, lactic, and other acids are also produced. The action on phosphates is hindered by the presence of calcium, magnesium, and ammonium carbonates, ferric and ferrous hydroxides, etc.

The action of the acids produced by bacteria varies considerably with different phosphates. Tricalcium and dicalcium phosphates and the tetracalcium phosphate of basic slag are dissolved much more rapidly, and in much greater quantities, than the sparingly soluble, crystalline, and amorphous crude phosphates.

The increased effect of the more sparingly soluble phosphates in humous soils, as compared with other soils, is attributed to the greater activity in such soils of acid-producing bacteria, fungi, and yeasts.

N. H. J. M.

Relation of Magnesium and Phosphorus to Growth of Fungi. HOWARD S. REED (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxiii; *J. Biol. Chem.*, 6).—Certain relations between these two elements in nutrient solutions have striking effects on growth, and especially on spore formation in *Aspergillus niger*; the latter may be almost inhibited by reducing the phosphorus to small amounts. W. D. H.

Enzymes of Some Lower Fungi. ARTHUR W. DOX (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxiv—xxv; *J. Biol. Chem.*, 6).—From *Penicillium* cultures, an enzyme resembling erepsin was obtained; this is most active at the neutral point of methyl-orange; a hippuric acid splitting enzyme was also found. In other kinds of *Penicillium* the enzyme activity was very variable. W. D. H.

Are Fungi Able to Utilise the Elementary Nitrogen of the Air and to Increase the Total Nitrogen in the Soil? BERTHOLD HEINZE (*Bied. Zentr.*, 1909, 38, 280; from *Annal. mycologici*, 1906, 4, 41—63).—Bluish-green algæ assimilate free nitrogen, although not to the same extent as *Azotobacter*. It is doubtful whether mould fungi

can fix nitrogen, but even if they can not, they are important as sources of carbon for nitrogen-fixing bacteria.

In the microbiological fixation of nitrogen, the first products are probably amino-acids, perhaps salts of carbamic acid. Higher amino-acids would next be formed, and from these, by mutual condensations, proteids would be produced.

N. H. J. M.

The Prochromogen of the Respiration Chromogen of Plants. WLADIMIR I. PALLADIN (*Ber. Deut. bot. Ges.*, 1909, 27, (3), 101—106).—The author adduces evidence to show that the chromogen of the leaf (Palladin, *ibid.*, 1908, 26, 125) exists in combination, to which he gives the name prochromogen. From this the chromogen is liberated as required by an enzyme, and is therefore not found in any quantity in the leaf as a general rule. In spring, however, when the physiological processes are intense, free chromogen can be found in larger quantity, which can be still further increased by feeding the leaf with sucrose.

E. J. R.

Theory of the Respiration of Plants. I and II. WLADIMIR I. PALLADIN (*Bull. Acad. Sci. St. Pétersbourg*, 1909, 459—478, 519—546 *).—The author discusses exhaustively previous work on aerobic and anaerobic respiration (compare Abstr., 1906, ii, 481, 570, 696; 1907, ii, 385; 1908, ii, 416, etc.), from which the following conclusions are drawn.

The first reactions of respiration are reactions of anaerobic decomposition, brought about by enzymes. These reactions are similar to the reactions resulting from dry distillation, consisting of a series of successive reductions and oxidations by means of combined oxygen in the net-work of organic substances. Besides dextrose, other substances may afford material for anaerobic respiration, which may proceed without formation of alcohol but with formation of other compounds. Anaerobic respiration transforms stable constituents of the plants which do not undergo direct oxidation into extremely unstable, readily oxidisable substances. Alcohol is formed only during anaerobic respiration, and not during normal respiration in air, intermediate substances which are formed earlier than alcohol, and are hence more labile, themselves undergoing oxidation. Aerobic plants are capable of living in media free from oxygen without developing carbon dioxide. Respiratory oxydases are ordinary pigment-forming enzymes, and are incapable of direct oxidation of the products of anaerobic decomposition which are related to compounds of the aliphatic series. The respiratory chromogens are very widely distributed in plants; they are not oxidised directly by the oxygen of the air, the presence of special oxydases being required for the various chromogens. The respiratory pigments formed in plants usually undergo immediate reduction to colourless chromogens, these chromogens being related to aromatic compounds. Dextrose, as the initial product of the assimilation of carbon, is the parent substance from which aromatic compounds are formed in plants; as in dry distillation, so also in plant tissues, the benzene ring is formed from dextrose. To

* and *Biochem. Zeitsch.*, 1909, 18, 151—206.

compounds, in the form of which the chromogens occur in a combined state in the tissues, the author gives the name "pro-chromogens" (compare preceding abstract). Absence of chromogens renders impossible, not only oxidation processes in plants, but also oxidation of pyrogallol by the latter. T. H. P.

Disassimilation in Plants. N. T. DELEANO (*Biochem. Zeitsch.*, 1909, 17, 225—230).—The mould *Lactarius sanguifluus* contains two kinds of lipase, one belonging to the mycelium, insoluble in the nutritive medium, soluble in glycerol and acting as serum lipase does, best at 42—50°. The other originates from the cells, passes into the nutritive medium, and acts like pancreatic lipase independently of temperature changes. At the time of fructification, lipase action is the dominating factor; after this stage is passed, lipase action can no longer be detected, the enzymes being either destroyed or their action inhibited. W. D. H.

New Methods of Colouring Vegetable Phosphorus Compounds. CORRADO BONGIOVANNI (*Staz. sperim. agrar. ital.*, 1909, 42, 116—120).—For detecting organic phosphorus compounds in plant tissues, the author recommends the following methods, which he has applied to the seeds of *Ricinus communis*, wheat, and *Tropaeolum majus*.

(1) Sections of the seeds are warmed gently with dilute hydrochloric acid, washed several times with water, treated with 10% ferric chloride solution, again washed, immersed in 10% potassium thiocyanate, and, after further washing, examined under the microscope, when the globoids are seen to be stained yellow.

(2) The sections are immersed for about fifteen minutes in a saturated solution of molybdic acid in hydrochloric acid and then placed, without washing, in a 10% stannous chloride solution containing a few drops of 5% potassium or ammonium thiocyanate solution. In this way the cell-sap is coloured a faint yellow, and the globoids of the aleurone granules an intense reddish-violet, whilst the protoplasm either remains colourless or assumes a faint violet coloration. T. H. P.

Distribution of Rennet in the Parts and Tissues of Plants. C. GERBER (*Compt. rend.*, 1909, 148, 992—995).—The coagulating power of the parts of various plants has been determined with reference to milk at 42°. In the green parts of the plant the rennet is roughly proportional to the chlorophyll. The reproductive apparatus contains more rennet than the vegetative organs, the *style* being more active than the *achene*. Rennet appears to be distributed in the plant in the same manner as the proteolytic ferment, so that both activities may be due to one and the same enzyme.

In the root and stalk, the *liber* alone contains any appreciable rennet activity, but rennet is also present in the green bark. In plants like the mulberry, the green parts of which contain pectase, rennet can be better studied in the *liber* of the stalk than in the leaves. R. J. C.

Fatty Oil from the Fruits of *Aesculus hippocastanum*. MORTEN STILLESSEN (*Chem. Zeit.*, 1909, 33, 497—498).—This oil was at one time used in medicine. The fruits yield on extraction with ether 1·5 to 3·0% of a yellowish-brown, rather viscid oil with a faint odour reminiscent of mustard oil, but on distilling 5 kilos. of the fruits in steam no volatile oil was obtained. The oil has D_{15}^{20} 0·9260, n_D^{20} 1·4747, saponification number 194·5, iodine number 95·4, Reichert-Meissl number 1·54, Hehner number 92·9, acetyl number 13·5, and unsaponifiable matter (phytosterol) 0·53%. By extracting the lead salts of the mixed fatty acids with ether and oxidising with permanganate the liquid acids thus separated, evidence was obtained that these consisted mainly of oleic acid with a little linoleic acid. The solid fatty acids, which were present only in small amount, appeared to consist of stearic and palmitic acids. All the acids are present in the oil as glyceryl esters.

T. A. H.

The Fruit of *Aralia hispida*. J. MILTON GILCHRIST (*Chem. News*, 1909, 99, 211).—The ripe fruit of this plant from Sylvan Beach, New York, was dried at 105—110°, when it was found to contain 41·72% of sugar, probably lævulose, also citric acid and tartaric acid as well as acetic acid. The results of analyses of the ash gave the following composition :

SiO ₂ .	Fe ₂ O ₃	Al ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	P ₂ O ₅ .	SO ₃ .
13·59	9·13	9·13	1·25	1·72	25·66	13·63	15·01	5·28

The nitrogen content of the fruit was found to be 1·5%, and potassium iodide iodine solution gave no indication of the presence of any alkaloid. From the nutlets contained in the fruit, by grinding them to powder, and successively extracting with ether, oils were obtained amounting to about 45% of the dried nuts. The saponification value was found to be 517, which corresponds with palmitic acid, and the products of saponification seemed also to contain oleic acid.

J. V. E.

Are the Cinchona Alkaloids a Protection for the Plant? P. VAN LEERSUM (*Pharm. Weekblad*, 1909, 46, 369—376).—From the results of experiments, the author concludes that the cinchona alkaloids do not protect the plants against the attacks of insects.

A. J. W.

Càscola (Falling) of the Flowers of Frappato Vines. ENRICO PANTANELLI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 406—411).—The author has investigated a case of càscola of the vine, and finds that healthy grapes and leaves contain considerably more carbohydrates of all sorts and considerably less of the various forms of nitrogen than the diseased grapes and leaves. The conclusion is drawn that the disease is due to excess of nitrogenous nutrition in a soil otherwise poor in nitrogen and in phosphoric acid.

T. H. P.

Indigo Products from Northern Nigeria. ARTHUR G. PERKIN (*J. Soc. Chem. Ind.*, 1909, 28, 353—355).—The author has published already the results of an investigation of the “Gara plant” (*Loncho-*

carpus cyanescens) of Sierra Leone (*ibid.*, 1907, 26, 389), the fermented leaves and stems of which were found to yield 0.65% of indigotin. In the present paper an account is given of the examination of a further sample of this plant and of indigo extracted from it.

A specimen of mixed stems and leaves from Northern Nigeria contained 0.65% of indigotin, whilst a sample of indigo also from this Colony contained 21.47 to 21.65% of indigotin, 1.1 to 1.3% of indirubin, and 12.15% of "brown matter" soluble in sodium hydroxide, the rest being moisture, inorganic matter, etc. The botanical origin of these two samples is uncertain, but comparison of fragments of leaves and stems present in each of them with corresponding parts of the "Gara plant" showed that they were probably, derived from this, and this is probably also the case with the samples of fermented leaves and indigo from Northern Nigeria examined by Rawson previously (*J. Soc. Chem. Ind.*, 1888, 17, 429). The presence of considerable quantities of "brown matter" appears to be characteristic of all these products. No samples of the plant containing the undecomposed glucoside from which the indigotin is presumably derived in the first instance have yet been obtained.

T. A. H.

Formation of Indigotin in Plants. OSKAR WALTHER (*Ber. Deut. bot. Ges.*, 1909, 27, 106—110).—The author considers that the enzyme, peroxydase, plays an important part in the formation of indigotin in plants. The hydrolysis of the glucoside indican to dextrose and indoxyl, and the subsequent oxidation of the latter to indigotin, are, he supposes, both brought about by enzymes. General oxidation processes in the plant are also discussed, with special reference to the respiration chromogen of Palladin (*Abstr.*, 1908, ii, 416).

E. J. R.

Amount of Hydrocyanic Acid in Reed-millet. JOHANN BEHRENS (*Bied. Zentr.*, 1909, 38, 282; from *Ber. Versuchs-Stat. Augustenberg*, 1906, 38).—Plants of *Sorghum saccharatum* when crushed in a mortar with water and distilled after two days yielded, 52 mg. of hydrocyanide per kilo. of fresh substance.

N. H. J. M.

Action of Fertilising Salts on Plant Enzymes. MICHAEL X. SULLIVAN (*Proc. Amer. Soc. Biol. Chem.*, 1908, xliv; *J. Biol. Chem.*, 6).—Potassium sulphate retards, whilst nitrate and mixtures of calcium hydrogen phosphate, sodium nitrate, and potassium sulphate accelerate, the oxidising action of wheat roots. The mixture of the three salts in equal quantities increases, the phosphate only increases, and the sulphate alone diminishes, the activity of malt diastase. Sodium nitrate has no action. Plants were grown in a mixture containing 100 parts per million of phosphoric acid, ammonia, and potassium oxide, and in a mixture of this with 200 milligrams of starch paste. The roots convert the starch into sugar. This activity was retarded by potassium sulphate and calcium hydrogen phosphate, but increased by sodium nitrate or by a mixture of the three salts.

W. D. H.

Influence of Environment on the Composition of Wheat. FRANK T. SHUTT (*J. Soc. Chem. Ind.*, 1909, 28, 336—338).—Results

are given showing the effect of soil moisture, especially during the period of maturation, on the quality of wheat grown under conditions of high temperatures. The amount of gluten largely depends on the character of the season, whilst the quality of the gluten is determined by the variety; the quality of the wheat is influenced by both factors. When the soil contains sufficient moisture to bring the wheat crop to maturity, a succeeding period of hot, dry weather is desirable.

N. H. J. M.

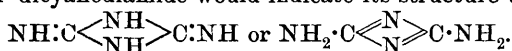
Manurial Experiments on Cereals with Calcium Nitrate. GIULIO PARIS (*Bied. Zentr.*, 1909, 38, 230—231; from *Staz. sper. agrar.*, 1908, 41, 171).—The employment of calcium nitrate, or sodium nitrate and lime, is recommended for non-calcareous, volcanic soils.

N. H. J. M.

Manuring Sugar Beet with Sodium Chloride. KARL ANDRLÍK and JOSEF URBAN (*Zeitsch. Zuckerind. Böhm.*, 1909, 33, 477—485).—The employment of sodium chloride cannot result in a marked decrease in the amount of sugar in sugar beet provided that the amount of sodium in the roots and in the whole plant is not increased. Further experiments are required to show whether such application can be beneficial.

N. H. J. M.

Nitrogenous Nutrition of Plants by means of Amino-compounds. RENATO PEROTTI (*Staz. sperim. agrar. ital.*, 1908, 41, 593—608).—Working under sterile conditions with maize, beans, wheat, and rice, as both young and adult plants, the author finds that dicyanodiamide can be used directly as a nitrogenous food by these plants to an extent not less than other amino-compounds and ammonium nitrate are used, provided that the amount of dicyanodiamide employed does not reach the toxic dose; this compound offers the great advantage, that its toxic action is extremely slight. The biochemical behaviour of dicyanodiamide would indicate its structure to be either



This view of the constitution is supported by the physiological behaviour of dicyanodiamide compared with that of cyanamide, the latter containing a $\cdot\text{C}:\text{N}$ group, which has a strong toxic action.

T. H. P.

Action of Ammoniacal Nitrogen [as Manure] Under the Influence of Lime. THEODOR PFEIFFER, ALBERT HEPNER, and L. FRANK (*Bied. Zentr.*, 1909, 38, 226—228; from *Mitt. landw. Inst. Univ. Breslau*, 1908, 4, 331).—On peaty soil ammonium salts only act favourably when lime is also applied. On sandy soil, injury due to the effect of ammonium salts is only to be feared when exceptionally large amounts of lime are applied, or when lime is applied too late. In the case of loamy soils, as much as 1% of calcium carbonate was without injurious effect.

N. H. J. M.

Analytical Chemistry.

Potassium Hydrogen Tartrate as Standard Substance. CONSTANTIN KOLLO (*Pharm. Zentr.-h.*, 1909, 50, 315—317).—The author proposes potassium hydrogen tartrate as a fit standard substance both in acidimetry and alkalimetry, on account of its being non-hygroscopic and readily obtainable in a pure condition.

As, however, its solubility in water is rather limited, a *N*/10-solution must be prepared by dissolving 18.819 grams in 600 c.c. of boiling water and diluting this when cold with water up to a litre. Free alkalis may then be titrated with phenolphthalein as indicator. If, however, mineral acids have to be standardised, 1.8819 grams are carefully ignited, and the resulting potassium carbonate is dissolved in water and titrated with the acid, using methyl-orange as indicator.

L. DE K.

Potassium Hydrogen Tartrate as Standard Substance. RUDOLF HEFELMANN (*Pharm. Zentr.-h.*, 1909, 50, 334—335).—The author observes that Kollo's use of potassium hydrogen tartrate (preceding abstract) is not novel, and that the use of this salt has been recommended from time to time by several analysts including himself.

L. DE K.

Potassium Chlorate Containing Bromate. ERNST PIESZCZEK (*Pharm. Zeit.*, 1909, 54, 325).—The author agrees with Klopstock (this vol., ii, 136) that commercial potassium chlorate (prepared electrolytically from carnallite lyes) frequently contains bromate. The amount may be estimated as follows: the sample is fused with an equal weight of ferric hydroxide until all effervescence ceases. The mass is then exhausted with water, and the filtrate evaporated to dryness. The residue is extracted repeatedly with strong alcohol, which dissolves the potassium bromide and leaves the bulk of the chloride undissolved. The alcoholic solution is evaporated to dryness, and the residue, dissolved in water and precipitated with silver nitrate, the silver bromide, and chloride, so obtained is washed, fused, and weighed. It is then heated in a current of chlorine, which expels the bromine, and re-weighed. From the difference in the weighings the bromine is calculated as usual.

L. DE K.

Estimation of Total Sulphur in Urine. F. W. GILL and HARRY S. GRINDLEY (*Proc. Amer. Soc. biol. Chem.*, 1908, xi; *J. Biol. Chem.*, 6).—There is a loss of sulphur attending the estimation of this element in urines when the sodium peroxide method is used.

W. D. H.

Quantitative Estimation of Tellurium. ALEXANDER GUTBIER and FERDINAND FLURY (*Chem. News*, 1909, 99, 217. Compare Abstr., 1903, ii, 328).—The possibility of satisfactorily estimating tellurium by Frerichs' gravimetric method (Abstr., 1903, ii, 41) is called into

question. The authors now publish a series of twelve results of most careful determinations of tellurium in extremely pure tellurium dioxide by Frerichs' method; these neither agree with the theoretical 79.95% Te nor amongst themselves, varying from 82.80 to 89.28% Te. On examining the precipitates obtained, they proved to be free from dioxide and from potassium, but, however, contained iodine, which could not be removed even by continued washing for some hours. The great affinity of iodine for tellurium (Abstr., 1902, ii, 653) being in this case very pronounced, renders it impossible to carry out quantitative estimations of tellurium by Frerichs' method, owing to formation of tellurium tetraiodide. J. V. E.

Estimation of Nitrogen by Kjeldahl's Method, especially in Milk. GEORG WIEGNER (*J. Landw.*, 1909, 57, 81—110).—About 10 grams of milk, weighed in the flask, are heated with 25 c.c. of sulphuric acid and a drop of mercury for about ten minutes, when frothing ceases; 10 grams of potassium sulphate are then added, and the heating continued until the liquid is colourless. The solution, diluted with 50 c.c. of water, is filtered to remove unoxidised fat before being distilled. Potassium hydroxide solution (600 grams in 1 litre of water) is added in sufficient quantity nearly to neutralise the acid, the mixture allowed to cool, and then the rest of the potash solution (making 175 c.c.) and 100 c.c. of 17.5% solution of potassium sulphide added. The distillation is carried out in a new form of apparatus, of which a sketch is given, and, with the amount of solutions employed, is continued for forty-five minutes. The ammonia is collected in 60 c.c. of *N*/10-sulphuric acid, which is finally diluted to exactly 250 c.c. Fifteen c.c. of 10% potassium iodide solution and 15 c.c. of 4% potassium iodate solution are then added, the flask closed, and left for forty-five minutes. It is then titrated with *N*/10-thiosulphate solution.

Copper sulphate should not be employed instead of mercury for milk, as low results are obtained. Potassium hydroxide is preferable to sodium hydroxide, as the solutions boil without bumping, and addition of zinc is unnecessary. N. H. J. M.

Estimation of Nitrogen in Saltpetre by means of Stannous Chloride and Iron Filings. ALB. KLEIBER (*Chem. Zeit.*, 1909, 33, 479—480).—Ten grams of the sample are dissolved in water up to 150 c.c., and 7.5 c.c. (0.5 gram) are placed in a 700—1000 c.c. distillation flask, and 5 grams of stannous chloride, 15 c.c. of strong hydrochloric acid, and 4—5 grams of iron filings are added. After warming for ten to fifteen minutes on the water-bath, 50—100 c.c. of water are added, also a small lump of paraffin, and then 60 c.c. of strong aqueous sodium hydroxide.

The ammonia formed is then distilled off and collected in a receiver containing 20 c.c. of *N*/2-sulphuric acid; the distillation should take about half an hour. L. DE K.

Estimation of Nitric Acid by Nitron in Liquids Containing Many Organic Substances. HARTWIG FRANZEN and E. LOHMANN (*J. pr. Chem.*, 1909, [ii], 79, 330—338).—The usual volumetric

methods for the estimation of a mixture of nitrous and nitric acids are inapplicable to bacteriological cultures; good results are obtained with nitron. The authors use Busch's method, in which the total nitric acid is estimated after the nitrous acid has been oxidised to nitric acid by hydrogen peroxide, and the residual nitric acid is determined after decomposition of the nitrous acid by hydrazine sulphate.

The estimation in the presence of Bouillon's solution gives too low results, owing to the retention of some nitron nitrate in colloidal solution. If this is prevented by the addition of 2 to 2.5 c.c. of concentrated sulphuric acid per 200 c.c. of solution, the estimation in the presence of Bouillon's solution is as accurate as in water only. Since oxalic acid is a common constituent of bacteriological cultures, the presence of sulphuric acid has the additional advantage of preventing the precipitation of nitron oxalate. A somewhat large excess of nitron should be used. C. S.

Estimation of Phosphorus in Foods, Fæces, and Urine.

F. W. GILL, J. B. PETERSON, and HARRY S. GRINDLEY (*Proc. Amer. Soc. Biol. Chem.*, 1908, xii; *J. Biol. Chem.*, 6).—The (a) magnesium nitrate, (b) nitric acid, (c) aqua regia, (d) Kjeldahl, (e) hydrochloric acid and potassium chlorate, (f) nitric and hydrochloric acids, and (g) direct ashing methods were compared; methods a, b, d, f, and g gave practically identical results. The uranium acetate volumetric method applied to urine, compared with the nitro-hydrochloric acid method, shows that the former gives lower results.

W. D. H.

Estimation of Phosphoric Acid with Uranium Acetate.

ROBERT B. GIBSON and CLARENCE ESTES (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxv—xxvi; *J. Biol. Chem.*, 6).—An excess of standard uranium acetate solution is added, and after decanting or filtering from the precipitated uranium phosphate, the uncombined uranium is estimated colorimetrically by addition of potassium ferrocyanide, and determination in the usual way of the depth of colour produced.

W. D. H.

Estimation of Phosphoric Acid in Ashes.

W. PLÜCKER (*Zeitsch. Nahr. Genussm.*, 1909, 17, 446—454).—The method of estimating phosphoric acid proposed by Lorenz (*Abstr.*, 1901, ii, 278), in which the precipitate of ammonium phosphomolybdate is weighed directly, was found by the author to be trustworthy. The method is particularly useful for the estimation of very small quantities of phosphoric acid, as each mg. of the latter yields 30.35 mg. of precipitate. The presence of iron, aluminium, and silica is without influence on the results obtained. For the estimation of phosphoric acid in the ash of organic substances, it is recommended that the substance should be first treated with calcium acetate solution or with milk of lime in order to prevent loss of volatile phosphorus compounds during the ignition. W. P. S.

The Simultaneous Estimation of Carbon Monoxide, Hydrogen, and Methane by Fractional Combustion. V. NESMJELOFF (*Zeitsch. anal. Chem.*, 1909, 48, 232—272).—The author arrives at the following conclusions. The fractional combustion by means of silver oxide is not suitable for practical purposes. A simultaneous combustion of carbon monoxide, hydrogen, and methane over palladium-asbestos allows of the estimation of the carbon monoxide alone if the velocity of the current does not exceed 1 litre per sixty minutes. The combustion of the mixture for the purpose of estimating the carbon monoxide, by passing it over copper oxide heated at 250°, gives good results, and the methane is not affected.

L. DE K.

Gases Disengaged by the Action of Copper Salts on Steel. E. GOUTAL (*Compt. rend.*, 1909, 148, 988—991. Compare Carnot and Goutal, *Abstr.*, 1897, ii, 520).—During the dissolution of cast-iron or steel in potassium cupric chloride, gaseous compounds of carbon are given off which appear to have been occluded in the metal. An error in the estimation of carbon in steel may arise if account is not taken of these gaseous products. To estimate them, the author dissolves 10 grams of steel filings or shavings in potassium cupric chloride at 45° in two hours. The solution is then boiled, and the gases are carried forward in a slow current of purified nitrogen and passed through baryta water to absorb carbon dioxide, sulphuric acid saturated with bromine to absorb unsaturated hydrocarbons, and finally through a tube, containing glass wool moistened with iodic acid, maintained at 75°. In the last, carbon monoxide is absorbed with liberation of iodine, which is carried forward into chloroform and afterwards titrated with standard thiosulphate. Carbon dioxide is estimated as barium carbonate and as barium sulphate.

The total volatile carbon is determined in a further sample of steel dissolved in the same way, the gaseous stream being mixed with oxygen and passed over a heated platinum spiral. The carbon dioxide produced is estimated in the usual way.

A typical hard steel contained 0.5960% solid carbon, 0.0185% carbon as carbon dioxide, 0.0059% as carbon monoxide, and 0.0171% as unknown hydrocarbons, etc.

R. J. C.

Estimation of Carbon and Phosphorus in Steel. ANDREW A. BLAIR (*J. Iron Steel Inst.*, 1909, i,*).—In the estimation of phosphorus, weighing the phosphomolybdate precipitate dried at 110° for two hours, and titrating its solution after reduction, give identical results, and the volumetric method is more rapid.

Experiments with potassium cupric chloride show that there is no production of hydrocarbons, and therefore no loss of carbon, when steel is dissolved in a solution of a copper salt. The carbon in steel is best estimated by direct combustion, carried out rapidly, so that the heat of oxidation causes complete oxidation, and fusion of the oxide formed. A platinum boat is used, with a layer of alumina under the steel. The experiments were made in a platinum combustion tube.

C. H. D.

* from *Advance proof*.

Estimation of Carbon in Aliphatic Hydroxy-compounds by the Wet Process. ERNST BERL and A. G. INNES (*Ber.*, 1909, 42, 1305—1309).—The necessity for a rapid and trustworthy method for estimating the amount of cellulose in a cuprammonium solution of this substance, coupled with the inapplicability of the ordinary combustion method, owing to the difficulty of filtering and purifying precipitated cellulose, led the authors to devise the following method.

A known weight of substance is introduced into a round-bottomed flask, which can be attached by means of a ground-glass junction to a Bunte burette. After evacuating the apparatus, 5—6 c.c. of a saturated solution of chromic acid are introduced into the flask from a tap funnel, which is fused into the side of the flask. After the reaction has subsided, 5 to 6 c.c. of syrupy phosphoric acid are introduced, and the reaction is completed by five to ten minutes' heating. The carbon dioxide is then driven over into the burette by running hot water into the flask from the tap funnel. After twenty minutes, the bottom of the burette is opened over a saturated salt solution, and the level of the liquid is read; the carbon dioxide is then absorbed by potassium hydroxide, and, after displacing the latter by salt solution, the level is again read, from which the volume of carbon dioxide can be calculated.

As shown by various accordant test analyses, the method is applicable to aliphatic hydroxy-compounds which are not volatile in a vacuum or with steam, but not to aromatic compounds, owing to the tendency to form carbon monoxide and gaseous hydrocarbons. In cases in which chromic acid and phosphoric acid alone do not suffice for complete oxidation, a globule of mercury should be added.

Since chromic acid and phosphoric acids are both liable to contain organic impurities, a blank experiment should be made. The phosphoric acid is best prepared by dissolving pure white phosphoric oxide in a small quantity of water. The use of sulphuric acid in place of phosphoric acid is not to be recommended, owing to the formation of sulphur dioxide.

The amount of material used for analysis must be sufficiently small to ensure the entire oxidation taking place under reduced pressure.

P. H.

Precipitation of Fischer's Salt (Potassium Cobaltinitrite). LUCIEN L. DE KONINCK (*Bull. Soc. chim. Belg.*, 1909, 23, 200—202).—For the detection of potassium by precipitation as cobaltinitrite, the author recommends the use of a solution prepared as follows: 50 grams of cobalt nitrate are dissolved in a litre of water with the addition of 25 c.c. of nitric acid (D 1.2), and this is mixed with a solution obtained by dissolving 300 grams of sodium nitrite in a litre. Before use, the orange-coloured solution is left for twenty-four to forty-eight hours to allow of the precipitation of any small quantity of potassium which may be present. With this solution, potassium can just be detected if present in a concentration of 1 in 10,000.

For the precipitation of cobalt, a solution prepared by dissolving 35 grams of sodium nitrite and 22 grams of potassium nitrate in

100 c.c. of water is recommended. This avoids the use of potassium nitrite, which is not easily obtainable in a pure condition.

H. M. D.

Compensation Apparatus for Rapid Methods of Electrolytic Analysis. ARTHUR FISCHER (*Chem. Zeit.*, 1909, 33, 337).—A description of a convenient arrangement of apparatus for making measurements of the cathode potential during the deposition of metals in the way described by Sand (*Trans.*, 1907, 91, 373).

The improvements introduced consist in using a voltmeter to measure the compensating *E.M.F.*, and a galvanometer as zero instrument in place of a capillary electrometer, the rheostat and measuring instruments being permanently connected in one box. T. E.

Constant Current Electro-analysis. HORACE W. GILLET (*J. Physical Chem.*, 1909, 13, 336—340).—In the separation of copper from zinc, when the copper remaining in solution has become too dilute to carry all the current, electrolysis of the acid begins and continues whilst the last traces of copper are deposited. The liberation of hydrogen prevents the separation of zinc, which requires a higher potential. If two metals, *A* and *C*, to be separated lie on the same side of hydrogen in the potential scale, it is usual to employ a constant voltage method, but if an excess of another metal, *B*, requiring an intermediate voltage is added, it will serve to prevent the deposition of metal *C*, even although the voltage used is higher than its deposition potential. The metal *C* must not be passive under the conditions employed, but must be capable of redissolving should it be locally deposited owing to local rise in current density or imperfect stirring. Thus in phosphate solution at 60° the following decomposition potentials were given by Root (compare *Abstr.*, 1903, ii, 683): Ag 1.3, Cu 1.6, Pb 2.2, H 2.25. The author shows that in separating silver from lead at 60°, excess of copper is a perfect preventative, the whole of the silver being readily deposited with some copper, but without a trace of lead, with a current of 1 ampere at 2.5 rising to 2.9 volts.

The number of possible applications of this method is small, because of the complications introduced by formation of alloys, amalgams, and solid solutions. R. J. C.

Microchemical Analyses. [V.] Analysis of the Iron Group. NICOLAAS SCHOORL (*Zeitsch. anal. Chem.*, 1909, 48, 209—231. Compare this vol., ii, 96).—Cobalt is best precipitated by means of a solution containing equal weights of ammonium thiocyanate and mercuric chloride. Nickel is best precipitated by means of an ammoniacal solution of dimethylglyoxime, or by means of lead acetate and potassium nitrite. Iron is detected by the ferrocyanide reaction. Aluminium is best precipitated as alum by means of potassium hydrogen sulphate; this is preferable to caesium sulphate, formerly employed. Chromium, which should be present as chromate, is best precipitated with benzidine hydrochloride in presence of sodium acetate. Zinc is best precipitated by adding sodium hydrogen carbonate to its solution in aqueous sodium hydroxide. Manganese is best precipitated by means of potassium hydrogen oxalate.

In all above-mentioned reactions, characteristic, microscopic appearances are observed.

In case of some, or all, of the metals being present, the usual course of separation must be adopted. For instance, nickel and cobalt are separated from the others by treating the mixed sulphides with dilute hydrochloric acid, and the cobalt is then separated from the nickel with potassium nitrite. Advantage is taken of the fact that iron and chromium oxides become very insoluble in acids on ignition, thus enabling the alumina to be extracted by dilute nitric acid, etc.

L. DE K.

Estimation of Tungsten. M. TSCHILIKIN (*Ber.*, 1909, 42, 1302—1304).—Tungstic acid is quantitatively precipitated by α -naphthylamine hydrochloride in the cold; for this purpose, 25 c.c. of a 2% solution of sodium tungstate are slowly added from a burette to 100 c.c. of a solution of 25 grams of α -naphthylamine with $1\frac{1}{2}$ molecular proportions of hydrochloric acid in 1 litre of water; after three hours, the precipitate is filtered and washed with the naphthylamine solution, diluted with five parts of water, and ignited while moist in a platinum crucible. The composition of the precipitate is expressed by the formula: $(C_{10}H_9N)_2(WO_3)_5 \cdot 3H_2O$, the formula of the corresponding precipitate formed with benzidine (compare von Knorre, *Abstr.*, 1905, ii, 286) being $(C_{12}H_{12}N_2)_2(WO_3)_5 \cdot 5H_2O$. Commercial sodium tungstate has the composition $Na_2WO_4 \cdot 2H_2O$.

P. H.

Estimation of Thorium in Monazite Sand. VINCENZO BORELLI (*Gazzetta*, 1909, 39, i, 425—448).—The author deals with the disgregation of the sand, the solution of the products of disgregation, precipitation of the oxalates of the rare earths, transformation of the oxalates into nitrates, and the separation of the thorium from the other elements. For the details of the various steps in the estimation, the original must be consulted.

T. H. P.

Precipitation of Antimony from Thioantimonate Solutions. WILLY SCHULTE (*Metallurgie*, 1909, 6, 214—220).—Aluminium or magnesium precipitates metallic antimony from solutions of alkali thioantimonates, or from a suspension of freshly precipitated antimony pentasulphide. The process is not quantitative, as the antimony at first precipitated is partly re-dissolved by the sodium sulphide formed if allowed to remain long in contact with the solution (compare Czerwek, *Abstr.*, 1906, ii, 708).

Magnesium is more active, and the method may be used quantitatively. Precipitated antimony sulphide, free from other sulphides, is dissolved in sodium sulphide solution and evaporated on the water-bath, and, when cool, magnesium powder is added. The solution becomes warm, and hydrogen sulphide is evolved. The process is continued until further additions of magnesium produce no further evolution of gas. After stirring and remaining overnight, the solution is stirred until no more gas is evolved. Dilute sulphuric acid is then added to remove magnesium hydroxide and excess of magnesium,

and the whole is filtered through a tared filter. The precipitated antimony is washed successively with warm water, dilute sulphuric acid, boiling water, and alcohol, dried at 110° , and weighed. The presence of sodium hydroxide in the solution must be avoided, as it prevents the action of the magnesium.

Small quantities of antimony hydride are formed when magnesium acts on a hot solution of thioantimonate.

When an alloy of 90% tin and 10% antimony (Britannia metal) is made the anode in a solution of sodium sulphide at $80-90^{\circ}$, the alloy may be deposited unchanged in composition on an iron cathode, copper and iron remaining in the anode mud. With an electrolyte consisting of sodium thioantimonate and sodium hydroxide at $65-70^{\circ}$, the tin may be dissolved, the antimony being deposited on the cathode in a practically pure state (99.66%). C. H. D.

Separation of Antimony and Tin. GEORG PANAJOTOW (*Ber.*, 1909, 42, 1296—1299).—Antimony sulphide is insoluble in a 15% solution of hydrochloric acid, whereas tin sulphide is soluble; this fact was made use of for the separation of antimony and tin by heating a mixture of the two salts, containing about 15% of hydrochloric acid, at $50-60^{\circ}$, and passing a rapid stream of hydrogen sulphide through the mixture for half an hour; the liquid was then cooled to 30° , and treated for ten minutes more with a slower stream of gas. The precipitate was filtered on a Gooch crucible, washed with water containing hydrogen sulphide to remove any tin, and weighed after treatment successively with alcohol, carbon disulphide, and ether. The tin contained in the filtrate was precipitated by hydrogen sulphide after neutralisation with ammonia. The method gives accurate results.

P. H.

Rhodium. ALEXANDER GUTBIER and M. RIESS (*Ber.*, 1909, 42, 1437—1441).—The reduction of rhodium salts to the metallic state by hydrazine (Gutbier and Hofmeier, *Abstr.*, 1905, ii, 533) may be utilised for the estimation of rhodium (compare Jannasch and Mayer; *Abstr.*, 1905, ii, 557). Experiments made with chloropentamminerhodium chloride and the bromo-bromide, and with several alkali rhodipentahalides (Gutbier and Hüttlinger, *Abstr.*, 1908, ii, 200), show that the precipitation should take place in hot alkaline solution, and that the concentration should not be too great. The rhodium hydrosol at first formed soon changes into a metallic, glistening precipitate, evolution of gas taking place owing to the catalytic action of the metal on hydrazine. The precipitate is dried at 105° , and heated first in air, then in hydrogen, and finally in carbon dioxide freed from oxygen. The metal does not retain alkali. C. H. D.

Naphthalene Picrate and the Estimation of Naphthalene. WILLEM P. JORISSEN and J. RUTTEN (*Chem. Weekblad.*, 1909, 6, 261—272).—A summary of the methods employed in the estimation of naphthalene. That of Stavorinus (*Het. Gas*, 1905, 477) is condemned on account of the decomposition of naphthalene picrate and the volatility of both naphthalene and picric acid at 100° . That of Colman

and Smith (Abstr., 1900, ii, 372) gives too low results, owing to solution of the naphthalene picrate in the washing water employed.

A. J. W.

Nylander's Reaction. M. E. REHFUSS and PHILIP B. HAWK (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxxi—xxxii; *J. Biol. Chem.*, 6).—Mercuric chloride and chloroform do not interfere with Nylander's test for sugar in urine (as stated by Bechhold) provided the urine is first boiled for five minutes. The reaction is regarded as a valuable confirmatory test, and details are given regarding the best way to effect it and the influence of other substances on it. Protein does not interfere with it, unless more than 2% is present.

W. D. H.

Barfoed's Test. WILLIAM H. WELKER (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxxiii—xxxiv; *J. Biol. Chem.*, 6).—In some cases where the test was used a greenish-white precipitate was produced; the cause was traced to the presence of sodium chloride, quite a small percentage of which interferes with the reaction. The nature of the precipitate is not yet clear.

W. D. H.

Correction of Acidity and a New Method for the Estimation of Free Volatile Acidity in Wines. NICOLÒ GALLO (*Staz. sper. agrar. Ital.*, 1909, 42, 37—50).—Experiments with wines to which acetic acid had been added show that when it is a question of diminishing the amount of this acid in a wine by 0.5—0.6‰, recourse should be had to normal potassium tartrate and never to the carbonate. Calcium carbonate should only be used when the proportion of acetic acid to be neutralised is very large.

The following method for estimating the free volatile acidity of wines depends on the observation made by the author that there exists a practically constant ratio between the quantity of acetic acid in a wine and the quantity extracted by ether in a single extraction. The method consists in shaking 25 c.c. of the wine and 30 c.c. of ether vigorously for a few seconds in a 100 c.c. cylinder with a ground stopper. When the ether has settled, 20 c.c. of it are removed by a pipette and shaken with water in a small beaker. The ether is then evaporated at a low temperature, and the remaining acid solution titrated with *N*/10-sodium hydroxide and phenolphthalein. The number of c.c. of alkali solution, multiplied by 0.24 and by 3.30, gives the parts of free acetic acid per 1000 of the wine.

T. H. P.

Estimation of Oxalic Acid in Urine. HUGH MACLEAN (*Zeitsch. physiol. Chem.*, 1909, 60, 20—24).—Autenrieth and Barth's method (Abstr., 1902, ii, 575) consists briefly in treating the dog's urine with excess of calcium chloride and ammonia until strongly alkaline; the mixture is filtered after eighteen to twenty hours, and the precipitate dissolved in 15% hydrochloric acid; this is shaken with a mixture of ether and alcohol, which dissolves the oxalic acid, and in the final aqueous solution acidified with acetic acid, the estimation of oxalic acid as calcium oxalate is made in the usual way. At Salkowski's suggestion, the accuracy of this method was tested, and the statement

of Autenrieth and Barth is confirmed that the method is exact; no oxalic acid is left in the filtrate after removal of the first precipitate.

W. D. H.

Estimation of Total Tartaric Acid in Tartaric Products.

P. CARLES (*J. Pharm. Chim.*, 1909, [vi], 29, 381—382; *Bull. Soc. chim.*, 1909, [iv], 5, 567—568; *Ann. Chim. anal.*, 14, 183—185).—In addition to the precautions already mentioned (*Abstr.*, 1907, ii, 655) as necessary in making this estimation, it is suggested that litmus paper should be used as an indicator. An aqueous solution of potassium tartrate or potassium sodium tartrate, whichever product will result from the titration, is prepared, and the coloration assumed by pieces of litmus paper placed in this is used as a standard of neutrality. The potassium hydrogen tartrate to be titrated is then dissolved in water, a few drops of phenolphthalein added and some pieces of litmus paper, and the titration proceeded with until the litmus paper assumes a blue tint. The liquid is then boiled, more litmus paper added, and the titration continued until the colour of the paper is the same as that in the standard liquid. At this stage the addition of a few more drops of alkali should cause the red coloration due to phenolphthalein to appear.

T. A. H.

Estimation of Amino-acids in Urine. VALDEMAR HENRIQUES (*Zeitsch. physiol. Chem.*, 1909, 60, 1—9).—See this vol., ii, 506.

Halphen's Reaction. LÉON RONNET (*J. Pharm. Chim.*, 1909, [vi], 29, 379—380).—The author has tried the modified form of this reaction described by Garnier (this vol., ii, 447), and finds that it is less sensitive than the test as originally described by Halphen. For the quantitative estimation of cotton seed oil, the author applies Halphen's reaction colorimetrically, the colour given by an oil containing a known quantity of cotton seed oil being used as a standard of comparison.

T. A. H.

Estimation of Added Water in Altered Milks. ANDRÉ KLING and PAUL ROY (*Compt. rend.*, 1909, 148, 1050—1052 *).—The estimation of added water in milk which has been kept for any length of time is complicated by the fermentations which occur in spite of preservatives and convert part of the non-fatty solids into volatile matter. The authors determine the total nitrogen by Kjeldahl's method, having first evaporated to dryness under reduced pressure. The total nitrogen per litre multiplied by the factor 6.39 gives the amount of protein matter, which is either compared with that in a milk of similar origin, or, in default, with the standard value 33 grams per litre. The authors show that this method is capable of yielding concordant results with the same milks when fresh and after two years' storage. The addition of 5% of water can be detected unmistakably.

R. J. C.

Distinctions between Natural, Artificial, and Synthetic Camphors. WILHELM LOHMANN (*Ber. Deut. pharm. Ges.*, 1909, 19, 222—226).—After a historical résumé of the processes available for

* and *Ann. Chim. anal.*, 1909, 14, 215—217.

the manufacture of synthetic camphor, the author points out that the melting point is not a safe means of distinguishing natural from synthetic camphor, and that the best means is the observation of the rotatory power, all the synthetic camphor so far placed on the market being optically inactive. Some commercial synthetic camphors are impure, and consist of mixtures of camphene, borneol or isoborneol, and camphor. The presence of such impurities can be detected by fractional sublimation, and estimated by acetylating the crude product, suitably diluted with turpentine oil, and determining the amount of acetic esters formed. The estimation might also be carried out by melting the crude product with phthalic anhydride, converting the bornyl hydrogen phthalate formed into the sodium salt by adding sodium hydroxide, and then shaking out the unchanged camphor with ether and weighing it. Artificial camphor (pinene hydrochloride) can be readily distinguished from natural camphor by heating it with potassium hydroxide until all volatile products have passed off, and then testing the residue for chlorides.

T. A. H.

Choline in Animal Tissues and Fluids. W. WEBSTER (*Bio-Chem. J.*, 1909, 4, 117—126).—The author is of the opinion that the tests hitherto employed for the detection of choline in the blood are untrustworthy, and denies that choline can be detected by their means.

W. D. H.

Estimation of Creatinine. F. C. COOK (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxiv; *J. Biol. Chem.*, 6).—Certain factors influence the estimation of creatinine by Folin's colorimetric method. If more than 10 c.c. of alkali are used, lower results are obtained, because the alkali dissolves creatinine picrate. Thirty c.c. of picric acid gave but slightly higher results than 15 c.c. The presence of protein and the period of standing are also factors that influence the results. Of four other methods examined, the autoclave method of Benedict and Myers gave the most satisfactory results.

W. D. H.

Alkaloid Reactions. Eserine (Physostigmine). C. REICHARD (*Pharm. Zentr.-h.*, 1909, 50, 375—384).—The author is investigating systematically the colour reactions and other distinctive characters of the chief alkaloids, and a considerable number of these have been dealt with in previous papers.

If a little eserine sulphate is placed on a glass slip and moistened with water, and to the drop of solution so formed a drop of sulphuric acid is added, characteristic crystals of a sparingly soluble sulphate separate. After a while, the preparation gradually becomes oily and eventually resinous, but the crystals retain their characteristic appearance for a considerable time. With nitric acid, a similar separation of crystals occurs, and if the preparation is not warmed, the acid remains colourless for a day. On addition of potassium chromate to eserine sulphate in presence of nitric acid, a green mass is formed, and a similar change occurs, but more slowly, in presence of sulphuric acid. The alkaloid reduces molybdic acid very slowly and slightly in the cold, but rapidly gives a blue coloration on

warming. No coloration is given by eserine sulphate in the cold with titanous acid in sulphuric acid, but on warming slightly a yellowish-brown tint, changing to reddish-brown, is obtained; this rapidly disappears, yielding a colourless solution. The foregoing are the most characteristic of the numerous reactions described. In each case detailed directions for the application of the colour reaction are given.

T. A. H.

Reaction of Hordenine and Urotropine. A. LABAT (*J. Pharm. Chim.*, 1909, [vi], 29, 433—435).—Denigès has shown (Abstr., 1908, i, 775) that hordenine, like other substances containing a *p*-tolyl nucleus, gives a green coloration when heated with formaldehyde and sulphuric acid. The author now points out that since urotropine yields formaldehyde under the conditions of this experiment, it can replace the latter in making the test, and conversely, that hordenine can be used for the detection of urotropine.

T. A. H.

Estimation of Urea. CLARENCE QUINAN (*J. Biol. Chem.*, 1909, 6, 173—179).—A modification of the hypobromite method is described, in which greater exactness is obtained by the use of a modified Lunge's gas-volumeter.

W. D. H.

Detection in Urine of Chromogens of Methylene-blue, Thionin, and Lauth's Violet by Oxidising Agents in Acid Media. C. FLEIG (*J. Pharm. Chim.*, 1909, [vi], 29, 513—520).—Methylene-blue may be eliminated in the urine as such or as (1) a "chromogen of elimination," which is stable and yields methylene-blue only after boiling with acetic acid and subsequent oxidation by exposure to air, or (2) a "chromogen of fermentation," formed by the action of micro-organisms in alkaline or feebly acid urines. This second chromogen is unstable and yields methylene-blue by mere exposure to the atmosphere.

The new test consists in adding either hydrogen peroxide or ammonium persulphate to urine supposed to contain either of these chromogens; the unstable one yields methylene-blue at once, the stable one only after the further addition of acetic acid and boiling for a few minutes. If methylene-blue is present to begin with, it is extracted by means of chloroform. Methylene-blue is eliminated in the faeces in the form of a chromogen different from those occurring in the urine. The same test may be applied to the detection of the chromogens of thionin and Lauth's violet in urine, but in the case of thionin, dilute hydrochloric acid is preferable to acetic acid as a hydrolysing agent, and, further, ferric chloride solution may be used as an oxidising agent in place of hydrogen peroxide or ammonium persulphate. The test is not applicable to the urinary chromogens of triphenylmethane dyes. Fluorescein is eliminated in the urine unchanged.

T. A. H.

Formation of Crystals of Hæmin by means of Alkali Iodides or Bromides. GEORGES GUÉRIN (*J. Pharm. Chim.*, 1909, [vi], 29, 377—378).—Fresh defibrinated blood was dialysed until it no longer contained chlorides. A drop of this preparation, placed on a micro-

scope slide and evaporated to dryness, gave on addition of a dilute solution of an alkali bromide or iodide, microscopic crystals identical in form with those of hæmin (hæmatin hydrochloride) produced in Teichmann's test for blood.

T. A. H.

Tests for Pus and Blood. JOSEPH H. KASTLE and NORMAN ROBERTS (*Proc. Amer. Soc. Biol. Chem.*, 1908, xlii—xlvii; *J. Biol. Chem.*, 6).—Peroxydases are absent from normal urine, but are present in active inflammatory conditions of the genito-urinary tract when pus appears in the urine.

Phenolphthalein as a reagent for the detection of blood is very sensitive; 1 part of blood in 80 million parts of water can be detected. Blood-stains more than a year old give the reaction.

W. D. H.

Animal Fæces. I. Comparison of the Analysis of Fresh and Air-dried Fæces. A. D. EMMETT and HARRY S. GRINDLEY (*J. Amer. Chem. Soc.*, 1909, 31, 569—579).—In the preparation of fæces for analysis, it is usual to dry them in the air, and afterwards reduce them to powder. It is desirable, however, to determine the composition of the fresh, undried material, since a loss of nitrogen usually occurs on drying. Moreover, the analysis of fresh dung facilitates the study of the nature of the metabolic and undigested products.

It has now been found that proteins, fat, moisture, ash, carbohydrates, and phosphorus can be easily and satisfactorily estimated in the fresh fæces of swine and cattle. In the case of swine-dung, it is considered that the losses which occur on drying are chiefly due to mechanical errors introduced by the manipulation of the material during the drying process, and not to the loss of any particular constituent. In cases in which there is any danger of loss of nitrogen or the products of fermentation, the analysis of the fresh material, preserved with thymol, is preferable to the dry method. In connexion with the analysis of fresh fæces, it is necessary that the food-stuffs supplied to the animals should be ground or chopped fairly small, otherwise the dung will contain coarse, undigested particles, and it will consequently be difficult to obtain an average sample.

E. G.

New Reaction of Abrastol. OTTORINO CARLETTI (*Boll. Chim. Farm.*, 1909, 6, 223—224).—The following reaction allows of the detection of 0.00005 gram of abrastol in the extract prepared from food materials in the manner described by Vitali (*Abstr.*, 1908, ii, 642). After removal of the solvent by evaporation, the residue is treated with 2—3 c.c. of concentrated sulphuric acid and then with 1 to 2 drops of a 10% aqueous or alcoholic tartaric acid solution, the capsule being then cautiously heated by means of a small flame. In presence of abrastol, emerald-green striae form in the liquid, which becomes uniformly green on shaking. The coloration disappears if the solution is diluted with water. This reaction has the advantage over that given by ferric chloride, that it is not influenced by the presence of organic acids.

T. H. P. C.

General and Physical Chemistry.

Measurement of the Optical Constants of Certain Liquid Crystals. ERNST DORN and WILHELM LOHMANN (*Ann. Physik*, 1909, [iv], 29, 533—565).—The refractive indices of the isotropic and the two anisotropic forms of ethyl ethoxybenzylideneamino- α -methylcinnamate and ethyl ethoxybenzylideneamino- α -ethylcinnamate have been determined. Values are recorded for the lithium, sodium, and the green and blue mercury lines.

The double refraction of the anisotropic modifications is very considerable, being about twice as large as that of calcspar. With increase of temperature, the refractive index of the isotropic liquids diminishes, whilst that of the crystalline liquids increases. In the anisotropic modifications which are formed at lower temperatures both substances behave like uniaxial solid crystals. This is regarded as evidence against the emulsion theory of crystalline liquids.

H. M. D.

Biaxial Liquid Crystals. FRÉDÉRIC WALLERANT (*Compt. rend.*, 1909, 148, 1291—1292).—The anisotropic liquid obtained by melting azoxyanisole possesses different optical properties when examined in a beam of convergent light from the anisotropic liquid which results when isotropic liquid anisole is cooled down. This is strong evidence in favour of the idea that such anisotropic liquids really contain liquid crystals, the orientation of the crystals depending on how the anisotropic liquid has been obtained.

T. S. P.

Magnetic Dichroism of Different Minerals. GEORGES MESLIN (*Compt. rend.*, 1909, 148, 1179—1180).—From an examination of thirty different minerals immersed in nine different liquids, it is shown that the magnetic dichroism of the mineral runs parallel with the amount of double refraction; for example, with siderite, where the difference between the indices of refraction is 0.31, the magnetic dichroism is strong, whereas with apatite, where the difference is only 0.004, there is no magnetic dichroism. Moreover, when there is a change in sign in the dichroism, it occurs when the mineral is immersed in a liquid of which the refractive index is approximately equal to the mean refractive index of the mineral.

T. S. P.

Secondary Spectrum of Hydrogen. A. DUFOUR (*Phil. Mag.*, 1909, [vi], 17, 854—855).—A claim for priority against Hogley (this vol., ii, 359). The stellar and secondary spectra were always obtained together in the author's experiments, even when the hydrogen was at atmospheric pressure.

H. M. D.

Arc Spectrum of Yttrium. G. EBERHARD (*Zeitsch. wiss. Photograph. Photochem.*, 1909, 7, 245—253).—The wave-lengths and intensities of the lines in the arc spectrum of yttrium have been

measured. By the use of a series of rare earth fractions, obtained by Urbain's method of fractionation, the gradual variation in the intensity of the yttrium lines was also observed. The results are tabulated and compared with previous measurements of Kayser and of Exner and Haschek. The differences in the recorded intensities of many lines are attributed to the different times of exposure of the plates.

H. M. D.

Quantitative Spark Spectra of Titanium, Uranium, and Vanadium. JAMES H. POLLOCK (*Sci. Proc. Roy. Dubl. Soc.*, 1909, 11, 331—337).—Photographs have been obtained of the spark spectra yielded by solutions containing 10, 1, 0.1, 0.01, and 0.001% of titanium, uranium, and vanadium. The wave-lengths, intensities, and persistencies of the various lines are recorded in tabular form. From a comparison of the spectra given by the fused metals, it was found that in all three cases the solutions give all the lines exhibited by the free metals.

H. M. D.

An Example of a Longitudinal Positive Zeeman Effect in the Emission Spectra of Vapours. A. DUFOUR (*Compt. rend.*, 1909, 148, 1311—1312).—An investigation of the action of a magnetic field of 28,000 units on the band $\lambda = 5789.7$ of oxide of iron has shown that the Zeeman effect parallel to the lines of force is positive. The deviation of the magnetic doublet is about five times less than that for the sodium *D*-line, and the circular polarisation of the components is complete. Observations perpendicular to the lines of force indicate that the band in question furnishes an ordinary triplet.

No general relation exists between the occurrence of a longitudinal positive Zeeman effect and the incomplete extinction of the components of the magnetic doublets by a circular analyser. This rule only applies to certain classes of compounds; the observed facts again show that different band spectra possess different characteristics, and that the Zeeman effect may be utilised to classify them. T. S. P.

Emission of Light in Banded Spectra. JOHANNES STARK (*Ann. Physik*, 1909, [iv], 29, 316—330).—In reference to the view of Lenard and Saeland (this vol., ii, 283) that the phenomenon of phosphorescence is genetically connected with the photo-electric effect, the author points out that this is in agreement with his general theory of banded spectra (compare Abstr., 1907, ii, 147, 417; 1908, ii, 138, 746, 911; 1909, ii, 106, 109). According to this theory both phosphorescence and fluorescence are dependent on the absorption of light of short wave-lengths, resulting in the separation of valency electrons; the emission of light is then due to the re-union of the valency electrons with the atomic residues. Whereas in a fluorescing substance the valency electrons recombine immediately or after a very short interval with the atomic residues, it is supposed that the special characteristic of phosphorescence is caused by a combination of part of the separated electrons with other atoms, energy being required for the resolution of

these combinations before re-combination of the electrons with the atomic residues can take place.

The author maintains the correctness of his previous view, that the line spectrum of an element is due to positively charged atoms of the element, and throws doubt on Lenard's theory, that the chief series of lines is due to electrically neutral atoms, and the secondary series to positively charged ions.

H. M. D.

Influence of their State in Solution on the Absorption Spectra of Dissolved Dyes. SAMUEL E. SHEPPARD (*Proc. Roy. Soc.*, 1909, 82, 4, 256—270).—The absorption spectra of solutions of certain dyes have been examined. The absorption spectrum of the *isocyanines*, *pinacyanols*, and *cyanine* in aqueous solution is quite different from that of the solutions in ethyl alcohol and other organic solvents. This difference is supposed to be due to the dye being present partly or wholly as a colloid in the aqueous solution. The fact that the aqueous solutions are coagulated by electrolysis and by repeated heating and cooling, and that they show the Tyndall effect, affords evidence in support of this view.

Dyes which are present in true solution show the smallest changes in the absorption spectrum when the concentration is varied. The absorption maxima are not displaced, and if the dyes are chemically stable, Beer's law is found to hold good. On the other hand, dyes which are wholly or partly present in the form of colloids exhibit considerable changes when the concentration alters and Beer's law does not hold. In solid media, like collodion and gelatin, similar relationships are found.

From his observations the author draws the conclusion that the process of dyeing is strictly analogous to the "solution" of dyes in liquid solvents, in that corresponding phases or grades of solution are to be found in the two cases.

H. M. D.

Absorption Spectra of Solid Tetramethylpicene and of its Solutions. JOHN E. PURVIS and ANNIE HOMER (*Proc. Camb. Phil. Soc.*, 1909, 15, 82—84. Compare *Trans.*, 1908, 93, 1319).—A comparison of the absorption spectra of the solid hydrocarbon and of its *N*/1000 solutions in benzene and ethyl alcohol has been made. In all cases three absorption bands are found, but the relative position of these varies. In the benzene solution both the general and selective absorption are shifted towards the red in comparison with the alcoholic solution, and there is a further shift in the case of the solid hydrocarbon. The phenomena are attributed to the differences in the damping effect exerted by the medium on the vibrations of the active molecules of the solute.

H. M. D.

Absorption Spectra of Concentrated and Diluted Solutions of Chlorophyll. JOHN E. PURVIS (*Proc. Camb. Phil. Soc.*, 1909, 15, 85—88).—A comparison of the absorption spectra of chlorophyll in concentrated and dilute solutions has been made. Ethyl-alcoholic solutions, the concentrations of which were in the ratio 719.8:1, were compared, photographic records of the absorption being taken

after the solutions had been allowed to remain for gradually increasing intervals of time. The two freshly prepared solutions show bands at λ 538 and 565, and the general absorption in both begins at about λ 510. After standing for several days, the strong solution shows well-marked bands at λ 538 and 508, together with a trace of the band at λ 565, and the general absorption is very much smaller than in the freshly prepared solution. In the dilute solution λ 565 is stronger, and λ 538 much weaker, than in the corresponding strong solution, and no band can be observed at λ 508. The observed gradual changes in the spectra are supposed to be due to enzyme action. H. M. D.

Polarisation by Lateral Diffusion. GEORGES MESLIN (*Compt. rend.*, 1909, 148, 1095—1097).—A limpid liquid illuminated by a ray of light and viewed from the side diffuses light, which is partly polarised in the plane defined by the incident and diffused beams. If crystalline particles are suspended in the liquid, the amount of diffused light is greater, but the proportion polarised is less, although in the same plane. This effect was found in more than 1000 different liquids. Boric acid suspended in liquids of refractive index greater than 1.42, such as terebenthene, benzene, aniline, etc., and also pyrogallol under certain conditions, exhibits the abnormal property of diffusing light which is polarised in a plane perpendicular to the plane of diffusion (negative dichroism). In this case the transmitted ray is polarised in the plane of diffusion (positive dichroism). In all other cases where the transmitted beam exhibits positive dichroism (such as potassium carbonate suspended in light petroleum), the diffused (reflected) beam is polarised in the same plane.

The peculiar spontaneous dichroism of boric acid suspensions is attributable to the orientation of the crystals by gravity. R. J. C.

An Ammonium Model. EDGAR WEDEKIND (*Ber.*, 1909, 42, 2142—2147).—The model is composed of two concentric circular hoops, one of which can rotate about a vertical diameter inside the other one; by attaching five spheres to the circumferences of the two circles, or by placing one in the centre and four on the circumference, it is possible to explain the isomerism and mechanism of the formation of quaternary ammonium salts. For a detailed account of this the original paper should be consulted. P. H.

Calculations in Photochemical Processes. FRITZ WEIGERT (*Ber.*, 1909, 42, 1783—1786).—Polemical. Reply to Byk (compare this vol., ii, 454). P. H.

Influence of Radium on Rate of Crystallisation. LOUIS FRISCHAUER (*Compt. rend.*, 1909, 148, 1251—1254 *).—Sulphur, carefully purified by successive fractional distillations, was sublimed on to a microscope slide, where it appeared in detached hemispherical drops. Drops with a diameter less than 30μ do not crystallise spontaneously, whilst those of diameter more than 180μ crystallise in a few minutes. Most of the drops were from 54 to 90μ in diameter, about 65 being

* and *Le Radium*, 1909, 6, 161—164.

deposited per square millimetre. These crystallised spontaneously at the rate of about one per day.

A slide was partly covered with lead sheet 5 mm. thick, and the remainder was exposed to the radiation from 25 mg. of radium contained in a glass bulb 0.9 mm. thick. The exposed part crystallised spontaneously, and by contact from drop to drop at such a rate that at the end of four days about 3 to 5 times as much was crystallised as on the protected part of the slide. The remaining drops in the exposed part all crystallised when the slide was heated at 70° for six hours, whereas only a moderate crystallisation occurred in the unexposed portion.

Solidification of superfused sulphur deposited inside a tube occurs spontaneously where radium emanation is allowed to settle down, but most of the rest of the sulphur remains liquid.

Röntgen rays are without effect on the rate of crystallisation, hence it is probable that radium γ -rays are also without effect. Since α -rays could not penetrate the glass of the bulb containing the radium, it follows that the crystallising action described was due to the radium β -rays.

R. J. C.

Radium and Uranium in Radioactive Minerals. ELLEN GLEDITSCH (*Compt. rend.*, 1909, 148, 1451—1453 *).—It is generally accepted from the experiments of Boltwood, McCoy, Rutherford, and Boltwood and Strutt (compare Abstr., 1905, ii, 295, 366, 568, 787) that the ratio of radium to uranium in all rocks is constant. The method of estimation by dissolving the mineral in acid and measuring the activity of the emanation given off is objected to by the author on various grounds, principally the fact that if the mineral contains sulphides, these, during the dissolution in nitric acid, give rise to barium and lead sulphates, which would carry down some radium sulphate.

The author estimates the radium in various minerals by dissolving them completely in suitable solvents. Alternate additions of barium chloride and sulphuric acid are made until the mother-liquors are no longer radioactive. The active precipitates are converted into carbonates by boiling with sodium hydroxide and sodium carbonate, and are then completely dissolved in hydrochloric acid. The radium in the solution is estimated by the emanation evolved. The ratio of radium to uranium is not constant in the minerals analysed. Joachimsthal pitchblende contains radium and uranium in the ratio given by Boltwood. A French autunite contains relatively less radium, and Ceylon thorianite more radium, than pitchblende. It might be supposed that since autunite is a secondary mineral, the original ratio may have become modified, as certain pyromorphites containing radium are free from uranium altogether. The discrepancy in the case of thorianite is more difficult to understand.

R. J. C.

Absorption of the γ -Rays of Radium by Lead. Y. TUOMIKOSKI (*Physikal. Zeitsch.*, 1909, 10, 372—374).—The absorption of the γ -rays from radium emanation by lead has been measured for different thicknesses reaching up to 19 cm. The value of the absorption coefficient decreases gradually as the thickness of the layer of lead

* and *Le Radium*, 1909, 6, 165—166.

traversed increases. Between 1.5 and 12 cm., it is, however, nearly constant, the value of λ being 0.52—0.50. The mean value of λ between 12.0 and 15.8 cm. is 0.39, and a further drop in the absorption coefficient then appears to take place, the mean value between 15.8 and 18 cm. being 0.25. H. M. D.

Radium Emanation. ANDRÉ DEBIERNE (*Compt. rend.*, 1909, 148, 1264—1267. Compare Rutherford, *Abstr.*, 1908, ii, 791; Rutherford and Royds, this vol., ii, 203).—The emanation from a solution of 0.2 gram of radium was purified from oxygen, hydrogen, and carbon oxides by successive treatment with heated copper, copper oxide, phosphoric oxide, and fused potash. Nitrogen was removed by slightly heated metallic lithium. The purified emanation was liquefied between -175° and -150° , and a residue consisting of helium with a little emanation was pumped off. The liquefied emanation was free from helium and neon.

The mean volume of emanation in equilibrium with 1 gram of radium was found to be 0.58 cub. mm., a value in exact agreement with that given by Rutherford (*loc. cit.*), although the method of isolation was quite different. The actual volumes of emanation determined were 0.60, 0.52, 0.61, 0.59 after three, six, nine, and thirty-two days accumulation in the radium solution respectively. The initial contraction of the emanation and the final development of helium noted by Rutherford were observed. The emanation had a half-period of 3.81 days (Rutherford found 3.75), but the small proportion of uncondensed emanation mixed with the helium appeared to have a somewhat longer half-period. The emanation at atmospheric pressure exhibits spontaneous electric discharges, particularly if the containing tubes are of fusible lead glass, which, moreover, turns violet under the influence of the radiation. The phenomenon is attributed to the accumulation of electric charges from α - and β -particles when the glass has sufficient insulating power. R. J. C.

Liberation of Heat from Radioactive Substances. WILLIAM DUANE (*Compt. rend.*, 1909, 148, 1448—1451).—An extremely sensitive calorimeter is described, consisting of two bulbs connected by a horizontal capillary tube and half filled with ether. The slightest temperature difference gives rise to a difference in vapour pressures, causing the ether to flow from the warmer to the cooler bulb until the difference in level in the two bulbs compensates the difference in vapour pressure. The bulbs are not completely evacuated, so that it is possible to get a small air bubble in the capillary tube to act as an index, which is either observed through a telescope or projected on to an enlarged scale. The whole calorimeter is supported on wax inside a block of lead, insulated by cotton wool from the containing zinc box, which is in turn placed in a thermostat. The apparatus, which is suitable for many physical, chemical, and biological measurements, is so sensitive that it is possible to detect with certainty in a few minutes a development of heat at the rate of 0.001 gram calorie per hour.

The radioactive substance or other source of heat to be examined is

placed in a tube, which is fused inside one of the bulbs, so that it hangs in the ether. The total displacement of liquid or the rate of displacement may be measured. The author makes use of the Peltier effect to measure the actual amount of heat produced. A thermocouple of nickel and iron is placed in the tube along with the radioactive substance, and the exact current is passed to absorb at the thermojunction all the heat given out by the radioactive substance, so that no motion of the liquid in the capillary tube is apparent. The thermojunction is previously calibrated in the same apparatus against a second electric circuit developing a known amount of heat.

A salt containing 0.80 mg. of radium chloride developed heat at the rate of 0.073 cal. per hour, so that 1 gram of radium should evolve 120 cal. per hour (previous investigators have given 110, 117, and 118 cal.). Radiothorium was found to emit heat, an actual development of 0.025 cal. per hour being measured. A radium salt of equal radioactivity would give 0.039 cal., so that radiothorium disengages a quantity of heat which is of the same order as that given by radium.

Polonium, free from radium and radiothorium, was found to emit heat.
R. J. C.

Secondary Röntgen Radiation from Air and Ethyl Bromide. J. ARNOLD CROWTHER (*Proc. Camb. Phil. Soc.*, 1909, 15, 101—105. Compare Abstr., 1907, ii, 922).—The relative amounts of ionisation produced in ethyl bromide vapour by the secondary Röntgen rays which are emitted by ethyl bromide and air have been measured. From this result, and the extent to which the two kinds of secondary rays are absorbed by ethyl bromide, it is found that the intensity of the secondary radiation from ethyl bromide is 105 times that from air.

By means of observations on the absorption of the two kinds of secondary rays by filter paper, the previous measurements of the ratio (*loc. cit.*) have been corrected, and the intensity ratio obtained in this way is 101. The two values obtained from measurements made respectively in air and in ethyl bromide are thus in good agreement.

H. M. D.

Absorption Spectra of Mesitylene and Trichloromesitylene. JOHN E. PURVIS (*Proc. Camb. Phil. Soc.*, 1909, 15, 89—90).—The author has compared the absorption spectra of mesitylene and trichloromesitylene in 0.001 molar ethyl-alcoholic solution. By the introduction of the three chlorine atoms the strong absorption band is shifted towards the red from λ 269— λ 254 to λ 287— λ 263. The persistence of the latter is very much greater than that of the mesitylene band.

H. M. D.

Condition of Electric Charges on Particles Suspended in Gases; Charge on Chemical Fumes. MAURICE DE BROGLIE and BRIZARD (*Compt. rend.*, 1909, 148, 1457—1458).—Smoke is examined by the ultramicroscope whilst subjected to an electric field. Ammonium chloride fume is found to consist of particles of one sign travelling

with a relatively high velocity. If the fume is first exposed to radium, the mobility of the particles when in the electric field is four to five times less, and both + and - charges are observed. It is therefore supposed that a single particle can hold more than one charge. After exposure to radium, the particles soon return to their normal state of mobility and charge.

Generally speaking, fumes which are produced by chemical action unaccompanied by rise in temperature have no electric charge. Such are the fumes produced by moist air with stannic chloride, silicon fluoride, hydrogen chloride, nitric acid, Nordhausen sulphuric acid, phosphorus pentachloride, arsenic chloride, etc. Sulphur dust distilled in nitrogen also belongs to this category. These substances give particles which are neutral, but transformable, by ionising rays into large ions of both signs.

Products of violent chemical action are already charged and of both signs. Such are the fumes produced by throwing sodium, sulphuric oxide, phosphoric oxide, and phosphorus pentachloride into water. Products formed with flame, such as by projecting powdered arsenic or antimony into chlorine, the spontaneous combustion of hydrogen phosphide, etc., are also charged, but the ionisation in this case is allied to the well-known ionisation by flames. The phosphorescence of phosphorus gives rise to ionisation, but that of sulphur does not.

R. J. C.

Dielectric Constants of Mixtures of Solids. ERNST RUDOLFI (*Zeitsch. physikal. Chem.*, 1909, 66, 705—732).—The melting-point curves and dielectric constants of a number of binary mixtures consisting mainly of naphthalene, anthracene, and their derivatives have been determined. The dielectric constants were measured by a modification of Drude's method, and only varied between 2.6 and 3.2. The equilibrium data are as follows: Naphthalene-bromocamphor, eutectic point 40.5° and 64% by weight of bromocamphor; naphthalene-phenanthrene, eutectic point 47.5° and 54% by weight of the latter component; naphthalene- α -naphthylamine, eutectic point 27.5° and 74% by weight of the latter component; naphthalene-*p*-toluidine, eutectic point 29° and 73% by weight of the latter component; naphthalene-anthracene, eutectic point 77° and 12% anthracene; mixed crystals may be formed between 0 and 12% anthracene; β -naphthol-anthracene, from 0—12% of anthracene mixed crystals separate, from 12—100% of anthracene this substance separates primarily from the fused mass; β -naphthylamine-anthracene behaves exactly like the last system; naphthalene- β -naphthol form a continuous series of mixed crystals, as do naphthalene and β -naphthylamine. In the latter case, however, the melting point of each of the pure components is lowered by the addition of the other. Finally, the system naphthalene-picric acid shows two eutectic points at 78.5° and 8% and 114° and 94% of picric acid respectively, and a compound containing the components in molecular proportions, which has been described by previous observers.

The dielectric constant of binary mixtures can be calculated from those of the pure components by means of a formula based on the

expression $(\sqrt{K} - 1)/d$, where d is the density, and it is shown that this formula applies whether the components exist separately or as mixed crystals. It also applies to the compound of picric acid and naphthalene, but no general conclusion can be drawn from a single example of this type. G. S.

Physico-chemical Interpretation of the Differences of Potential Existing in Living Tissues. PIERRE GIRARD (*Compt. rend.*, 1909, 148, 1186—1189).—In a previous paper (this vol., ii, 463) the author has shown that when a membrane is placed in a concentration cell which is slightly acid or alkaline the polarisation of the membrane is, among other things, inversely proportional to the coefficient of viscosity of water. The alteration of *E.M.F.* of the cell with temperature will consequently not be proportional to the absolute temperature, as demanded by Nernst's equation, but will vary more rapidly in accordance with the variation with temperature of the viscosity of water. If the *E.M.F.* of polarisation is of opposite sign to that of the concentration cell, rise in temperature will lower the voltage of the cell more rapidly than corresponds with proportionality to the absolute temperature, whereas when the *E.M.F.*'s are of the same sign, the effect of a rise in temperature is to increase the voltage more rapidly than corresponds with proportionality to the absolute temperature. These conclusions have been verified by experiments on different concentration cells. Since the cell contents of living tissues deviate more or less from neutrality, an explanation is thus afforded of the results obtained by Lesser and others in experiments on the skin of a frog. T. S. P.

Modified Oxy-Hydrogen Gas Coulometer. J. W. TURRENTINE (*J. Physical Chem.*, 1909, 13, 349—354).—A modified form of the Walter-Neumann coulometer is described, in which the electrodes are readily detachable. The new form of apparatus is much less liable to breakage than the old. H. M. D.

Conductivity of Non-luminous Sodium Vapour and the Relationship between the Ionisation of Gases and the Absorption of their Line Spectra. CHRISTIAN FÜCHTBAUER (*Physikal. Zeitsch.*, 1909, 10, 374—377).—An experiment is described which indicates that sodium vapour begins to conduct electricity at about 200°. It has also been found that sodium vapour exposed to an arc light shows the characteristic absorption lines when the temperature reaches 190°. These observations support the view that sodium ions are the source of the lines in the absorption and emission spectrum. The other alkali metals also absorb the lines of the primary spectrum at low temperatures, and it is therefore probable that the electro-positive metals generally have a tendency to ionise in the form of vapour. H. M. D.

Conduction of Electricity in Mixtures of Metals and their Salts. A. H. W. ATEN (*Zeitsch. physikal. Chem.*, 1909, 66, 641—671).—The electrical conductivity of mixtures of bismuth chloride and

bismuth in different proportions has been determined at different temperatures up to 350°. The measurements were made in an atmosphere of carbon dioxide, and, in order to obtain a sufficiently high resistance, the fused salt was contained in a capillary tube.

At low temperatures (250—280°) addition of bismuth lowers the conductivity of bismuth chloride, but at higher temperatures the conductivity first increases and then diminishes with progressive increase of bismuth, so that the curves obtained by plotting the composition as abscissæ against the conductivity as ordinates show very distinct maxima at the higher temperatures. The observations cannot be carried much beyond 40 mol. % of bismuth, owing to the limited solubility of the latter in the chloride, even at the higher temperatures. The temperature-coefficient of the conductivity of bismuth chloride is greater at high than at low temperatures, but that for mixtures containing a fair proportion of bismuth does not vary much with the temperature.

As regards mixtures rich in bismuth, it was only possible to examine those containing 98.9—100 mol. % of the metal, owing to the slight solubility of the chloride in the fused metal. Further, satisfactory measurements could only be made above 320°, owing probably to crystallisation of salt in the capillary at lower temperatures. Addition of bismuth trichloride causes a steady diminution in the conductivity of bismuth at all temperatures. The solubility of the trichloride in fused bismuth is smaller than the values given by Eggink (*Abstr.*, 1908, ii, 1043).

The viscosity of bismuth trichloride and of mixtures of the salt and bismuth in varying proportions has been determined at a series of temperatures between 260° and 320° by a modified form of the Ostwald apparatus. The densities of the mixtures have also been determined within the same limits of temperature, which admits of the calculation of the viscosity in absolute measure. For a mixture of given composition the viscosity, η , diminishes and the limiting conductivity, λ , increases with temperature, but $\lambda\eta$ is not constant, nor does there appear to be any simple relationship between λ and η .

The theoretical bearing of the results is discussed, but considerable uncertainty is introduced owing to the fact that the proportion of the compound BiCl_3 in the various mixtures is not known. G. S.

Electrical Conductivity and Dissociation of Sulphuric Acid in Aqueous Solutions at High Temperatures. YOGORO KATO (*Mem. Col. Sci. Eng. Kyōto*, 1908, i, 332—351).—The measurements were made in Noyes's laboratory by means of the platinum-lined bomb already described (Noyes and Coolidge, *Abstr.*, 1904, ii, 226). Observations have been made at 18°, 100°, 156°, and 218°, and the equivalent conductivity, in reciprocal ohms, of solutions containing 0.5—12.5 milli-equivalents of the acid per litre are given in tabular form.

The ionisation of sulphuric acid takes place mainly according to the equation $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4'$ (1), but the latter ion undergoes partial ionisation in dilute solution as follows: $\text{HSO}_4' \rightleftharpoons \text{H}^+ + \text{SO}_4''$ (2). It is shown that the ionisation relations can be calculated from the

conductivity data when the H^+ ion concentration and the concentration of the unionised acid are known, but the latter cannot be determined directly. On the assumption that the limiting conductivity for the $H^+HSO_4^-$ dissociation is equal to that for acetic acid, the degree of dissociation, according to equation (1), is calculated, and is shown to correspond fairly closely with that for hydrochloric acid, especially at higher temperatures. On the assumption that this agreement holds throughout, the concentration of the unionised part of the acid, and hence the complete equilibrium relations at different temperatures and concentrations, have been calculated. The results are tested by applying van't Hoff's equation connecting displacement of equilibrium with temperature with the heat of reaction, the results being moderately satisfactory. G. S.

Conductivity of Solutions of Lithium Nitrate in Ternary Mixtures of Acetone, Methyl Alcohol, Ethyl Alcohol, and Water. Viscosity and Fluidity of the Mixtures. HARRY C. JONES and EDWARD G. MAHIN (*Amer. Chem. J.*, 1909, 41, 433—442).—The electrical conductivity of ternary mixtures (containing the components in varying proportions) of water, acetone, methyl and ethyl alcohols in dilutions of 10 to 1600 litres has been determined at 0° and 25° , and the results, as well as the temperature-coefficients of the conductivity, are given in tabular form. The viscosity and fluidity of the mixtures at 0° and 25° are also given. The results are very briefly discussed. G. S.

Relation between Electrical Conductivity and Thermo-electric Power of Alloys of Silver with Zinc. NICOLAI A. PUSHIN and M. S. MAXIMENKO (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 500—524).—The authors' measurements of the specific resistances, the temperature-coefficients of the latter, and the thermo-electric forces of alloys of silver and zinc, in conjunction with the results of Pushin (*Abstr.*, 1907, ii, 618) and Petrenko (*Abstr.*, 1906, ii, 284), lead to the following conclusions.

Silver dissolves in zinc to a small extent, forming solid solutions, and silver dissolves zinc, forming solid solutions containing not less than 30 atom % of zinc.

The results also indicate the presence of the following compounds of the two metals: (1) Zn_6Ag , analogous to Hg_6K , Hg_6Cs , Hg_6Rb , Cd_6Na , and Zn_6Cu (compare Kurnakoff and Kusnetzoff, *Abstr.*, 1907, ii, 171; Kurnakoff and Schukowsky, *Abstr.*, 1907, ii, 345); (2) Zn_4Ag (compare Maey, *Abstr.*, 1905, ii, 146); (3) Zn_3Ag_2 , which exhibits the maximum specific resistance, the maximum temperature-coefficient of the latter, and the maximum absolute thermo-electric voltage; (4) $ZnAg$; (5) $ZnAg_3(?)$, $Zn_2Ag(?)$, and $Zn_{10}Ag(?)$, which may be compounds or solid solutions of definite concentrations.

Experimental confirmation is obtained of the view of Kurnakoff (*loc. cit.*) and Guertler (*Abstr.*, 1907, ii, 65), that the formation of a solid solution is accompanied by considerable increase of the resistance of the alloy, which increases also with the concentration of the solid solution.

Comparison of the resistance and thermo-electric force curves demonstrates for silver-zinc alloys the truth of the view expressed by Thomson and by Liebenoff (*Der elektrische Widerstand der Metalle*), that the first current passing through an alloy usually produces in the latter a thermo-current which acts as a supplementary resistance.

T. H. P.

Validity of Faraday's Law at Low Temperatures. WENDELL G. WILCOX (*J. Physical Chem.*, 1909, 13, 383—387).—The electro-deposition of silver from pyridine solutions of silver nitrate has been investigated at temperatures between 0° and -55°. As the temperature falls, the amount of silver deposited by a given quantity of electricity gradually diminishes; this is attributed to decomposition of the pyridine. It is shown that the difference between the amount of deposited silver and that required by Faraday's law increases with increase in the change of concentration at the electrodes. In spite of the observed discrepancies, the conclusion is drawn that Faraday's law regulates the electro-deposition at the temperatures of the experiments.

H. M. D.

Chemical Changes Produced by Different Kinds of Rays.
II. **Action of the Direct Electric Current.** CARL NEUBERG (*Biochem. Zeitsch.*, 1909, 17, 270—292. Compare Abstr., 1908, ii, 915).—Electrolysis of a number of substances was carried out between platinum electrodes in pure aqueous solution in closed vessels shielded from the light. In general, oxidative and hydrolytic changes were brought about. The multivalent alcohols give corresponding hydroxy-aldehydes or hydroxy-ketones. The carbohydrate acids with unbranched carbon chains give aldoses containing one atom of carbon less. Mono-saccharides form osones and carboxylic acids; di- and tri-saccharides are hydrolysed, and undergo further changes like the monosaccharides. Glucosides and paired glycuronic acid derivatives are hydrolysed.

Amino-acids lose ammonia, and are converted into aldehydes with an atom of carbon less. Hydroxy- and diamino-acids behave similarly; Aminodicarboxylic acids form aldehydic acids. Peptones and proteins are hydrolysed, and in part converted into aldehydes; phosphatides and nucleic acids are decomposed, and the decomposition products further changed. In general, the electric current, like the enzymes, tends to form carbonyl compounds of great potential activity from indifferent substances; its action is analogous to the catalytic action of light.

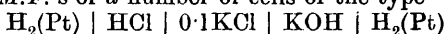
E. F. A.

Calculation of Ionic Hydration from Transport Numbers and Ionic Velocities. ERNST H. RIESENFELD and B. REINHOLD (*Zeitsch. physikal. Chem.*, 1909, 66, 672—686).—On the basis of Nernst's theory as to the movement of water with the ions in transport measurements, the authors derive the formula: $n_c = w_c - cx(1)$, where n_c is the experimental transport number (referred to the anion), w_c is the true transport number, c is the concentration, and x is a measure of the hydration of the anion. A number of curves are given in which the observed transport number is plotted against the con-

centration, and the following conclusions are drawn: (1) if in great dilution the anion wanders more rapidly than the cation; the latter is in general more highly hydrated than the former; (2) in such a case the transport number increases at first with increasing concentration; in the contrary case it diminishes.

The hydration cannot be calculated from equation (1) alone, but this can be done by combining the latter equation with another obtained by applying Stokes' law regarding the motion of a sphere in a medium of considerable resistance to the data for ionic velocities, and also from the ionic velocity data alone. The following values are thus obtained for the hydration of a number of ions at infinite dilution from the data for the ionic velocities, and very similar values are obtained from the alteration of the transport numbers with the temperature. The numbers denote the number of mols. of water per mol. of ion, and are presumably valid for 18°. $H^+ = 0$, $K^+ = 22$, $Na^+ = 71$, $Li^+ = 158$, $Ag^+ = 37$, $\frac{1}{2}Cd^{++} = 55$, $\frac{1}{2}Cu^{++} = 56$, $OH^- = 11$, $Br^- = 20$, $I^- = 20$, $Cl^- = 21$, $NO_3^- = 25$, $ClO_3^- = 35$. G. S.

Theory of Electrolytic Ions. II. Electrolytic Dissociation of Water. RICHARD LORENZ and A. BÖHI (*Zeitsch. physikal. Chem.*, 1909, 66, 733—751. Compare Lorenz and Mohn, Abstr., 1907, ii, 838).—The *E.M.F.*'s of a number of cells of the type



have been carefully measured at temperatures between 0° and 90°, and from the results the degree of dissociation of water calculated by Ostwald's method. The acid and alkali were used in *N*, *N*/10, and *N*/100 solution, but the most trustworthy results were obtained for *N*/10 solutions, and only these were used at higher temperatures. The contact differences of potential were corrected for by Planck's formula. The necessary data for calculating the degree of dissociation were found in the literature, except as regards the conductivity of *N*/10 potassium hydroxide at high temperatures, which was determined directly.

The values obtained for the degree of dissociation of water at different temperatures are as follows:

Temperature	0°	18°	25°	40°	60°	80°	90°
Degree of dissociation ...	0.37	0.85	1.10	1.98	3.55	5.92	$7.30 \times 10^{-}$

The results are in good agreement with those obtained by other methods, and the values for the heat of dissociation calculated by substituting the above values in van't Hoff's formula connecting displacement of equilibrium with temperature agree well with recent measurements of the heat of neutralisation of strong acids and bases.

G. S.

Magnetic Character of Compounds Prepared from Non-magnetic Elements. EDGAR WEDEKIND (*Zeitsch. physikal. Chem.*, 1909, 66, 614—632. Compare Abstr., 1907, ii, 353; Binet du Jassonneix, Abstr., 1906, ii, 520).—The magnetic properties of the following alloys of manganese, a boride, MnB , two antimonides, $MnSb$ and Mn_2Sb , and a phosphide, MnP , have been investigated. Some experi-

ments were made with the powdered materials, but the most trustworthy results were obtained with rods about 3 cm. long, which were obtained with considerable difficulty by fusing the materials in tubes of quartz or zirconium oxide in absence of air. The measurements of magnetic induction, etc., were made by a modification of the ordinary method in which a ballistic galvanometer is used.

The induction, magnetic permeability, and magnetic intensity for different strengths of field are given in tabular form, with similar observations on cobalt and wrought iron for comparison. They are also represented graphically, the magnetic induction being plotted against the field strength. The results are confirmed by a magnetometric method.

Of the compounds in question, the antimonide, MnSb , shows the greatest temporary magnetism and the phosphide the least. The compound (or end member of a series of mixed crystals) MnSb is five times more magnetic than the phosphide, and is only two and a-half times less magnetic than incompletely fused cobalt. A satisfactory comparison with iron is not practicable.

The weakly magnetic compounds retain their magnetism very strongly, being more effective than cast iron in this respect; the retaining power of the boride for magnetism is four times greater than that of the antimonide. The permanent magnetism is, however, in all cases less than that of steel.

The polarity of the boride is diminished by heating, and becomes zero at 450° G. S.

Coefficients of Expansion of Gases. ANATOLE LEDUC (*Compt. rend.*, 1909, 148, 1173—1176).—From an exact knowledge of the molecular volumes of different gases (Abstr., 1909, ii, 381) and by means of formulæ which the author has previously developed, the mean and true coefficients of expansion at constant pressure and the mean and true coefficients of increase in pressure at constant volume have been calculated for twenty different gases. The mean coefficients hold for a range in temperature from 0° to 100° , and the true coefficients for 0° . The errors in the numbers obtained probably do not exceed one in a thousand. In all cases, including that of hydrogen, the coefficient of increase in pressure at constant volume is greater than that usually given for a perfect gas: 3663×10^{-6} .

T. S. P.

Specific Heat of Hydrogen Chloride from Explosion Experiments. MATHIAS PIER (*Zeitsch. physikal. Chem.*, 1909, 66, 759—762. Compare Abstr., 1908, ii, 352).—It is shown that from the results of the explosion experiments described in the earlier paper the specific heat of hydrogen chloride at constant volume can be calculated. The results are in fair agreement with those calculated by means of the general formula for diatomic gases: $C_v = 4.6000 + 0.0005t$.

G. S.

Specific Heat of Ferromagnetic Substances: Alloys of Iron and Nickel. ANTOINE DUMAS (*Arch. Sci. phys. nat.*, 1909, 27, 352—382, 453—478).—The author has made measurements of the

specific heats of various alloys of nickel and iron, more especially in the region comprising the point of magnetic transformation (compare Weiss and Beek, *Abstr.*, 1908, ii, 659).

The curves expressing the mean specific heat as a function of the temperature all follow similar courses. The specific heat increases at first slowly, then more and more rapidly up to a certain point at which the curve becomes horizontal; this point corresponds exactly with the point of magnetic transformation. Curves connecting the true specific heat with the temperature show that this specific heat at first exhibits increasingly rapid, parabolic augmentation, then a sudden fall to a lower value, and subsequently renewed rapid rise. The absolute value of the discontinuity of the true specific heat at the point where ferromagnetism disappears is proportional to the square of the absolute temperature of this transformation point.

The positions of the points of transformation do not obey the law of mixtures, but vary with the content of nickel in an ill-defined manner. Apparently, the other ferromagnetic properties obey a law similar to that determining the positions of the points of transformation.

T. H. P.

Thermo - endosmosis. AUBERT (*Compt. rend.*, 1909, 148, 1254—1255. Compare Lippmann, *Abstr.*, 1907, ii, 668).—Two films of the same liquid, each 0.4 mm. thick, separated by a membrane, were maintained at different temperatures, and the direction of flow through the membrane was observed by means of capillary tube gauges. The membranes employed were gelatin, pigs' bladder, parchment, potato skin, and carrot skin. The rate of flow is proportional to the area of the membrane and to the temperature difference, and does not alter with time. The flow was always from the cooler to the warmer side of the membrane, whether the liquid used was pure water or a solution of acid, base, or salt. If the flow was obstructed, a pressure was developed which in some cases could exceed one atmosphere.

R. J. C.

Dissociation of a Compound in a State of Equilibrium. RUDOLF RUER (*Zeitsch. physikal. Chem.*, 1909, 66, 633—636).—The author points out that van Laar's criticism (this vol., ii, 376) of his results (*Abstr.*, 1908, ii, 819) is based on a misunderstanding. G. S.

The Sintering-point Curve: a Simple Means of Detecting Chemical Compounds between Two Components. ALFRED STOCK (*Ber.*, 1909, 42, 2059—2061).—The position of the maximum in a freezing-point curve corresponding with a binary compound is not always easy to fix, and Tamman's method of thermal analysis is not applicable to fused viscous substances of low conductivity. The sintering point is the temperature at which the eutectic begins to melt, and is readily observed. The sintering-point curve of a series of binary mixtures coincides approximately with the solidus, the sintering temperatures lying, however, slightly above the true eutectic temperatures. The curve shows a sharp cusp directed upwards at the composition corresponding with a compound.

C. H. D.

Methods of Preventing Superheating. A. KRÖNER (*Zeitsch. physikal. Chem.*, 1909, **66**, 637—640).—The superheating in a Beckmann's apparatus may be to a great extent overcome by the use of small, bell-shaped bodies, which are placed mouth downwards on the heated surface, or may be suspended in the boiling liquid. A still better effect is obtained when necessary by using a porous sheet of glass-wool or asbestos pressed against the heated surface. G. S.

A Source of Error but little Considered in the Determination of Boiling Points Under Diminished Pressure. C. VON RECHENBERG (*J. pr. Chem.*, 1909, [ii], **79**, 475—491).—In the ordinary apparatus used for distillation under diminished pressure the temperature of the vapour is measured in the distilling flask itself, whereas the pressure manometer is connected with some other part of the apparatus which is more or less far removed from the distilling flask. With this arrangement it is assumed that the pressure in the distilling flask is the same as that given by the manometer. Strictly speaking, this assumption is never true; in the distilling flask there is a flow of vapour from higher to lower pressures, and the pressure and temperature must vary at different heights above the liquid. These variations will only be noticeable with substances having a high boiling point under very low pressures, and the author shows that in some cases the excess of pressure in the distilling flask may be as much as 3—4 mm., which in the case of a liquid boiling above 200° would cause an error in the boiling point of 3—5° per mm. It follows that in all cases the manometer should be directly connected with the distilling flask.

It is further pointed out that quantitative conclusions cannot be drawn from the results obtained by Krafft and others in their work on distillation in a "cathode light vacuum," since the pressure in the distilling flask must have been much greater than 0·001 mm. It is, in fact, shown that if the pressure were really 0·001 mm., 1 gram of heneicosane would take 44·7 hours to distil, and the amount of vapour present at any time would not be enough to heat the glass and mercury of the thermometer to the temperature of the vapour.

T. S. P.

Dephlegmator with Heated Jacket. MICHAEL M. TICHWINSKY (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 386—387).—When 500 grams of caraway oil were distilled with a five-bulbed jacketed dephlegmator, the first fraction contained 3·66% of carvone, the constituent with the higher boiling point, whilst when the distillation was carried out with the same dephlegmator, but in a current of steam, the proportion of carvone in the first fraction was 3·21%. These results compare favourably with those obtained by Schimmel & Co. (*Semi-annual Report*, April, 1908, 161—165) on distilling large quantities of the oil (compare also Hardy and Richens, *Abstr.* 1907, ii, 531). T. H. P.

Evaporation of Aqueous Solutions. PIERRE VAILLANT (*Compt. rend.*, 1909, **148**, 1099—1102. Compare *Abstr.*, 1908, ii, 460).—It has been shown that the addition of sulphuric acid to water does not alter the value of the constant *B* in the evaporation formula:

$\phi = B.S(F-f)H$, where ϕ is the weight of water evaporated in unit time from surface S , F being the vapour tension of the liquid, f that of the air, and H the barometric pressure. The rate of evaporation of solutions of potassium and sodium hydroxides, phosphoric acid, potassium bromide and iodide, sodium chloride and nitrate, lithium and calcium chlorides, and glycerol has now been measured under exactly similar conditions of surface, and B calculated in each case with the aid of Dieterici's values of the vapour tension of these solutions. With the single exception of potassium hydroxide solutions, the value of B is remarkably constant. Thus the rate of evaporation does not depend on the nature of the solution, but only on its vapour pressure and surface. It is supposed that a layer of saturated air is formed in the immediate neighbourhood of the surface, and that evaporation is regulated solely by the rate of diffusion of the water vapour out of this layer.

R. J. C.

Freezing Points of Gaseous Mixtures at very Low Temperatures. GEORGES BAUME (*Compt. rend.*, 1909, 148, 1322—1324).—The author has investigated the freezing-point curves of the following binary systems: methyl ether-hydrogen chloride, methyl ether-sulphur dioxide, methyl ether-methyl chloride.

The curve for the system methyl ether-hydrogen chloride has two maxima, the one (at -94°) corresponding with Friedel's compound OMe_2HCl , whereas the other, at -102° , corresponds with the formula $\text{OMe}_2\cdot 4\text{HCl}$. The greater part of the curve lying between the two maxima could not be investigated, the mixtures forming uncrystallisable glasses.

Methyl ether and sulphur dioxide form one compound only $\text{OMe}_2\cdot\text{SO}_2$, the melting point of which is -91.7° .

The results for the system methyl ether-methyl chloride are to be published later.

Incidentally, the melting points of the pure constituents have been determined as follows: hydrogen chloride, -111° ; sulphur dioxide, -72.3° ; methyl chloride, -91.5° ; methyl ether, -138.5° .

T. S. P.

Freezing of Hydrogels. H. W. FISCHER and O. ROBERTAG (*Biochem. Zeitsch.*, 1909, 18, 58—94. Compare Abstr., 1908, ii, 1024; this vol., ii, 303; Lottermoser, *ibid.*, 27).—Experiments have been made by comparing the thermal effects of plunging tubes containing water and hydrogels in low temperature baths. In each experiment a tube of water (with a cake of gelatin) and a tube containing a gelatin gel were used. The tubes were made from the same glass and were exactly alike; they were placed in a vessel similar to a Dewar flask, and then immersed in a good freezing mixture and allowed to freeze. Differences of temperature in the two tubes were measured by means of a thermo-electric couple and a millivoltmeter. The results are expressed in curves, where the times are plotted against the readings of the voltmeter. They show that at the beginning there is no difference in temperature, then for a few minutes there is a slight difference, but ultimately this disappears. Preliminary experiments,

using two tubes containing benzene, gave no temperature differences. Analogous experiments, including determination of both cooling and heating curves, have been made with myricyl alcohol gels.

The general conclusion drawn is that the view that the forces acting between a reversible gel and a liquid are enormous is quite erroneous, and this conclusion is supported by Pauli's experiments on the evaporation of water from gels, and by the authors' experiments on the evaporation of chloroform from a myricyl alcohol gel.

It is also pointed out that the presence of colloids does not appear to favour under cooling. J. J. S.

Phenomena of Condensation for Mixtures of Carbonic Acid and Urethane in Connexion with Double Retrograde Condensation. PHILIPP KOHNSTAMM and J. CHR. REEDERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 11, 913—921).—The pressures corresponding with the co-existence of two liquid phases in the system carbon dioxide-urethane have been determined for temperatures between 26.1° and 37.3°. The phenomena of condensation of carbon dioxide are considerably modified by a very small quantity of urethane, for a mixture containing somewhat less than 0.4% of urethane gives rise to the three-phase system and shows a very pronounced retrograde condensation. H. M. D.

The Conditions Necessary for Direct Reactions, and the Direction of the Electric Current Produced when Metals are Attacked by Sulphur. ALBERT COLSON (*Compt. rend.*, 1909, 148, 1183—1186).—The author demonstrates by the following experiments that if two substances are each capable of combining with a third, the compound formed at a given temperature is not necessarily that with the greater heat of formation. 1. Although the heat of formation of aluminium oxide is much greater than that of copper oxide, when a mixture of the two metals is heated in the air, the copper oxidises first. 2. Copper and silver are readily blackened by sulphur when kept together in a vacuum, whereas aluminium and magnesium are not affected, although the heats of formation of the sulphides of copper and silver are less than those of aluminium and magnesium. The same is true if the metals are suspended in a solution of sulphur in light petroleum. 3. When copper and aluminium form the electrodes in a solution of yellow ammonium sulphide, the copper is attacked; similarly, if the copper is replaced by silver. 4. When copper is brought into contact with sulphur vapour, cupric sulphide is formed, although the heat of formation of cuprous sulphide is much greater than that of cupric.

The author considers that reactions are conditioned at constant pressure by the temperatures at which a compound is formed or decomposed. This range of temperature limits the "zone of reaction" (*Abstr.*, 1899, ii, 205). According to this view thermite reactions do not take place by reason of the great heat of formation of aluminium oxide, but because this oxide is not dissociated at the temperature of reaction (about 2000°), whereas the oxide to be reduced, for example, Cr_2O_3 , is dissociated. Thus in non-reversible reactions temperature plays a much more important part than heat of reaction. T. S. P.

Thermochemical Investigations of Organic Compounds.

III. Nitrogen Compounds. W. SVENTOSLAVSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 387—429. Compare this vol., ii, 23, 213).—In this paper the author analyses the thermochemical data for nitriles, amines, amides, acetylamino-compounds, nitro-compounds, nitrites, and nitrates. From the available numerical data the following conclusions are drawn.

All the linkings of nitrogen with oxygen and carbon exhibit variable thermochemical functions, their heats of formation increasing with increase of the molecular weight and with change of the structure of the compound in the direction of overloading of the neighbouring spheres surrounding the given unsaturated linking. With progressive increase of the molecular weight, the increases, $d\beta$, $d\mu$, etc., of the heat of formation of the unsaturated atomic linking are not uniform, but depend on the loading of the atoms connected by the unsaturated linking. For instance, $d\beta$ for the linking C-N increases considerably if the remaining affinities of the nitrogen atom are satisfied by hydrogen atoms, whilst it is diminished if the primary amine is changed to a tertiary one, in which the nitrogen is loaded with "heavy" radicles.

The heat of neutralisation of the amino-group in an aliphatic chain is considerably less than when the amino-group is attached to an aromatic nucleus; this fact the author regards as due to the equilibrium of the carbon linkings of the nucleus being disturbed.

The law of change of the heat of formation of atomic linkings is confirmed by studying the progressive change from ammonia to primary, secondary, and tertiary amines. Further, the characteristics of the linkings $C:N$ and $C \cdot N \begin{smallmatrix} < \\ O \end{smallmatrix}$ indicate that change from one class of compounds to another produces some variation in the heats of formation of the atomic linkings, this variation being, however, unimportant; such variation depends on the dynamic influence of the surrounding spheres. These facts indicate the use of the general law of valency of the elements, but also show that this law is valid only in a qualitative sense.

Equations are given expressing the thermochemical characters of the linkings C-C, C-H, C-N, and N-H, and combinations of these.

The heats of formation of the linking $C-N \begin{smallmatrix} \leq \\ O \end{smallmatrix}$ increase with the molecular weight, the formation of the grouping $N \begin{smallmatrix} \leq \\ O \end{smallmatrix}$ from its elements being accompanied by development of heat. Replacement of hydrogen by a radicle causes an increase in the heat of formation of the grouping $-O-N \begin{smallmatrix} \leq \\ O \end{smallmatrix}$. The formation of the linking N-O from the elements is accompanied by absorption of heat.

T. H. P.

Relation of the Surface Tension to the Internal Pressure and to van der Waals' Constants, a and b . PAUL WALDEN (*Zeitsch. physikal. Chem.*, 1909, 66, 385—444. Compare this vol., ii, 119, 123).—According to Stefan, the work, $(K-p)V$, required to

bring particles from the interior to the surface of a liquid is half that required to vaporise them (K = internal pressure, p = vapour pressure of liquid, $V = M/d$ = volume of a molecule of the liquid). Neglecting p in comparison with K , the formula $KV = M\lambda/2$ is obtained, where λ is latent heat of vaporisation of the liquid. Combining this with the equation already deduced for non-associated liquids (*loc. cit.*), $M\lambda/V = 3.64\gamma_\sigma$, where γ_σ is the surface tension at the boiling point, the equation $K = 1.82\gamma_\sigma$ is obtained; otherwise expressed, the ratio of the internal pressure and the surface tension at the boiling point is constant. An alternative expression for the internal pressure, valid through a wider range of temperature, is $K = 196\gamma_\sigma/\log T'_\sigma$, which gives the results in absolute measure. Further, according to van der Waals, $K = a/V^2$, and combining this with an expression for a in terms of T_σ and V_σ , a third expression, $K = 424T_\sigma/V_\sigma$, is obtained for K . The values of K are calculated by means of these three formulæ for a large number of non-associated and associated liquids, and the results are tabulated. Only for non-associated liquids is there fair agreement in the values obtained by the three formulæ, as is to be anticipated from the mode of deriving the latter.

As regards the relationship between internal pressure and chemical constitution for non-associated liquids, it is shown that in any one homologous series an increase of CH_2 always produces approximately the same diminution in the internal pressure, but the magnitude of the diminution is not the same for different homologous series. The halogens and halogen acids have very different internal pressures; the values for the elements, in atmospheres, are as follows: $\text{F}_2 = 1060$, $\text{Cl}_2 = 2135$, $\text{Br}_2 = 2660$, $\text{I}_2 = 2830$. On the other hand, the halogens in non-associated organic compounds can be interchanged without altering the internal pressure. The transition from saturated to unsaturated carbon compounds is accompanied by an increase in the internal pressure.

The nature of valency and residual affinity is discussed in this connexion, and it is shown that the greater the attractive forces between the molecules the greater is the internal pressure and also the tendency to association. Further, the greater the internal pressure of the solvent, the greater is its effect in producing simplification or ionisation of the solute. Internal pressure and mutual solubility are also connected; the smaller the difference of the internal pressures of two media, so much the greater is their reciprocal solubility.

The constant a of van der Waals' equation at the boiling point can be calculated in absolute measure by means of the formula $a_\sigma = 424VT'_\sigma$. A comparison of the values for non-associated liquids calculated by this formula with the values, a_k , under critical conditions given by Guye and Friderich (Abstr., 1900, ii, 709; 1902, ii, 599) shows that $a_k = 1.25a_\sigma$. By making use of this result, the relationships between a_k and the surface tension and heat of evaporation respectively are given by the equations $a_k = 245\gamma V^2/\log T'_\sigma$ and $a_k = 25.83V_m\lambda$, where the symbols have the usual significance. The values of a_σ thus obtained are not identical with those calculated

from van der Waals' equation, but the relationship a_σ/a_1 approximately holds, where a_1 represents the values of van der Waals. For associated liquids, a_k/a_σ is greater than 1.25.

From the known relationships of a and b expressions corresponding with the above are established for b , and are compared with the values obtained by other methods. For non-associated liquids, the expression $b_k = 1.26V_\sigma$ holds, but for associated liquids b_k/V_σ is greater than 1.26. The critical pressure, π , can be calculated by means of the formula $V_\sigma\pi/T_\sigma = 12.46$, and it is shown that the observed and calculated values are in good agreement.

A number of relationships between the surface tension, the internal pressure, and the critical pressure are deduced and tested. For a wide range of boiling points, the critical pressure, π , can be calculated by means of the formula $\pi = (6.5\gamma/\log T_\sigma) - 0.102T_\sigma$. Further, the critical pressure is proportional both to the internal pressure and the surface tension, $K/\pi = 34.2$ and $\gamma/\pi = 0.45$, and the molecular heat of evaporation, $M\lambda = \pi V_\sigma$.

The critical volume is 2.675 times the specific volume at the boiling point. The relationship $V_k\pi/T_k \sim 21.8$ is also deduced theoretically; this has already been given by Young and Thomas, and is written by van't Hoff in the form $V_k\pi/T_k \sim 22.0$. The experimental data show, however, that this formula is in many cases not valid; it holds approximately for normal liquids, but not for associated solvents or for liquefied gases. A modified form: $(V_k\pi)/T_k = 53.5/\log T_k + 0.004T_k$, represents the experimental results more accurately.

G. S.

An Hypothesis Relative to the Internal Pressure in Liquids.

ÉMILE H. AMAGAT (*Compt. rend.*, 1909, 148, 1359—1366).—In a preceding paper (*ibid.*, 1135) the author has shown that the total internal pressure of a liquid may be considered as the sum of two pressures, π and π'' . Further investigation of the value of π'' shows that it is always negative for all gases, and that it continually increases (negatively) as the volume diminishes. The pressure π'' thus acts in opposition to the molecular attraction and the internal pressure as if it were a perfect fluid (gas) occupying the intermolecular spaces. If this fluid follows Boyle's Law, then at constant temperature: $\pi''(v - \epsilon) = \pi''(v_1 - \epsilon) = \dots$, where ϵ is the volume of the molecules, and $v - \epsilon$, $v_1 - \epsilon$, \dots etc., are the volumes of the hypothetical fluid at pressures π'' , π_1'' , etc. As the external pressure on the gas increases, ϵ should decrease and finally attain a constant value; this is found to be the case for nitrogen at 0° . For pressures above 1600 atmospheres, ϵ has a value equal to 0.001125. This limiting value is called the co-volume ($=a$), and is independent of the temperature. For pressures where this limiting value holds, π''/π_1'' should equal $(v_1 - a)/(v - a)$, and this is demonstrated to be true.

Taking into account the variation of π'' with the temperature, keeping the volume constant, and assuming that the hypothetical fluid behaves as a perfect gas, it is shown that $1/273v - dp/dt = 1/273(v - a)$, and this is found to be true for nitrogen for pressures where ϵ has its limiting value ($=a$).

Similar results have been found with carbon dioxide, ethylene, oxygen, air, and ether.

Theory shows that if equal volumes of different gases are compared under the same conditions of temperature and (low) pressure, the internal pressure should be proportional to the square of the molecular weight of the gas. The experimental results, however, are not in accord with the theory. T. S. P.

Internal Pressure of a Gas. ANATOLE LEDUC (*Compt. rend.*, 1909, 148, 1391—1394).—Utilising the formulæ given in a previous paper (*ibid.*, 1174), the author has calculated the internal pressures of eighteen different gases under normal conditions, that is, for external pressures less than three atmospheres. This internal pressure is not found to be proportional to the square of the molecular weight of the gas, as it theoretically should be.

A comparison at 15° of ammonia and the methylamines shows that the substitution of CH_3 for H increases the internal pressure by 21·1-thousandths of an atmosphere.

In the case of acetylene and benzene at 129·6° and atmospheric pressure, the ratio of the internal pressures is found to be 10·1, which is approximately equal to the ratio of the square of the molecular weights of these substances. The deviation is probably due to the different complexities of the molecules. T. S. P.

Van der Waals' Equation of Condition and the Solid State. ISIDOR TRAUBE (*Ber. Deut. physikal. Ges.*, 1909, 231—236).—From van der Waals' equation the author deduces that the product of the internal pressure and the square root of the atomic (or molecular) compressibility should be approximately constant. As in a previous paper (*Abstr.*, 1903, ii, 355), the equation is applied to the solid state, and by making use of the compressibility values given by Richards, the author finds that the above product is very nearly constant for fourteen elements in the solid state. The higher value obtained in the case of iron is attributed to the great influence exerted by small traces of foreign substances on the internal pressure. H. M. D.

Influence of Temperature on the Change of Volume on Neutralisation for Various Salts at Different Concentrations. IDA FREUND (*Zeitsch. physikal. Chem.*, 1909, 66, 555—613).—The measurements were made by Ostwald's method, a special form of Sprengel pycnometer, which proved very suitable for experiments extending through a wide range of temperature, being used for the density measurements. The changes of volume on the formation of the chlorides and nitrates of potassium and sodium, of ammonium chloride, and of the acetates and fluorides of potassium and ammonium, have been calculated from the density determinations for a series of temperatures between 0° and 100°, and for 0·125 to 2*N*-solutions (in the case of the ammonium salts only up to 0·25 normal solution), and the results are expressed graphically and in the form of tables. In the first place the measurements were expressed in gram-equivalents

per kilo. of solution, but they are also approximately calculated for gram-equivalents per kilo. of solvent. The average accuracy is 3 in 100,000 ; above 70° the experimental difficulties become much greater.

In agreement with the results of previous observers, it was found that $\Delta v/c$ (where Δv is the change of volume and c is the concentration) increases with dilution, and approaches a limiting value independent of the nature of the salt. The influence of temperature is greater the more dilute the solution. For the chlorides and nitrates of potassium and sodium, $\Delta v/c$ diminishes at first with increase of temperature, attains a minimum value, which in the most dilute solutions lies at 45°, and beyond that point increases with the temperature. On the other hand, the changes of volume for the salts of weak acids and the ammonium salts diminish regularly with increase of temperature.

The theoretical bearing of the changes of volume with the concentration and the temperature are discussed, mainly with reference to Tammann's views as to the connexion of these factors with the internal pressure of the respective solutions. G. S.

Relation between the Orthobaric Densities of Homologues. G. TER GAZARIAN (*J. Chim. Phys.*, 1909, 7, 273—288. Compare Abstr., 1908, ii, 666).—From a study of the experimental data of Young and his co-workers, it is shown that for the members of a homologous series the densities corresponding with temperatures distant the same number of degrees from the critical temperature differ only by a factor. For example, if d is the density of pentane at the temperature t , the density d' of one of its homologues at the temperature $t + \theta$ (where θ is the difference in the critical temperatures of pentane and the other substance) is given by the formula $d' = d + (d'_c - d_c) - at$, where d'_c and d_c are the critical densities of pentane and its homologue, and a is the factor referred to above ; a varies from one natural group to another, and in some cases is zero. Its value increases with the molecular weight of the homologues.

The above rule is tested by application to the experimental data for certain hydrocarbons and esters, the results being given in tabular form. In the case of esters, a is practically zero.

A similar rule appears to hold for viscosities ; the details will be given in a later paper. G. S.

Adsorption by Clays. PAUL ROHLAND (*Biochem. Zeitsch.*, 1909, 17, 220—224. Compare this vol., ii, 27 ; Michaelis and Rona, this vol., ii, 125).—Kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), of all the clays, is least suited for adsorption experiments. The plasticity is very small, and likewise the tendency to form colloidal hydroxides, which in reality bring about the adsorption of proteins. Better suited are dark-coloured plastic clays, which form a large proportion of these colloidal hydroxides on contact with water, and are characterised by a loss of 12% or more on ignition. Such clays absorb a large number of substances possessing colloidal characters, and absorb further some crystalloids, in particular, dyes of complicated nature, such as Prussian- or Turnbull's-blue, aniline, and animal dyes, but not simple substances such as copper sulphate or potassium dichromate. They further absorb carbonates, and to some extent phosphates, but allow other simple salts to diffuse.

The colloidal hydroxides of silicon, aluminium and iron, and the organic colloids of the clays, are regarded as forming a complicated network of cellular structure, and presenting a very large number of dividing surfaces, whereas a compact crystalloid substance only presents one such surface. It is to be supposed that the meshes of the coagulated colloidal network swollen with water molecules are too fine to allow coarse colloid molecules to diffuse through them, but they are large enough to allow the passage of the much smaller crystalloid molecules. The more complicated a substance is the more readily it will be adsorbed; compounds will also be more readily adsorbed from concentrated solution in which their molecules are aggregated to complexes than in dilute solution in which they are probably dissociated.

E. F. A.

Adsorption by Means of Clay. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1909, 18, 207).—The authors point out that Rohland (preceding abstract) had misquoted from their original paper (compare this vol., ii, 125).

J. J. S.

Relation between Density and Degree of Dissociation of Aqueous Solutions. S. TERESCHIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, ii, 155—160; *Ber. Deut. physikal. Ges.*, 1909, 211—214).—It has been shown by Heydweiller (*Ber. Deut. physikal. Ges.*, 1909, 11, 37) that for a large number of salts the excess, $s-1$, of the density of the solutions over that of water at the same temperature may be calculated by means of the formula: $(s-1)/m = A_s i + B_s(1-i)$, where m represents the number of gram-mols. per litre, i the degree of dissociation, and A_s and B_s constants independent of the concentration.

For Heydweiller's two constants, A_s and B_s , the author derives the equations: $A_s = N(\mu' - \mu'_0)/1000m + N(\mu'' - \mu''_0)/1000m$ and $B_s = N(\mu - \mu_0)/1000m$, in which N represents the number of gram-mols. of a binary electrolyte per litre, μ_0 the mass of the solvent in the volume of the spheres of action of the molecules, and μ the mass of all the molecules with the mass of the layers of solvent of changing density surrounding them; μ'_0 and μ' represent the corresponding magnitudes for one ion, and μ''_0 and μ'' for the other. The values of A_s and B_s calculated in this way for a large number of salts are in good agreement with the experimental values.

T. H. P.

The Diametral Line of Acetylene. ÉMILE MATHIAS (*Compt. rend.*, 1909, 148, 1102—1105).—The densities of liquid acetylene and its saturated vapour have been determined with an accuracy of 1 in 5000 at temperatures ranging from -23.75° to $+32.93^\circ$. The mean of the two densities at each temperature obeys the Cailletet-Mathias law, its graph being a rectilinear diameter to the density curve. In spite of the unsaturated character of acetylene, there is little sign of abnormally high density at low temperatures, such as is met with in the substituted ammonias. The critical temperature of acetylene was found by Young's method to be $+37.05^\circ$ or 310.05° absolute ($=\theta$). The critical density calculated by the mean density

law is 0.2346 ($=\Delta$). The angular coefficient a of the mean density graph is 0.00064.

If the law of corresponding states holds for the density curves of all substances, the constants $a(=a.\theta/\Delta)$ and $b(=-a\sqrt{\theta}/\Delta)$ should be independent of the nature of the substance. The values of a and b in the case of acetylene are 0.8605 and 0.0489, whereas carbon dioxide gives 0.858 and 0.0493. Thus, in the case of acetylene and carbon dioxide, the critical temperatures of which are very close together, the law of corresponding states holds, in spite of the difference in constitution of the two molecules.

R. J. C.

Theory of Organic Bases Based on the Viscosity of their Solutions. D. E. TSAKALOTOS (*Compt. rend.*, 1909, 148, 1324—1326).—In aqueous solution organic bases are supposed to combine with a molecule of water, the resulting compound, or aquo-base, then dissociating to a greater or lesser extent with the formation of hydroxidions. From measurements of other observers on the viscosities of aqueous solutions of various bases, the author deduces that combination between the base and water does take place, and hence support is given to the theory mentioned.

Aqueous solutions of triethylamine, pyridine, piperidine, and nicotine each give solutions possessing a maximum viscosity, and this maximum viscosity is considered to point to the formation of a definite compound between the water and the base.

T. S. P.

Contribution to the Study of Capillarity. PIETRO PALLADINO (*Chem. Zentr.*, 1909, i, 973; from *Giorn. Farm. Chim.*, 1909, 58, 5—6).—The rising of the capillary meniscus when a solid is wetted by a liquid indicates a pressure between the solid and the liquid substance. A solid substance inserted in two liquids remaining in layers one on the other, causes the under liquid to form a convex meniscus at the point of contact of the two liquids. The nature of the solid substances influences the meniscus; methylene dibromide or di-iodide under water gives a convex meniscus with quartz, glass, mica, magnesium, aluminium, etc., and concave with platinum, gold, lead, zinc, tin, copper, etc. The same solid substance may give a different meniscus according to the nature of the lower liquid; thus, methylene dichloride under water gives with magnesium or aluminium a concave meniscus. When the lower liquid is made up of two miscible components, which by themselves give different forms of meniscus, according as one or the other substance predominates, so is the meniscus changed. Although in saturated solutions the meniscus is practically reduced to nothing, the presence of solid or gelatinous substances does not produce a reverse effect.

J. V. E.

"Dynamic" Osmotic Pressures. EARL OF BERKELEY and ERNALD G. J. HARTLEY (*Proc. Roy. Soc.*, 1909, 82, A, 271—275).—The rate at which water passes through a copper ferrocyanide membrane into solutions of sucrose has been measured, and compared with the rate at which known hydrostatic pressures force water through the membrane. The measurements of the osmotic flow refer to the initial

velocity, for it is found that this diminishes considerably when the membrane is allowed to remain in contact with the solution. In order to prevent local changes of concentration, the solutions were efficiently stirred.

For the hydrostatic flow the velocity is proportional to the pressure. When the rates of osmotic flow are divided by the rate of hydrostatic flow for a difference of pressure of one atmosphere, the so-called dynamic osmotic pressures of the various sucrose solutions are obtained. For dilute solutions, these pressures agree fairly well with the equilibrium osmotic pressures, but for the more concentrated solutions the dynamic values are considerably smaller than the equilibrium values. The experiments indicate that osmotic phenomena can be measured kinetically, and that for dilute solutions the results are the same as when measured statically. H. M. D.

Osmotic Pressures of Calcium Ferrocyanide Solutions. II. Weak Solutions. EARL OF BERKELEY, ERNALD G. J. HARTLEY, and J. STEPHENSON (*Phil. Trans.*, 1909, A, 209, 319—336. Compare this vol., ii, 126).—The osmotic pressures at 0° of calcium ferrocyanide solutions of from 7 to 21·8% strengths were measured in the apparatus described previously with addition of a more sensitive pressure gauge, since the pressures measured did not exceed 25 atmospheres.

It was found that the osmotic pressure of 7% and 12·2% solutions agree very well with those calculated on the assumption that the gas laws hold for solutions, whereas 17·6% and 21·8% solutions give values higher than the calculated. As this is the reverse of what would be expected on the dissociation hypothesis, the osmotic pressures of dilute solutions of strontium ferrocyanide and potassium ferrocyanide were also measured. Potassium ferrocyanide in accordance with current theory gives osmotic pressures which diverge more and more from the calculated as the solution is diluted, until at 1·5% strength the salt appears to be dissociated into three ions or molecules. On the other hand, strontium ferrocyanide, the crystals of which contain 14H₂O, exhibits the same anomaly as the calcium salt, but somewhat more markedly, the osmotic pressure in 6·18% solution being actually less than the calculated. A few measurements were made of the osmotic pressures of magnesium camphorate, potash alum, sodium and calcium naphthionates, barium, lead, and potassium benzenesulphonates, barium o-nitrobenzoate, luteocobalt chloride, and calcium acetate, all of which behave normally, giving in dilute solution osmotic pressures in excess of the calculated.

The conductivities of calcium and strontium ferrocyanide solutions from about 20% strength down to a high dilution were carefully measured by the Fitzpatrick and Whetham commutating method at 0°. The equivalent conductivities of these salts show a steady increase, until at infinite dilution the equivalent conductivity is about five times that of a 20% solution. The normal electric and abnormal osmotic properties of calcium and strontium ferrocyanides may be explained as due to (1) association to double molecules which are ionised, and (2) ionisation with subsequent association of the ions to complexes. On the former assumption, allowing for ionisation, the calculated osmotic

pressures are in equally satisfactory agreement with experiment whether it be supposed that five or six ions are formed from the double molecule. Erlenmeyer's formula (1865) for the ferrocyanides appears best to express the constitution: $[\text{Ca}(\text{CN})_6]_2\text{Fe} = \text{Fe}[(\text{CN})_6\text{Ca}]_2$, the ions being 4Ca^+ and $2\text{Fe}(\text{CN})_6^-$ or 4Ca^+ and $\text{Fe}_2(\text{CN})_{12}^-$.

Erlenmeyer's formula in the case of potassium ferrocyanide requires nine or ten ions, and leads to values of the osmotic pressure which are also in tolerable agreement with the experimental ones. Quantitative agreement is not to be expected in view of the assumptions made.

The evidence is held to prove that calcium and strontium ferrocyanides, at least, are associated in solution, although tetraethyl ferrocyanide is known to have the single molecule $\text{Et}_4\text{Fe}(\text{CN})_6$ (compare Buchböck, Abstr., 1897, i, 452). R. J. C.

The Measurement of Osmotic Pressure. JOSEF KÖNIG and J. HASENBÄUMER (*Zeitsch. angew. Chem.*, 1909, 22, 1009—1018, 1070—1074. Compare Abstr., 1908, ii, 888).—The primary object of the authors was the measurement of the osmotic pressures of different soils, but the present paper is mainly concerned with the apparatus used and the results obtained with different inorganic and organic compounds. A satisfactory semi-permeable membrane was formed in the walls of a porous pot, according to a modification of the method used by Walden (Abstr., 1893, ii, 203). The pot, after being cleaned in the usual manner and heated in a drying oven, was filled with a hot 6% solution of gelatin; as soon as the solution had penetrated to the outside, the pot was emptied, washed with hot water, and treated with formaldehyde vapour in order to harden the gelatin. The semi-permeable membrane of copper ferrocyanide was then deposited in the walls of the pot in the usual manner, full particulars being given in the original paper. Pots which have been prepared in this way can be used over and over again for osmotic experiments if care is taken to clean them by repeated treatment with water between each set of experiments, any gelatin which has become soluble being hardened by fresh treatment with formaldehyde.

In the first set of experiments the osmotic cell was connected with an open manometer in the usual manner, and measurements were made with dilute solutions of sodium nitrate, potassium nitrate, potassium chloride, potassium sulphate, ammonium sulphate, magnesium sulphate, and sucrose in order to test the membrane. The experiments were made at room temperature, and the results were in good agreement with those obtained by Pfeffer (*Osmotische Untersuchungen*, 1877).

For experiments with soils it was necessary to use the osmometer in a different way. In place of the open manometer was a U-tube and goose-neck, the latter containing oil of known density. The cell and its contents were placed in water, and the quantity of water entering the cell was measured by weighing the oil expelled from the goose-neck, the weighings taking place every twenty-four hours. The contents of the cell consisted of soil saturated with water, asbestos being added to prevent the soil caking together. Tests on six different soils, varying in nature from a sandy soil to a shaly one,

gave fairly concordant results for the "osmotic water absorption" in twenty-four hours.

Further experiments were made with different inorganic and organic salts and organic compounds (chiefly sugars) in order to test the method of "osmotic water absorption." It was found that equimolecular solutions show the same osmotic water absorption, allowance of course being made for dissociation in the case of salts. The salts of the fixed alkalis, such as potassium sulphate, diffuse through the membrane to a much greater extent than ammonium and magnesium sulphates.

In the last part of the paper the "osmotic water absorption" is used to determine the molecular weights of various sugars and dextrans, either dextrose or raffinose being taken as the normal substance. Good results could only be obtained when the temperature was kept constant at 25°. Stachyose was found to be $C_{18}H_{32}O_{16} \cdot 3H_2O$. The following multiples of $C_{12}H_{20}O_{10}$ were found for the dextrans named: Acid achroodextrin I + $\frac{1}{3}$ achroodextrin II, 5; Erythroedextrin IIa, 11; Erythroedextrin (SreEnl'), 13; diastatic achroodextrin, 8.

The apparatus can also be conveniently used for determining the isotonic coefficients of salts.

T. S. P.

Velocity of Molecular and Chemical Reactions in Heterogeneous Systems. I. MEYER WILDERMANN (*Zeitsch. physikal. Chem.*, 1909, **66**, 445—495. Compare Nernst and Brunner, *Abstr.*, 1904, ii, 315; Bruner and Tolloczko, *Abstr.*, 1901, ii, 10; 1902, ii, 62; 1903, ii, 470).—An adverse criticism, based both on theoretical and experimental grounds, of Nernst's diffusion theory of reaction velocities in heterogeneous systems. Nernst's equation is a special form of the author's general equation: $dt/d\tau = C\Sigma\tau(t_0 - t)$ (compare *Abstr.*, 1900, ii, 200; 1901, ii, 544), which indicates that the reaction velocity at the time τ is proportional to the distance of the system from equilibrium ($t_0 - t$) and to $\Sigma\tau$, the total surface in contact of the reacting parts of the heterogeneous system, but the interpretation of the factors given by Nernst is not justified.

The experimental part deals mainly with the rate of dissolution in water of benzoic acid and of a number of varieties of calcium sulphate. The materials were compressed under several thousand atmospheres' pressure, and were then found to dissolve uniformly. It was, however, found impossible to compress pure magnesium hydroxide so as to form a block which did not disintegrate when placed in water, and the author considers that the hydroxide used by Nernst and Brunner was contaminated with carbonate.

The measurements were made in a large beaker containing 1500 c.c. of water, which was placed in a bath at constant temperature. A double stirrer was used, and the block of material was fastened to the stirrers and rotated with them. Great precautions were taken to secure a uniform rate of stirring, and the methods employed for this purpose are fully described. In the case of benzoic acid, the rate of dissolution was measured by titrating a portion of the solution from time to time. For calcium sulphate, the rate of change of the conductivity of the solution was measured. The constants were calculated by means of the general formula given above.

The effect of temperature on the rate of solution of benzoic acid has been measured between 1° and 60° . The results are calculated by means of the formula: $\log.k_0 - \log.k_1 = A(T_0 - T_1)/T_0T_1$, which is valid for homogeneous systems. Between 1.5° and 17.5° A increases by 5.1%, and between 40° and 60° by 3.64% per degree. As the rate of increase of diffusion with temperature is only 2.5% per degree, this is regarded as a strong argument against the diffusion theory. The rate of solution increases proportionately with the stirring from 3 to 180 turns per minute, beyond this point it falls off, and above 400 turns attains a maximum value, independent of further increase in stirring. The greater the solubility the more rapidly is the maximum reached.

The rate of dissolution of three varieties of calcium sulphate, selenite, fibrous gypsum, and alabaster, under comparable conditions are in the ratio 1:3.5:5.4, whereas according to the diffusion theory they should be identical. Sections of selenite cut at right angles to each other give for the respective rates of solution 3.376:0.6378. Powdered and compressed selenite and powdered and compressed gypsum dissolve at the same rate.

As regards the theoretical objections to the diffusion theory, it is pointed out that Nernst's assumption of "infinitely great" forces acting at surfaces of contact is untenable, (1) because then the rate of evaporation of a liquid should be very rapid, whereas it is very slow; (2) molecules in contact, such as those of aniline and acetic acid, should react with very great velocity, which is contrary to fact. The author considers that the "diffusion layer" in contact with the solid does not exist, and that efficient stirring moves the solution in contact with the solid up to molecular distance from the latter. G. S.

Temperature-coefficient of Chemical Reaction Velocities.
II. The Physical Meaning of the Chemical Reaction Velocity in Gases and its Calculation from Purely Thermal Data Pertaining to the Reacting Substances. MAX TRAUTZ (*Zeitsch. physikal. Chem.*, 1909, 66, 496—511. Compare Abstr., 1908, ii, 824).—By a thermodynamical method a very complicated expression is derived for the temperature-coefficient of the reaction velocity in terms of the heat of formation from the atoms, vapour pressures, and molecular heats of the condensed components, and another expression is given for the velocity constant in terms of the same thermal factors, the time, and an unknown integration constant. The available data are not sufficient to admit of the formulæ being tested by application to special cases, but it is shown that they are in general agreement with the experimental results. G. S.

Chemical Action in Gaseous Mixtures Submitted to very High Pressures. E. BRINER and A. WROCZYNSKI (*Compt. rend.*, 1909, 148, 1518—1519 *).—In highly compressed gaseous mixtures at relatively low temperatures, since the atoms are very close together, the conditions are those where chemical attraction will exert its maximum effect and exothermic actions may be accelerated. The mixtures nitric oxide-carbon monoxide, nitric oxide-hydrogen chloride, and nitric oxide-sulphur dioxide at 50 atmospheres retain their normal

* and *Zeitsch. anorg. Chem.*, 1909, 63, 49—52.

character. If, however, they are condensed in liquid air in stout glass tubes which are two-thirds filled and then sealed off, a pressure of more than 500 atmospheres is reached when the liquids are allowed to warm up beyond their critical point and chemical action at definite rates takes place. The mixture nitric oxide-hydrogen chloride condenses in liquid air to a deep reddish-violet solid, doubtless an additive compound. At the ordinary temperature, the highly compressed mixture is a colourless gas, which after a time deposits two liquid layers gradually increasing from day to day. The pale red layer is nitrosyl chloride, and the pale yellow layer is water containing dissolved nitrosyl chloride. The action $4\text{NO} + 4\text{HCl} \rightarrow 2\text{NOCl} + 2\text{H}_2\text{O} + \text{Cl}_2 + \text{N}_2$ is strongly exothermic. If the tube contains excess of nitric oxide, the two liquid layers are slowly converted into one deep green liquid of unknown composition.

The system $\text{NO} + \text{SO}_2$ gives rise under high pressure to a pale green solid, which is stable at ordinary pressures and apparently consists of nitric oxide dissolved in sulphur trioxide, formed according to the exothermic equation $2\text{NO} + 2\text{SO}_2 \rightarrow 2\text{SO}_3 + \text{N}_2$. The mixture hydrogen chloride-sulphur dioxide condenses to an orange-yellow additive compound in liquid air. The beginnings of chemical action have been observed in the systems hydrogen chloride-sulphur dioxide, nitric oxide-methyl chloride, and sulphur dioxide-oxygen at high pressures.

R. J. C.

The System Water-Liquid Ammonia. Agreement of the Results with the Existence of a Hydrate of Ammonia. E. BAUD and L. GAY (*Compt. rend.*, 1909, 148, 1327—1329).—In order to determine what hydrates exist in aqueous solutions of ammonia, the heat developed by mixing water and liquid ammonia in different proportions has been measured. This was effected by measuring the heats of dilution of the various mixtures, and of anhydrous liquid ammonia, in a large excess of water.

The curve showing the relation between the heat developed and the percentage composition of the mixture shows a maximum which corresponds with the composition $\text{NH}_3, 1.109\text{H}_2\text{O}$.

When water and liquid ammonia are mixed, contraction takes place; the maximum contraction occurs with the mixture of composition $\text{NH}_3, 0.9\text{H}_2\text{O}$.

The above results point to the existence of a hydrate, $\text{NH}_3, \text{H}_2\text{O}$.

The heat of solution of 1 gram-molecule of liquid ammonia in water at 12° is found to be 3.485 Cals.

T. S. P.

Equilibrium in the System Ammonium Sulphate, Ammonium Chloride, Ethyl Alcohol, and Water. J. P. WIBAULT (*Chem. Weekblad*, 1909, 6, 401—409).—The author has examined the system ammonium sulphate, ammonium chloride, ethyl alcohol, and water. His results are expressed by Schreinemaker's graphic method, a tetrahedron, the angles representing the components.

A. J. W.

Chemical Affinity in Reversible Systems. H. GOLBLUM (*J. Chim. Phys.*, 1909, 7, 289—336).—The general formulæ for the

representation of chemical affinity are tested on the basis of an experimental investigation of the reversible reaction: $\text{BaCrO}_4 + \text{K}_2\text{CO}_3 \rightleftharpoons \text{BaCO}_3 + \text{K}_2\text{CrO}_4$, already investigated by Guldberg and Waage. It is shown by Berthelot's rule that the left-hand system is the more stable, as its heat of formation exceeds that of the system on the right hand by 6.4 calories, and the same conclusion is reached by a consideration of solubilities, the solubility product of the substances on the left-hand side being about one-tenth of that on the right.

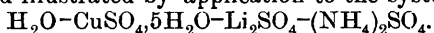
The equilibrium diagram of the system has also been constructed. On the basis of the phase rule, there are four points at which the system is univariant, and the positions of these points have been determined by solubility measurements in the usual way. The points represent solutions saturated with reference to the salts as follows: (A) potassium and barium chromate; (B) potassium and barium chromate and potassium carbonate; (C) potassium and barium carbonate and barium chromate, (D) potassium and barium carbonate. Measurements were made at 25°, and for B and C also at 40°.

Further, solubility determinations have been carried out in which solutions containing different molar proportions of potassium chromate in water have been shaken with barium carbonate until equilibrium was attained, and the solutions then analysed; similar measurements were made with solutions of potassium carbonate and solid barium chromate, so that the equilibrium was reached from both sides. From the results, the equilibrium constant $K = [\text{K}_2\text{CO}_3]/[\text{K}_2\text{CrO}_4]$ has been calculated, and it is shown that K is not constant; it decreases at first with the concentration, reaches a minimum value, and beyond that point increases. The deviation from the simple law is ascribed to the electrolytic dissociation of the salts, and the modifications required to take ionisation into account are considered.

From the values of the equilibrium constant at 25° and 40°, the heat of the reaction is calculated by van't Hoff's formula; it amounts to 5997 calories, in fair agreement with the value, 6400 calories, calculated according to Hess's law.

G. S.

Certain Deductions for Quaternary Systems. FRANS A. H. SCHREINEMAKERS (*Zeitsch. physikal. Chem.*, 1909, 66, 699—704).—A method for the graphic representation of quaternary systems is described, and illustrated by application to the system:



G. S.

Kinetics of the Hydrolytic Decomposition of Methyl Acetate by the Catalytic Action of Acetic Acid. KOZO IKAWA (*Mem. Col. Sci. Eng. Kyōto*, 1908, i, 320—324).—Ostwald found that the "constants" for the hydrolytic decomposition of methyl acetate by acetic acid diminished somewhat during the action, a result which he ascribed to vaporisation of the ester during the very slow reaction. The author has carried out the reaction in closed vessels, the rate being deduced from electrical conductivity measurements made at intervals up to thirty-five days for a single experiment, and obtains good constants.

G. S.

Kinetics of two Simultaneous Reactions in a System. KOZO IKAWA (*Mem. Col. Sci. Eng. Kyōto*, 1908, 1, 375—385).—It is shown that when mixtures of methyl and ethyl acetate, and of ethyl acetate and butyrate, undergo hydrolysis in the presence of hydrochloric acid in a dilute aqueous solution, the reactions exert no mutual influence.

G. S.

Catalysis by Moisture. J. MEYNIER (*Compt. rend.*, 1909, 148, 1516—1517).—Langevin demonstrated that the atmosphere contains ions which are drops of liquid water of the order $1/100$ of a micron in diameter, and that these can be removed by filtration through cotton wool. The part played by moisture in the explosion of hydrogen and oxygen, the oxidation of nitric oxide, etc. (compare Brereton Baker, *Trans.*, 1902, 81, 400), might be ascribed to these ions. The author mixes steady streams of nitric oxide and oxygen in equivalent proportions by means of a Y-tube, and measures their speed of combination by the temperature attained at a fixed point further along the tube. Neither drying the gases by means of fused potash and phosphoric oxide nor filtration through 30 cm. of cotton wool have any effect on the rate of combination. It follows that gaseous water alone brings about the action—the speed of which, however, is not proportional to the amount of water, but attains its full value in presence of the merest trace.

R. J. C.

Determination of Solubility by means of Pulfrich's Refractometer. II. YUKICHI OSAKA (*Mem. Col. Sci. Eng. Kyōto*, 1908, 1, 290—303).—The results of further solubility determinations by the refractometer method already described (*Abstr.*, 1907, ii, 934) are given. The applicability of the formula $ax + bx^2 = d - d'$ to the observations is confirmed.

The solubility of certain compounds in water at 25°, expressed in grams per 100 grams of water, is as follows: mercuric chloride, 7.42; sodium chlorate, 101; sucrose, 212; disodium hydrogen phosphate (as anhydrous salt), 12.2; borax (as anhydrous salt), 3.33. The following results are expressed in grams per 100 grams of solution: mercuric chloride in 99.2% alcohol, 33.8; coumarin in chloroform, 49.4; benzophenone in benzene, 78.6; mercuric chloride in a normal aqueous solution of sodium chloride, 25.08; sodium chloride in water, 26.5 (36.0 in 100 grams of solvent); potassium sulphate in water, 10.72 (12.0 in 100 grams of solvent). The agreement of the observed and calculated values of x for mercuric chloride in a solution of sodium chloride indicates that the formula holds even when a chemical reaction occurs in solution. A method is described by which the formula, the constants of which have been determined for a particular temperature, may be used for observations at other temperatures.

G. S.

Relations between Density and Crystallographic Constants in Certain Groups of Substances. LUIGI COLOMBA (*Atti R. Accad. Sci. Torino*, 1909, 44, 399—434).—If the molecule M of any substance is composed of a definite number, n , of groups r' , r'' , $\dots r^n$, and

V be its molecular volume and $v', v'', \dots v^n$ the molecular volumes of the component groups, then, if there is no modification of molecular volume in passing from the components to the molecule, $V = v' + v'' + \dots v^n = \Sigma v^n$. If V is less or greater than Σv^n , there is said to be positive or negative deformation. The ratio $A = \Sigma v^n / V$ is termed the index of deformation of volume.

With certain groups of cubic substances, the values of the indices of deformation approximate to the numbers 1.60, 1.075, and 0.93. Thus, for the series CaS, SrS, BaS, MgS, Li₂S, and NiSe, taking v' to be the atomic volume of the sulphur or selenium and v'' that of the metal, and calculating the density of the compound on the assumption that the index of deformation is 1.60, numbers are obtained in good agreement with the experimental densities. The same is the case with the series galena, argentite, zinc blende, alabandite, Cu₂S, naumannite, berzehanite, ZnSe, and MnSe, in which the index of deformation is equal to 1.075.

A group in which the deformation is negative is that of the spinels, the index of deformation being 0.93. With these substances v' is taken as the molecular volume of the sesquioxide, Al₂O₃, etc., and v'' as that of the basic oxide, MgO, etc. Excepting in the cases of jacobsite, which always contains an appreciable proportion of magnesium, and of the zinc compounds, ZnAl₂O₄ (gahnite), ZnFe₂O₄, and ZnCr₂O₄, with which slight discrepancies occur, the calculated and observed densities are in good agreement.

The second value given for A , 1.075, is almost exactly two-thirds of the first, 1.612, whilst the third, 0.93, is the reciprocal of the second, 1.075. To these the author adds a fourth, 0.62, the relations between these four values being given by the equations: $A_1 = 1.075$; $A_2 = 3A_1/2 = 1.612$; $A_3 = 1/A_1 = 0.930$, and $A_4 = 2/3A_1 = 0.620$. If the cubic system is taken to be a special case of the rhombohedral, the value of the angle 0001:10 $\bar{1}\bar{1}$ in the general equation

$$c = \tan(0001:10\bar{1}\bar{1}) \sqrt{3/2}$$

becomes 54°44', and the value of c becomes $\sqrt{3/2}$ or 1.2246. Now, taking cA_1 to be constant, the latter will have the value 1.316, which will also be the value of A_2/c , c/A_3 , and $1/cA_4$. All the cases in the cubic system are hence referable to the general equation:

$$C = \text{const. } xf(R),$$

in which C is made equal to c , and the values found for the indices of deformation are substituted for $f(R)$.

These principles are extended to other groups of compounds crystallising in other systems. For details the original must be consulted.

T. H. P.

New Proof of the Existence of Molecules. II. THE SVEDBERG (*Zeitsch. physikal. Chem.*, 1909, **66**, 752—758).—The measurements described in the previous paper (this vol., ii, 277) have now been extended to colloidal solutions of ferric hydroxide and of arsenious sulphide, and the results confirm the conclusions already given. Some further experiments with colloidal gold are described.

G. S

New Atomic Theory. JAMES MOIR (*J. Chem. Metal. Min. Soc. S. Africa*, 1909, 9, 334—341).—It is suggested that the atoms are built up of different arrangements of four or five primary materials, and the structural formulæ are so selected as to give the best possible agreement with all the known chemical and physical properties of the atoms. It is assumed that the carbon atom is made up of four similar sub-atoms of atomic weight 3, arranged tetrahedrally, and these sub-atoms, termed zoikon (symbol z), represent one of the primary materials. The second sub-atom is hydrogen, which is assumed to possess an intrinsic, repulsive force, and the third is a hypothetical element of atomic weight 2, symbol x , univalent like hydrogen, yet not fully saturating another element when joined to it. Helium (at. wt. = 4.09) and neon (at. wt. = 19.7) complete the list of primary elements. Further, it is assumed that the metals contain hydrogen as the cause of their electro-positive character, and that the sub-atom x confers an electro-negative character.

It is shown how all the other elements can be built up from these five primary materials, and many of the formulæ are illustrated graphically. Nitrogen is z_4x , the x being placed differently with reference to the carbon tetrahedron, according as the nitrogen is bivalent or quinquivalent. Oxygen is z_4x_2 , fluorine, z_3x_5 , and lithium, H_2xz . The theory may afford satisfactory explanations of certain isomeric changes.

G. S.

Reform of Chemical and Physical Calculations. C. J. T. HANSEN (*Chem. News*, 1909, 99, 229).—The author states that Hinrich's discovery of the atomic weight of pantogen has enabled him to prove that the atomic weights of the elements are exact multiples of the atomic weight $H=1$, and that the proportion $H:O=1:16$ is absolutely correct.

J. V. E.

Mathematically Harmonising the Elements. F. H. LORING (*Chem. News*, 1909, 99, 241—242. Compare this vol., ii, 392).—The present communication deals with certain interesting chemical regularities amongst the elements when classified by the author's method. Acidic and peroxide regularities, a specific heat sequence, and also the position of the magnetic elements are considered. The theory of satellites is found to be too hypothetical to be seriously entertained without the support of experimental evidence, and the figure 0.2684 previously given (*loc. cit.*) must be only regarded as roughly approximate.

J. V. E.

Chance Identity of Numbers with Atomic Weights and Approximate Agreement with Mendeléeff's Series. PIETRO PALLADINO (*Chem. Zentr.*, 1909, i, 970—971; from *Giorn. Farm. Chim.*, 1909, 58).—The author explains the existence of definite simple forms of aggregations of material particles by the assemblage of spheres. Four spheres closely packed give a tetrahedron, the addition of six more gives another tetrahedron, etc., leading to a series of tetrahedra. In addition to this simple form, several others are given, namely, octahedron, regular tetrahedron with truncated edges, six-faced double pyramid with

triangular base, the pyramid having truncated edges; from combinations of these fundamental forms all others may be derived. The number of spheres in the simplest aggregation is called the *absolute weight*, and by dividing this number for every series of different forms by $1/16$ of that aggregation which corresponds with oxygen ($O:16=3274.625=M$), numbers are obtained which agree with the atomic weights, and the order followed is approximately that of Mendeléeff.

J. V. E.

True Atomic Weights. Stas' Determinations. LOUIS DUBREUIL (*Bull. Soc. chim.*, 1909, [iv], 5, 604—610, 610—613. Compare this vol., ii, 475).—In these two papers the method of calculating atomic weights already outlined (Abstr., 1908, ii, 936), based on that of Hinrich's (Abstr., 1907, ii, 945), is applied to the data obtained by Stas in ascertaining the ratio between (a) potassium chloride and potassium nitrate, and (b) sodium chloride and sodium nitrate. The first paper deals with the first of these ratios, and in it the following corrected atomic weights are deduced: potassium, 38.9985; chlorine, 35.4941; oxygen, 16.013, and nitrogen, 14.0043.

The second paper deals with the second ratio, and in it the following corrected atomic weights are arrived at: sodium, 22.9965; chlorine, 35.4889; oxygen, 16.0229; nitrogen, 14.0076.

T. A. H.

Permeability of Glass for Gas. ALFRED STOCK and HANS HEYNEMANN (*Ber.*, 1909, 42, 1800—1801. Compare Zengelis, this vol., ii, 134).—A piece of silver foil was placed in a small glass flask, which was completely evacuated and sealed. It was placed inside a larger vessel containing iodine, which was likewise closed. After three months there was not the slightest indication of any iodine having passed through the glass. This is contrary to the observations of Zengelis (this vol., ii, 134), whose results are explained as being due to his having sealed his vessels with paraffin.

E. F. A.

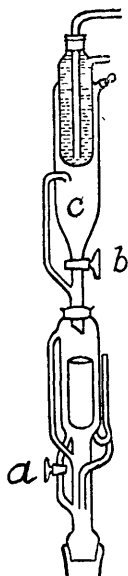
A Useful Oil-bath. LOUIS W. BOSART, jun. (*J. Amer. Chem. Soc.*, 1909, 31, 724).—A mixture of 10 parts of refined cotton-seed oil and one part of beeswax makes a very satisfactory oil-bath. It emits very little fume below 250° , and can be safely used almost throughout the range of the ordinary mercury thermometer, having a flash point above 300° when heated in an open cup. The mixture is solid at the ordinary temperature; it melts quickly, and can be used almost immediately after heat is applied.

T. S. P.

Extraction Apparatus for Plant Products. SAMUEL J. M. AULD and SAMUEL S. PICKLES (*Chem. News*, 1909, 99, 242).—The apparatus described and figured consists of an arrangement of two flasks so connected that the boiling saturated solution is syphoned into a second flask placed at a lower level, from which it is simultaneously distilled back again into the first flask. The extract thus accumulates in the lower flask, while the distilled solvent extracts still further the substance placed in the first flask. With this apparatus large quantities of material can be readily and rapidly dealt with.

J. V. E.

New Condenser for Extraction Apparatus. CARLO FRASCHINA (*Chem. Zentr.*, 1909, i, 1633; from *Giorn. Farm. Chim.*, 1909, 58, 111—112).—The apparatus described (annexed figure) is arranged for use with a Soxhlet extraction apparatus, and is so constructed that when the extraction is complete, by opening tap *a* and closing tap *b*, the solvent may be collected in reservoir *c*. J. V. E.



[Lecture Experiments.] **Quantitative Volumetric Gas Analysis and Synthesis.** P. RISCHBIETH (*Chem. Zentr.*, 1909, i, 1224; from *Zeitsch. phys. chem. Unter.*, 1909, 22, 19—29).—A number of quantitative experiments are described which are easily and rapidly carried out with a modified form of Bunte's gas burette, namely, the synthesis of water, analysis of atmospheric air, of marsh gas, ethylene, and acetylene, the volumetric analysis of nitric oxide, the oxidation of nitric oxide by oxygen, and the volumetric analysis of nitrous oxide. J. V. E.

Lecture Experiments. [Oxides of Copper.] WILLEM P. JORISSEN and H. FILIPPO, jun. (*Chem. Weekblad*, 1909, 6, 377—380).—Two lecture experiments are described. One illustrates the formation of cuprous oxide when copper is heated in a limited supply of air; there is, in the paper, a sketch of the apparatus employed. The other demonstrates the partial decomposition of cupric oxide, with evolution of oxygen, at a high temperature. A. J. W.

Inorganic Chemistry.

Apparatus for the Purification of Gaseous Hydrogen by means of Liquid Hydrogen. H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 11, 883—886).—An apparatus for the purification of hydrogen by liquefaction and subsequent evaporation is described. When impure commercial hydrogen is employed, a preliminary purification is effected by freezing out the admixed gases.

H. M. D.

The Precipitation of Metals from Aqueous Solutions of their Salts by Hydrogen at High Temperatures and Pressures. WLADIMIR N. IPATIEFF and W. WERCHOWSKY (*Ber.*, 1909, 42, 2078—2088).—Experiments on the reduction of dissolved salts to the metallic state by hydrogen under pressure have given negative results in many cases (compare Nernst and Tammann, *Abstr.*, 1892, 561). By employing the

apparatus used for organic reductions under high pressure (Abstr., 1908, i, 330), pressures up to 600 atm. may be obtained. Under 200 atm., silver and mercury are precipitated even from *N*/10 solution at the ordinary temperature. Copper is not precipitated even under 500 atm.

At 60–70° cupric salts deposit cuprous oxide in the form of carmine-red crystals, above 90° the product is a mixture of cuprous oxide and copper, and above 120° it consists of pure copper in branched crystals. A pressure of 100 atm. is sufficient, but precipitation does not occur under atmospheric pressure.

Nickel, cobalt, lead, and bismuth are similarly precipitated at a high temperature. Nickel is completely precipitated at 200° under 180 atm.

Iron salts have been examined at 350° under 230 atm. Ferric acetate then deposits the whole of its iron as anhydrous red ferric oxide, soluble in hydrochloric acid. At 400° under 420 atm. a small quantity of metallic iron was also found, but each experiment only lasted a few minutes, owing to the bursting of the steel tubes.

If Nernst's hypothesis is accepted, the electrolytic solution tension must be regarded as a variable, depending on the pressure, temperature, and ionic concentration. It is suggested that hydrolysis first takes place, the metallic hydroxide being then reduced to metal by the hydrogen. Against this, however, is the fact that the addition of sulphuric acid to copper sulphate, although reducing the hydrolysis, does not hinder precipitation. Preliminary experiments also indicate that oxides or hydroxides under a layer of water are only reduced with difficulty by hydrogen.

C. H. D.

Composition of Atmospheric Air. GEORGES CLAUDE (*Compt. rend.*, 1909, 148, 1454–1456).—The continuous apparatus described previously for separating nitrogen and oxygen from air (Abstr., 1906, ii, 16) and obtaining a residue of the rare gases has been subjected to a prolonged test, which shows that the separation of neon, helium, and hydrogen is of a sufficiently quantitative nature to lead to an estimate of these gases in air. The mixture of gases obtained was passed over magnesium to remove traces of nitrogen, and then over cupric oxide to remove hydrogen, which was weighed as water. The residual mixture of neon and helium had an extremely constant density, 0.53 to 0.57 (air = 1), corresponding with a ratio of neon to helium of 412:143. The proportion of the gases obtained from air was also fairly constant, 360 cubic metres of air yielding 7.25 litres. The proportion of hydrogen in air was found to vary considerably, the purest air obtainable containing less than one part in a million. The variation was found to be largely due to a leaky gas producer in the same building as the air compressor. With a view to showing the delicacy of the apparatus and method, one millionth of its volume of hydrogen was added to 180 cubic metres of air, and the mixture passed through the machine. About half the hydrogen was recovered as water (69 milligrams) in thirty minutes.

One million volumes of air contain 15 volumes of neon, 5 volumes of helium, and less than 1 volume of hydrogen.

R. J. C.

Method for the Preparation of Colloidal Sulphur. ALFRED HIMMELBAUER (*Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 307—308).—If pieces of gelatin or agar-agar are placed in a solution of ammonium polysulphide, they begin to opalesce at the end of a few hours, and finally become white and non-transparent. A similar effect is obtained with a solution of hydrogen sulphide. In the separation of the colloidal sulphur from the aqueous solutions, the gelatin and agar-agar appear to act as catalysts and accelerate the process. H. M. D.

Action of Pyrosulphuryl Chloride, $S_2O_5Cl_2$, on Sulphur, Selenium, and Tellurium. WILHELM PRANDTL and PAUL BORINSKI (*Zeitsch. anorg. Chem.*, 1909, 62, 237—249. Compare this vol., ii, 310).—Pyrosulphuryl chloride is without action on sulphur in the cold; on warming, sulphur chloride distils. The oxytetrachloride, $S_2O_3Cl_4$, if formed, decomposes at once.

When selenium is heated with excess of pyrosulphuryl chloride at 120—140° until dissolved, and the excess of solvent driven off under reduced pressure, white crystals of sulphur selenium oxytetrachloride, SO_3SeCl_4 , m. p. 165°, b. p. 185°, are obtained. Constitutional formulæ have been assigned to this compound by Rose (*Ann. Phys. Chem.*, 1838, [i], 44, 315) and Clausnizer (Abstr., 1879, 201), but the authors regard it as an additive compound analogous to such double halides as $SeCl_4.PCl_5$. In confirmation of this, it is found that selenium tetrachloride reacts with an excess of sulphur trioxide to form the compound, $2SeCl_4.3SO_3$, white crystals, m. p. 145°. When heated above its melting point, this substance loses sulphur trioxide and yields the compound $SeCl_4.SO_3$, identical with that described above. Ammonia forms selenium nitride, SeN .

Selenium tetrabromide and sulphur trioxide yield bright yellow needles of a compound, $SeBr_4.2SO_3$, which sinters without melting, and at 170° forms the yellow compound, $SeOBr_2.SO_3$.

Tellurium and pyrosulphuryl chloride form the compound, $TeCl_4.SO_3$, which crystallises in glistening cubes, or, if allowed to separate slowly, in crystals up to 1 cm. in length, which change into a second modification. It melts at 180° without decomposition. Dry ammonia forms a complex product containing tellurium nitride.

Tellurium tetrachloride and sulphur trioxide form white crystals of a compound, $TeCl_4.2SO_3$, m. p. 85°, which decompose at 120°, yielding the compound described above.

Tellurium tetrabromide and sulphur trioxide form a yellowish-brown, crystalline compound, $TeOBr_2.2SO_3$.

Sulphuryl chloride is without action on selenium or tellurium in the cold; the tetrachlorides are formed on heating; chlorosulphonic acid forms coloured, unstable solutions containing the compounds $SeSO_3$ and $TeSO_3$. C. H. D.

Caro's Acid. RICHARD WILLSTATTER and EMIL HAUENSTEIN (*Ber.*, 1909, 42, 1839—1850).—The methods hitherto adopted have been insufficient to decide between the two formulæ for Caro's acid, H_2SO_5 (Baeyer and Villiger, Abstr., 1901, ii, 380) and $H_2S_2O_9$ (Armstrong

and Lowry, Abstr., 1902, ii, 558). The analysis of salts is inconclusive, since a salt, MHSO_5 , is indistinguishable from $\text{M}_2\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$.

The acyl derivatives, however, are monobasic acids, and behave as mixed peroxides of persulphuric acid and acyl peroxides, confirming the formula H_2SO_5 for Caro's acid. The benzoyl derivative is thus decomposed by alkalis into Caro's salt and benzoate: $\text{COPh} \cdot \text{O} \cdot \text{O} \cdot \text{SO}_3\text{H} + \text{H}_2\text{O} = \text{OH} \cdot \text{O} \cdot \text{SO}_3\text{H} + \text{Ph} \cdot \text{CO}_2\text{H}$, and by acids into sulphuric acid and benzoyl hydrogen peroxide: $\text{COPh} \cdot \text{O} \cdot \text{O} \cdot \text{SO}_3\text{H} + \text{H}_2\text{O} = \text{H} \cdot \text{O} \cdot \text{O} \cdot \text{COPh} + \text{H}_2\text{SO}_4$.

Caro's reagent is better prepared from sodium or ammonium persulphate than from the less soluble potassium salt; it crystallises in hard prisms.

In the analysis of Caro's reagent, the three estimations, of hydrogen peroxide, sulphonyl hydrogen peroxide, and persulphuric acid, may be carried out with one solution. Twenty-five c.c. of a solution containing 40 grams of Mohr's salt and 150 c.c. of sulphuric acid per litre, standardised with permanganate, are diluted with 300 c.c. of water and cooled to 0° . The Caro's solution is diluted ten times, and 10—20 c.c. added to the mixture of titrating solution and ice. After stirring, the solution is at once titrated with permanganate. This gives the Caro's acid; reduction of the warm solution gives the Caro's acid + persulphuric acid.

Caro's reagent decomposes rapidly when alkali carbonate or a small quantity of alkali hydroxide is added. It is much more stable in presence of a large excess of alkali hydroxide.

Caro's acid may be prepared from hydrogen peroxide. On adding ammonium sulphate-hydrogen peroxide (Abstr., 1903, ii, 537) to concentrated sulphuric acid at -10° , and adding ice after all has become liquid, the product is found to consist of Caro's acid with a little persulphuric acid.

Benzoyl chloride reacts with neutral Caro's reagent at 0° , and crystals of the sparingly soluble *potassium benzoylperoxysulphonate*, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{O} \cdot \text{O} \cdot \text{SO}_3\text{K}$, H_2O , separate. The salt is neutral, and may be recrystallised from water below 50° . The water of crystallisation is lost in a vacuum over sulphuric acid. The salt may also be obtained anhydrous by crystallisation from alcohol. The active oxygen is estimated by titration with iodine.

The anhydrous salt explodes on rubbing, and the hydrated on contact with sulphuric acid or on warming to $70-80^\circ$. Ferrous sulphate gives a violet coloration even in $N/2000$ solution; ferric chloride gives the same coloration on heating. The acid is stable in acid solution, but is hydrolysed by alkalis to Caro's salt and benzoate. The hydrolysis to sulphuric acid and benzoyl hydrogen peroxide is accomplished by the action of ethereal sulphuric acid.

A dilute solution of Caro's acid reacts with benzenesulphonyl chloride at $8-12^\circ$, but not at lower temperatures, to form *potassium benzenesulphonylperoxysulphonate*, $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{O} \cdot \text{O} \cdot \text{SO}_3\text{K}$, which crystallises from water below 40° in glistening prisms, and explodes on rubbing or warming.

In order to show that derivatives of hydrogen peroxide arise from $\text{H} \cdot \text{O} \cdot \text{O} \cdot \text{H}$, and not from $\begin{array}{c} \text{H} \cdot \text{O} \cdot \text{H} \\ \text{O} \end{array}$, ethyl peroxide and benzoyl peroxide

have been reduced with platinum and hydrogen in the cold. Ethyl alcohol was obtained in the first, and benzoic acid in the second, case. Benzoyl peroxide must thus have the formula (I), as (II) would give rise to benzoic anhydride: (I.) $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{O} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{O} \end{array}$; (II.) $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CO} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CO} \end{array} > \text{O} : \text{O}.$

C. H. D.

Molecular Weight of Selenium. F. OLIVARI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 465—468).—A reply to Paternò's criticism (this vol., ii, 118) of the author's work on this subject (this vol., ii, 39).

T. H. P.

Selenium and Iodine. GIOVANNI PELLINI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 463—465).—A reply to the criticisms of Paternò (this vol., ii, 118) on the work of Pellini and Pedrina (*Abstr.*, 1908, ii, 833).

T. H. P.

Nitrosyl Perchlorate, the Anhydride of Nitrous and Perchloric Acids. KARL A. HOFMANN and (GRAF) ARMIN ZEEDTWITZ (*Ber.*, 1909, 42, 2031—2034).—When mixed oxides of nitrogen, prepared from sodium nitrite and 68% nitric acid, are passed into concentrated perchloric acid (a mixture of dihydrate and monohydrate), colourless, doubly refracting leaflets separate; when these are drained and dried over phosphoric oxide in an atmosphere of nitrogen oxides, and finally in a vacuum, a 20—30% yield of *nitrosyl perchlorate*, $\text{NO} \cdot \text{O} \cdot \text{ClO}_3 \cdot \text{H}_2\text{O}$, is obtained. By evaporating the mother liquor at 140° , and again passing nitrogen oxides, a further yield is obtained. For analysis, the nitrogen is estimated in the nitrometer, the substance being soluble in concentrated sulphuric acid without evolution of gas. The perchloric acid is estimated by saturating with alkali, igniting, and estimating the chloride, the hydrogen by passing the vapour over lead peroxide and a copper spiral, and the nitrous acid by titration with permanganate.

Nitrosyl perchlorate only absorbs moisture from the air very slowly. A little water decomposes it, forming a green solution. Methyl alcohol forms methyl nitrite, and ethyl alcohol, acetone, or ether ignite with explosion. Violent explosions occur with primary aromatic amines, probably owing to the formation of diazonium perchlorates. Phenols give the colorations of the Liebermann reaction. C. H. D.

Revision of the Atomic Weight of Phosphorus; Density of Hydrogen Phosphide. G. TER GAZARIAN (*Compt. rend.*, 1909, 148, 1397—1399).—Hydrogen phosphide was prepared by the action of water on calcium phosphide, and was purified by repeated liquefaction and fractional distillation. The density was determined by direct weighing, and was found to be 1.1829 compared with air. One litre of the gas under normal conditions weighs 1.5293 grams. After correcting for deviations from the gas laws, the molecular weight of hydrogen phosphide is found to be 33.930, which is accurate to one part in 3000, and

hence the atomic weight of phosphorus is 30.906, or in round numbers, 30.91.

T. S. P.

The Compounds of Sulphur and Phosphorus. IV. The Existence of Phosphorus Disulphide, P_3S_6 . ALFRED STOCK [with H. VON BEZOLD, B. HERSCOVICI, and M. RUDOLPH] (*Ber.*, 1909, 42, 2062—2075).—The literature of the phosphorus sulphides is reviewed. Mixtures of the two phosphorus sulphides, P_4S_3 and P_2S_5 , in different proportions have been examined in sealed, exhausted glass tubes. Three temperatures have been determined for each mixture, that at which the substance becomes moist, that at which sintering takes place, and the melting point. The melting-point curve has only a single maximum at 310° , corresponding with the formula P_4S_7 , and eutectic points at 47.5% S and 127° and 69% S and 248° respectively. The sintering-point curve (this vol., ii, 543) also clearly indicates the compound P_4S_7 , and there is no indication of P_3S_6 .

The same results are obtained whether mixtures of the sulphides or mixtures of sulphur and phosphorus are used for the experiments, provided that the mixtures are heated to 300° in an atmosphere of carbon dioxide to ensure combination. Giran's results (*Abstr.*, 1906, ii, 226) are explained by imperfect equilibrium, his mixtures only having been heated to 200° .

The sulphide P_4S_7 may be purified by repeated recrystallisation from carbon disulphide, or by careful fractional distillation. It is also obtained when a solution of P_4S_3 and P_2S_5 in carbon disulphide is heated above 100° .

There is no evidence of the existence of a phosphorus disulphide, PS_2 or P_3S_6 . All the substances previously described as such are mixtures of P_4S_3 and P_2S_5 .

C. H. D.

Compounds of Boron with Certain Metals. ARMAND BINET DU JASSONNEIX (*Ann. Chim. Phys.*, 1909, [viii], 17, 145—216).—A résumé of work already published (compare *Abstr.*, 1907, ii, 30, 95, 691, 692, 779).

G. S.

The Coking Test. O. BINDER (*Zeitsch. anal. Chem.*, 1909, 48, 372—375).—The well-known method of estimating the amount of coke yielded by heating a known weight of coal in a covered platinum crucible until no more gases are evolved has been applied by the author to some other substances having the same elementary composition (gum, starch, cellulose, and dextrin), and, no doubt, owing to a different structure, the amount of coke yielded is very different. Gum gave 17.73% (ash-free) of coke; starch, 9.9%; cellulose, 6.71% (according to Muck), whilst dextrin gave only 4.40%. The coke from gum is very solid, that of starch loose and covered with soot, and that of dextrin very porous, hollow, and lustrous.

Sucrose yielded 7.79%; lactose, 5.71%, and catechol, 36.55%, of coke. Sucrose-coke is lustrous, highly fused, and hollow, that of lactose, also fused and brown, with a tinge of blue. The coke from catechol is very similar to that yielded by soft coals.

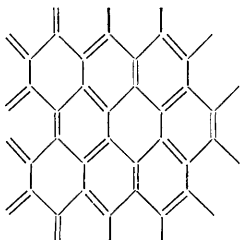
A number of illustrations are given, showing the characteristic appearance of the various cokes.

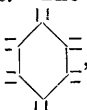
L. DE K.

Constitution of Wood Charcoal. OSSIAN ASCHAN (*Chem. Zeit.*, 1909, 33, 561).—The annexed representation of the molecule of wood charcoal as two concentric benzene nuclei (Dewar, *Chem. News*, 1908, 97, 16) does not harmonise with the tension theory, for whilst wood charcoal is an exceedingly stable substance, the strain in such a molecule must be greater even than that in a molecule of an explosive substance, such as acetylene.



The representation of the molecule of wood charcoal must, according to the author's views, explain its great stability, its intense colour, the formation of mellitic acid by oxidation, and the presence of a small quantity of hydrogen, oxygen, and possibly nitrogen. These two (or three) elements are probably essential constituents of wood charcoal, which may be possibly a highly carbonaceous organic substance. The analysis of wood charcoal prepared above 1500° gives numbers almost identical with those required by the formula $(C_{130}H_{10})_x$ or $(C_{132}H_{10}O)_x$. The author suggests that an unstrained arrangement of benzene nuclei, such as that figured, satisfies these requirements. The colour may be attributed to



the group , and the addition of hydro-

gen and oxygen may take place at the outermost carbon atoms; moreover, the web-like structure may account for the great absorptive power of charcoal, whilst its property of retaining dyes and other coloured substances may be due to the formation of loose additive compounds with the serried benzene nuclei. Bone charcoal contains about 1% of nitrogen, and Stollé has observed that the proportion of carbon to nitrogen is about 10:1. This fact is brought into agreement with the preceding representation by assuming that one or more of the bounding CH groups is replaced by N.

C. S.

Liberation of Helium from Radioactive Minerals by Grinding. J. A. GRAY (*Proc. Roy. Soc.*, 1909, 82, A, 301—306).—The author has determined the amount of helium which is liberated when thorianite is reduced by grinding to a more or less finely divided state. After grinding in an agate mortar, the mineral was shaken up with water, and, after the particles had been allowed to settle out for a definite time, the upper part of the water was syphoned off. The mineral suspended in this was left to settle out, and a weighed portion of the dry substance was then heated with nitric acid in an exhausted tube, the helium being afterwards pumped off and its volume determined. From a microscopic examination of the different samples of mineral, an estimate of the size of the particles was obtained.

In general, the amount of helium liberated increases with the fineness of the particles. When the diameter of the particles exceeds 10μ , very little helium is liberated. On the other hand, a temporary

limit to the amount of helium liberated is reached when the mineral is reduced to particles of a diameter of about 3μ . This limit corresponds with the liberation of about 28% of the contained helium. The conclusion is drawn that part at least of the helium in thorianite is retained in a structure which is very large compared with the molecular structure.

H. M. D.

Molecular and Some Other Constants of the Inactive Gases. GEORGE RUDORF (*Phil. Mag.*, 1909, [vi], 17, 795—813 *).—The velocities, mean free paths, and diameters of the molecules of the inert gases have been calculated. The molecular velocities calculated from the mean kinetic energy are respectively: helium 13.11, neon 5.845, argon 4.13, krypton 2.86, and xenon 2.28×10^4 cm. per second. The mean free paths are for helium, 2.85, and for argon, 1.006×10^{-5} cm.

The calculation of the molecular diameters was made by three different methods, involving respectively the mean free path, the number of molecules in unit volume of gas, and the viscosity coefficient. In the case of the first two methods, the required value of the volume occupied by the molecules themselves in unit gas volume was obtained in four different ways: (a) from the density of the liquid (as an upper limit), (b) from the coefficient b of van der Waals' equation, (c) from the dielectric constant, and (d) from the refraction. The separate values thus obtained for the molecular diameters vary very considerably, and indicate that even in the case of the simple monatomic gases, the kinetic theory is far from satisfactory. In the case of helium, for example, the numbers vary from 0.426 to 28.5×10^{-5} cm.

The number of molecules contained in unit volume of helium and argon has also been calculated in different ways, and in this case, also, the numbers show considerable discrepancy.

By making use of the formula of Lorentz and Lorenz, the following values were obtained for the refractive index of the inactive elements in the form of liquid: helium 1.03, argon 1.23, krypton 1.26, and xenon 1.46. These numbers are for infinitely long waves. In the absence of a value for the density of liquid neon, its refractive index could not be calculated, but it is shown that this density is probably 1.24.

Attention is directed to an error in the estimation of the molecular mean free paths and diameters of certain gases by Lord Kelvin (*Abstr.*, 1902, ii, 649).

H. M. D.

The Occurrence of Ammonia and Nitrate in Deposits of Potash Salts. WILHELM BILTZ and E. MARCUS (*Zeitsch. anorg. Chem.*, 1909, 62, 183—202).—Small quantities of ammonium salts have been previously detected in salt deposits, but nitrates and nitrites have not been observed.

Systematic profiles have been taken through the Stassfurt and the Vienenburg deposits. The ammonia was estimated colorimetrically with Nessler's solution, special precautions having to be taken on account of its small quantity. Potassium was estimated as perchlorate, and chlorine by titration.

* and *Ann. Physik.*, 1909, [iv], 29, 751—779.

The Stassfurt results show that the quantity of ammonia follows that of the carnallite, being practically zero in the rock-salt and anhydrite regions. It is independent of the total potassium. The distribution of bromine in the deposits is very similar (Boeke, Abstr., 1908, ii, 505), and it is probable that the two substances are present entirely as ammonium carnallite and bromo-carnallite respectively. The Vienenburg deposits give similar results. The younger carnallites are less rich in ammonia than the older. A sea-water obtained from these salts would contain 0.056 mg. NH_3 per litre, whilst a modern sea-water contains 0.2 mg. These figures confirm Erdmann's view *Zeitsch. angew. Chem.*, 1908, 21, 1685), that these salt deposits were not formed by the direct evaporation of sea-water.

Nitrites were not detected in any of the deposits. Nitrates were only found in the salt clays, which are also the only strata of the series in which organic remains are found. C. H. D.

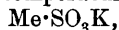
Formation of Potassium Nitrate from Sodium Nitrate and Potassium Carbonate from the Standpoint of the Phase Rule. ROBERT KREMANN and A. ŽITEK (*Monatsh.*, 1909, 30, 311—340).—The system represented by the equation $2\text{NaNO}_3 + \text{K}_2\text{CO}_3 \rightleftharpoons \text{Na}_2\text{CO}_3 + 2\text{KNO}_3$ has been investigated, solubility determinations having been made at 10° and 24.2° . Complete diagrams are given.

The mutual solubilities of the four salt pairs were determined with the following results: (1) Sodium nitrate and potassium nitrate do not form a double salt, although the solubility of each is increased by the addition of the other. (2) Sodium carbonate and potassium carbonate form the double salt, $\text{Na}_2\text{CO}_3 \cdot \text{K}_2\text{CO}_3 \cdot 6\text{H}_2\text{O}$. (3) At 24.2° the addition of sodium nitrate to solutions saturated with respect to sodium carbonate changes the solid phase from $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ to $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ at a definite concentration. At 10° the solid phase under such conditions is always $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, there being no transition point. (4) With the exception of the case just mentioned the relations at 10° are similar to those at 24.2° .

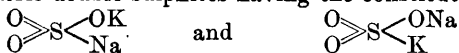
The solubility relations of the single salts showed that the systems containing three solid phases were the following: potassium nitrate-sodium carbonate-sodium nitrate; potassium nitrate-sodium carbonate-double salt; potassium nitrate-double salt-potassium carbonate. The compositions of the solutions corresponding with these three systems were determined, and the results present the following points of interest: (1) In solutions saturated with respect to sodium carbonate and potassium nitrate, which also contain sodium nitrate, the carbonate is present as $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ in the solid phase at 24.2° ; at 10° it is $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. (2) When potassium nitrate is added to the solution saturated with respect to sodium carbonate and double salt, the latter is almost completely precipitated.

In the last part of the paper the results obtained are applied to show how potassium nitrate and sodium carbonate can be technically prepared from sodium nitrate and potassium carbonate. Experiments on a small scale gave very satisfactory results. T. S. P.

Existence of Isomeric Double Sulphites of Potassium and Sodium. ALEXANDER E. ARBUSOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 447—451).—The double sulphites obtained by neutralising (1) potassium hydrogen sulphite by means of sodium carbonate, and (2) sodium hydrogen sulphite by means of potassium carbonate, give with methyl iodide at the ordinary temperature the same compound,



the methyl group replacing the sodium atom in each case. If, therefore, two isomeric double sulphites having the constitutions



are capable of existing, the form in which the potassium atom is united with sulphur is unstable, and changes readily into the other isomeride (compare Godby, *Proc.*, 1907, 23, 241).

T. H. P.

Solubility of Disodium Hydrogen Phosphate in Water. TSUTOMU SHIOMI (*Mem. Col. Sci. Eng. Kyōto*, 1908, i, 406—413).—The solubility of disodium hydrogen phosphate in water has been determined by a direct method at a number of temperatures between 0° and 100°. Some of the results, in grams of anhydrous salt in 100 grams of water, are as follows: 3·55 at 10·26°; 12·02 at 25·15°; 54·88 at 40·29°; 83·00 at 60·23°; 102·15 at 99·77°. There are three breaks in the curve, at 36·45°, 48°, and 95·2°. The first corresponds with the transition from dodecahydrate to heptahydrate, and the second and third probably represent the transitions from heptahydrate to dihydrate and dihydrate to anhydrous salt respectively. The investigation of the latter points is, however, not complete.

G. S.

Sub-oxides of Cæsium. ÉTIENNE RENGADE (*Compt. rend.*, 1909, 148, 1199—1202).—When an alkali metal is burned in an insufficient supply of air (or oxygen), it is difficult to tell by ordinary methods whether the substance produced is a definite sub-oxide or a mixture of metal and protoxide. The author has made use of the fact that the protoxides of the alkali metals dissolve in the metals themselves, and in the case of cæsium the fusion curves of the system cæsium-cæsium monoxide have been studied. The curves show the existence of four oxides other than the protoxide, namely: Cs_7O , Cs_4O , Cs_7O_2 , and Cs_3O . Only Cs_7O gives a maximum in the curve, the other three oxides transforming one into the other, and finally into Cs_2O as the percentage of oxygen increases. Besides the stable eutectics consisting of Cs - Cs_7O and Cs_7O - Cs_4O , there is a metastable eutectic consisting of Cs_7O - Cs_7O_2 . Pure crystals of the oxide Cs_7O_2 have been obtained; they resemble those of potassium permanganate both in shape and colour. The sub-oxides of cæsium, which have thus been proved to exist, do not possess formulæ in accordance with the univalent character of the alkali metals.

T. S. P.

Rubidium Peroxide Hydrate and Rubidium Percarbonate. ERICH PELTNER (*Ber.*, 1909, 42, 1777—1782).—*Rubidium peroxide hydrate*, $\text{RbO}\cdot\text{OH}\cdot\text{H}_2\text{O}_2$, is obtained as an oily precipitate which, on cooling, solidifies to a mass of white crystals, on mixing molecular proportions of rubidium hydroxide and of 30% hydrogen peroxide, both dissolved in alcohol; the substance is a snow-white, deliquescent solid, which is fairly stable below 0° , and when freshly prepared dissolves in water without decomposition; at the ordinary temperature, however, it undergoes violent decomposition, and evolves oxygen with a considerable rise of temperature. After the reaction has subsided, a hard, yellow solid remains, which dissolves in water with evolution of oxygen. From a determination of the available oxygen in this substance it appears to be a hydrated form of the oxide, Rb_2O_4 .

Rubidium percarbonates of the composition $\text{Rb}_2\text{CO}_4\cdot 2\text{H}_2\text{O}_2\cdot\text{H}_2\text{O}$, $\text{Rb}_2\text{CO}_4\cdot\text{H}_2\text{O}_2\cdot 2\text{H}_2\text{O}$, and $\text{Rb}_2\text{CO}_4\cdot 2\frac{1}{2}\text{H}_2\text{O}$ are obtained by dissolving one molecular proportion of rubidium carbonate in one, two, or three molecular proportions of 30% hydrogen peroxide solution, and sufficient water to obtain a clear solution; on adding alcohol to the cooled solution these substances are precipitated in the form of white, crystalline solids; they are all very hygroscopic, and evolve oxygen on being dried in a vacuum, but if kept dry they do not turn yellow. The dried substances evolve more oxygen on moistening with water.

P. H.

Conditions of Solubility of Silver Iodide in Sodium Iodide Solutions. W. S. KRYM (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 382—385).—The author has determined the solubility of silver iodide in sodium iodide solutions of various concentrations. The curve giving mols. of sodium iodide as abscissæ and mols. of silver iodide as ordinates for the temperature 25° consists of three branches, the corresponding solid phases being silver iodide, double salt, $\text{AgI}\cdot\text{NaI}\cdot 3\frac{1}{2}\text{H}_2\text{O}$, and sodium iodide respectively. The solubility of silver iodide increases continuously when the solid phase is silver iodide, and decreases continuously when this phase is double salt or sodium iodide.

T. H. P.

Hydrates of the Halogen Salts of Calcium. P. I. KUSNETZOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 367—379).—The author's results confirm the existence of two forms of tetrahydrated calcium chloride, one stable (α -form) and the other unstable (β -form).

The following hydrates have also been prepared: $\text{CaBr}_2\cdot 4\text{H}_2\text{O}$, with transition temperature about $+55^\circ$; $\text{CaI}_2\cdot 4\text{H}_2\text{O}$, with transition temperature about $+65^\circ$; $\text{CaI}_2\cdot 7\text{H}_2\text{O}$, decomposing between $+1^\circ$ and -2° .

T. H. P.

Red Lead. JAROSLAV MILBAUER (*Chem. Zeit.*, 1909, 33, 513—514, 522—523).—The temperature at which red lead is technically produced being uncertain, the author has experimentally studied the temperature-limits of its formation and the reversibility of the reaction. A special form of gas furnace is described, capable of maintaining a temperature constant within $\pm 2^\circ$, the gas supply being regulated

by an electro-magnetic regulator, actuated by the pressure of carbon dioxide contained in a spiral tube of silvered copper placed in the furnace. The temperature was measured by means of a thermocouple.

The substance was contained in a horizontal tube of Jena glass, one end of which was carried by a slowly rotating spindle, the other being conically ground and fitted into the conical end of the gas delivery tube, the joint being lubricated with gold-leaf, thus maintaining a gas-tight joint during rotation. The air or oxygen supplied was heated before entering by passing through a tube containing porcelain and copper oxide in the upper part of the furnace, and was passed through at constant velocity by means of a special gasometer (Abstr., 1907, ii, 252).

The lead oxide used was prepared by twice precipitating from purified lead nitrate and drying in a vacuum at 130° until free from water. The red lead formed was estimated by titration (Topf, Abstr., 1887, 997).

The formation of red lead proceeds faster at first, then more slowly, approaching a state of equilibrium. The velocity of the air or oxygen is without influence, provided that sufficient oxygen is present. Measurable oxidation occurs even at 240° , the yield increasing up to 450° , and altering little beyond that. A fuller study of the influence of temperature is in progress. Below 450° the product is always brown, true red lead only being obtained from 450° upwards (compare Liebig, *Zeitsch. angew. Chem.*, 1904, 11, 167).

The yield increases exponentially with the partial pressure of the oxygen, and is practically independent of the amount of moisture present in the gas.

C. H. D.

Solubility of Lead Sulphate. J. SEHNAL (*Compt. rend.*, 1909, 148, 1394—1396).—Owing to the discrepancies in the literature, the author has redetermined the solubility of lead sulphate in water. At the ordinary temperature, forty-eight hours are necessary for saturation to be attained. 0.0824 Gram of lead sulphate dissolves in 1000 c.c. of water, or 1 part in 12,135 parts of water; moreover, the solubility is the same at 100° as at the ordinary temperature (18°). The discrepancies in the results of previous observers are ascribed to impurities in the lead sulphate, it being shown that a trace of sulphuric acid has a considerable effect on the solubility.

The fact that lead sulphate dissolves in water is ascribed to hydrolysis, and in support of this it is shown that the solubility of hydrated oxide of lead ($\text{PbO}, \text{H}_2\text{O}$) in dilute sulphuric acid is the same as the solubility of lead sulphate in water.

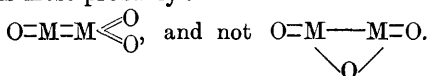
T. S. P.

A New Type of Sesquioxides. Selenite of Lead Sesquioxide and Thallic Selenite. LUIGI MARINO (*Zeitsch. anorg. Chem.*, 1909, 62, 173—182).—Lead sesquioxide, prepared either by the action of sodium hypochlorite on an ice-cooled solution of sodium plumbite, or by decomposing the selenite, $\text{Pb}_2\text{Se}_2\text{O}_7$, with sodium hydroxide, reacts with a warm concentrated solution of selenious acid, forming $\text{Pb}_2\text{Se}_2\text{O}_7$. After the reaction is over, the whole is heated to boiling, filtered,

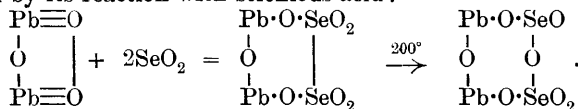
digested with cold 7% nitric acid, and washed. The product is identical with that formerly described (Abstr., 1908, ii, 833). Only traces of selenate are formed, showing that there is not an intermediate production of lead dioxide.

A selenite of this type differs from those obtained from other sesquioxides, such as those of iron, aluminium, or yttrium, in not forming acid or basic salts under any conditions. Thallium behaves like lead, the sesquioxide reacting with selenious acid to form a white, crystalline selenite, $Tl_2(SeO_3)_3$. Experiments with tin are difficult to perform, owing to the difficulty of preparing a pure tin sesquioxide.

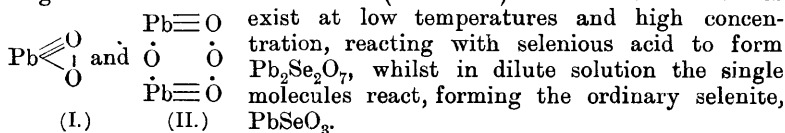
When a sesquioxide reacts with sulphurous acid to form a dithionate, its constitution is most probably :



Lead sesquioxide, on the other hand, probably has the constitution indicated by its reaction with selenious acid :



This leads to the assumption that lead dioxide can exist in single and in double molecules (I and II). The double molecules



The constitution of lead metaplumbate is also discussed.

C. H. D.

Dyeing Properties of Lead Chromate. LÉO VIGNON (*Compt. rend.*, 1909, 148, 1329—1331; *Bull. Soc. chim.*, 1909, [iv], 5, 675—678).—Fabrics are usually dyed with lead chromate by passing the material through the aqueous solution of a soluble lead salt and then through a solution of potassium or sodium chromate. The author finds that dyeing also occurs if the material is agitated in a suspension of precipitated lead chromate in water; equally good results are obtained with silk, wool, or cotton. The lead chromate does not combine chemically with the material dyed.

Dyeing also takes place if the lead chromate is suspended in alcohol or benzene, but the resulting colours are not so deep as those obtained when water is the medium of suspension.

T. S. P.

Some New Compounds and Double Compounds of Tervalent Thallium. JULIUS GEWECKE (*Annalen*, 1909, 366, 217—236).—An investigation on the preparation and properties of several halogen derivatives of trivalent thallium. It is shown that the supposed thallic fluoride of Willm (*Ann. Chim. Phys.*, 1865, [iv], 5, 5) is in reality thallic oxyfluoride, $TlOF$. Attempts to prepare thallic fluoride

were unsuccessful, owing to the great tendency of this substance to hydrolyse; further, the only double salt of thallic fluoride which could be isolated was the potassium salt, $2\text{TlF}_3 \cdot \text{KF}$, which is likewise unstable, being decomposed by atmospheric moisture with evolution of hydrogen fluoride.

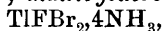
The following salts of the types $2\text{TlCl}_3 \cdot \text{M}''\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ and $2\text{TlCl}_3 \cdot \text{M}'\text{Cl}_2 \cdot 8\text{H}_2\text{O}$, analogous to the corresponding gold double salts, were obtained by allowing a solution of the components in water acidified with hydrochloric acid to evaporate in a vacuum over sulphuric acid. *Thallic nickel chloride* ($8\text{H}_2\text{O}$), bright green crystals. *Thallic cobalt chloride* ($8\text{H}_2\text{O}$), hygroscopic, red crystals. *Thallic calcium chloride* ($6\text{H}_2\text{O}$), large, colourless, transparent crystals. *Thallic strontium chloride* ($6\text{H}_2\text{O}$) was also prepared; the corresponding barium salt could not be obtained in a pure state. *Thallic magnesium chloride* ($6\text{H}_2\text{O}$), large, transparent, colourless crystals. *Thallic zinc chloride* ($6\text{H}_2\text{O}$), colourless prisms.

Thallic manganese chloride ($6\text{H}_2\text{O}$), long, silky, pale pink needles, and *thallic copper chloride* ($6\text{H}_2\text{O}$), large, pale blue crystals, are obtained only from neutral aqueous solutions.

Thallic oxyfluoride, TlOF , obtained by the action of dilute hydrofluoric acid on thallic hydroxide at the ordinary temperature, is a dark olive-green powder.

Potassium thallic fluoride, $2\text{TlF}_3 \cdot \text{KF}$, is prepared by fusing potassium hydrogen fluoride with thallic fluoride and treating the product with anhydrous hydrofluoric acid; it is obtained as a white mass.

Thallic fluoro-chloride, $\text{TlFCl}_2 \cdot 3\text{H}_2\text{O}$, prepared by passing chlorine into a solution of thallic fluoride in 40% hydrofluoric acid, crystallises in colourless needles. It yields the *anhydrous* salt, a white, crystalline powder, when kept in a vacuum over phosphoric oxide. *Thallic fluoro-chloride potassium chloride*, $2\text{TlFCl}_2 \cdot \text{KCl}$, forms colourless crystals. The anhydrous fluoro-chloride combines with ammonia, forming the *salt*, $\text{TlFCl}_2 \cdot 4\text{NH}_3$, a white substance, and with pyridine, forming the *salt*, $\text{TlFCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, crystallising in slender, white needles. *Thallic fluoro-bromide*, TlFBr_2 , a pale yellow, crystalline substance, is more stable than the analogous chloride; *thallic fluorobromide ammonia*,



is a yellowish-white powder.

W. H. G.

Theory of the Fusion of Copper in Cupola Furnaces.
N. JUSCHKEVITSCH (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 469—472).—The author has studied the reactions occurring in an atmosphere of dry nitrogen in an electric furnace between the following pairs of compounds, finely powdered and well mixed, taken in the proportions indicated.

(1) $\text{Cu}_2\text{O} + \text{FeS}$.—These substances begin to react according to the equation: $\text{Cu}_2\text{O} + \text{FeS} = \text{Cu}_2\text{S} + \text{FeO}$ at $280\text{--}285^\circ$, the velocity of the reaction increasing as the temperature is raised. At 700° , after two hours' heating, it was found that 95.65% of the sulphur had passed from the iron to the copper.

(2) $2\text{CuO} + \text{FeS}$.—Evolution of sulphur dioxide in this reaction is

very slow, a large proportion of the sulphur remaining in the mixture passing from the iron to the copper.

(3) $\text{Cu}_2\text{S} + \text{Fe}$.—The formation of ferrous sulphide when this mixture is heated at 600° is very slight, only 5% of the sulphur passing from the copper to the iron after six hours' heating.

(4) $2\text{Cu} + \text{FeS}$.—The reaction $2\text{Cu} + \text{FeS} = \text{Cu}_2\text{S} + \text{Fe}$ proceeds considerably more slowly than the change: $\text{Cu}_2\text{O} + \text{FeS} = \text{Cu}_2\text{S} + \text{FeO}$, six hours' heating at 600° only resulting in 26.1% of the sulphur passing from the iron to the copper.

By fusing CuO and FeS in presence of silica, coarse metals were obtained containing (1) 74.7% Cu, 3.45% Fe, and 20.75% S; and (2), 72.64% Cu, 4.48% Fe, and 21.28% S. T. H. P.

Influence of Small Quantities of Arsenic and Antimony on Copper. ARTHUR H. HIORNS and S. LAMB (*J. Soc. Chem. Ind.*, 1909, 28, 451—457).—Alloys were prepared by melting a rich copper-arsenic alloy with copper. The electrical conductivity falls rapidly with the increase of arsenic. Alloys containing up to 2.5% As are quite ductile, and can be rolled cold. Copper-antimony alloys are less malleable.

Both series of alloys are found to consist of solid solutions, which only attain equilibrium after prolonged heating. Traces of a blue arsenide, probably Cu_3As , appear above 0.21% As. The compound Cu_3Sb also appears in small quantity on slow cooling. C. H. D.

Reduction of Copper Sulphate with Hydroxylamine. MAXWELL ADAMS and ELIZA OVERMAN (*J. Amer. Chem. Soc.*, 1909, 31, 637—640).—When solutions of hydroxylamine and anhydrous copper sulphate in methyl alcohol are mixed at -10° , pale green crystals of the compound $\text{CuSO}_4 \cdot \text{NH}_2 \cdot \text{OH}$ are formed if the copper sulphate is in excess, whereas deep green crystals having the composition $\text{CuSO}_4 \cdot 2\text{NH}_2 \cdot \text{OH}$ are obtained when the hydroxylamine is in excess. These salts are stable when dry, but are changed into cuprous oxide when warmed with water to which a drop of alkali has been added; when left in contact with excess of hydroxylamine in methyl alcoholic solution, they become violet in colour, hydroxylamine being absorbed. By treating a saturated solution of copper sulphate in methyl alcohol with a large excess of pure hydroxylamine, violet crystals were obtained, which could not be dried without partial decomposition. Analysis indicated the formula: $\text{CuSO}_4 \cdot 5\text{NH}_2 \cdot \text{OH}$.

A cold aqueous solution of hydroxylamine acts on the compound $\text{CuSO}_4 \cdot 2\text{NH}_2 \cdot \text{OH}$ with the formation of a bright green, non-crystalline compound, $\text{Cu}_2\text{OSO}_4 \cdot 2\text{NH}_2 \cdot \text{OH}$; this compound also results from the interaction of cupric hydroxide and a solution of hydroxylamine sulphate.

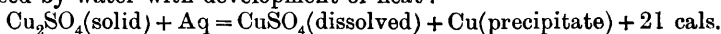
All the above compounds, with the exception of the one containing $5\text{NH}_2 \cdot \text{OH}$, are stable in alcohol or ether, or water at zero. In water, decomposition begins at 15° , and proceeds rapidly with rise in temperature; a drop of alkali solution changes them into cuprous oxide.

When a salt of hydroxylamine is added to a solution of copper

sulphate, the further addition of sodium hydroxide is supposed to give rise to the following compounds in succession: $\text{CuSO}_4 \cdot \text{NH}_2 \cdot \text{OH}$, $\text{CuSO}_4 \cdot 2\text{NH}_2 \cdot \text{OH}$, $\text{CuSO}_4 \cdot 5\text{NH}_2 \cdot \text{OH}$, $\text{Cu}_2\text{OSO}_4 \cdot 2\text{NH}_2 \cdot \text{OH}$. The last compound is then decomposed by the alkali with evolution of nitrogen and formation of cuprous oxide; in the presence of excess of hydroxylamine the cuprous oxide is reduced to copper.

T. S. P.

Cuprous Sulphate. ALBERT RECOURA (*Compt. rend.*, 1909, 148, 1105—1108).—Cuprous sulphate is not known in the free state, although the compounds $\text{Cu}_2\text{SO}_4(\text{CO})_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}_2\text{SO}_4 \cdot 4\text{NH}_3$ have been described. The author shows that by operating in absence of water, methyl sulphate and cuprous oxide may be made to yield cuprous sulphate, $\text{Cu}_2\text{SO}_4 : \text{Cu}_2\text{O} + \text{Me}_2\text{SO}_4 \rightarrow \text{Cu}_2\text{SO}_4 + \text{OMe}_2$. Ethyl sulphate will react in the same way, the corresponding ether being evolved. The reaction is carried out by heating 2 grams of powdered cuprous oxide with 20 c.c. of methyl sulphate at 160° until methyl ether ceases to be evolved (about a quarter of an hour). The cuprous sulphate is obtained as a greyish-white powder, which is washed with ether, carefully excluding air, and finally dried in a vacuum. When dry, cuprous sulphate is stable in dry air, but is immediately decomposed by water with development of heat:



The development of heat in this decomposition is contrary to the behaviour of other cuprous salts, and explains why cuprous sulphate cannot be prepared in aqueous solution. Freshly prepared cuprous sulphate if allowed to oxidise before drying is converted into a soot-black powder, from which cupric sulphate is dissolved by water, leaving an oxide with all the properties of Rose's oxide, Cu_4O . Dry Cu_2SO_4 , oxidised at 200° , yields the basic salt, $\text{CuO} \cdot \text{CuSO}_4$.

Cuprous sulphate is soluble in concentrated hydrochloric acid, in ammonia, and in glacial acetic acid, the last giving an intensely violet solution.

R. J. C.

Copper Complexes in Ammoniacal Solution. ARTHUR HANTZSCH and PHILIP WILFRED ROBERTSON (*Ber.*, 1909, 42, 2135—2137. Compare this vol., ii, 44).—Polemical. A reply to Dawson (this vol., ii, 316).

W. H. G.

Action between Metals and Acids and the Conditions under which Mercury Causes Evolution of Hydrogen. SAMUEL W. J. SMITH (*Phil. Mag.*, 1909, [vi], 17, 833—848).—Pure mercury displaces hydrogen from solutions of hydrochloric and sulphuric acid in the same way as the more strongly electropositive metals. The reaction ceases before a perceptible quantity of hydrogen has been evolved, because of the inhibiting influence of a very small quantity of mercury salt. An arrangement is described by means of which the reaction is made continuous. In this, mercury is allowed to escape from a containing tube in the form of a very fine jet, which impinges on the solution of acid. When this jet of mercury is in direct communication with a mercury surface at rest in the same solution, the concentration

of the mercury salt at this surface is prevented from becoming or remaining large enough to stop the evolution of hydrogen, and this is evolved continuously. The amount of mercury salt which is sufficient to stop the action at the still surface diminishes with the concentration of the acid solution, and, as a consequence, it is impossible to decompose the acid by means of the action of the jet when the concentration of the acids fall below a certain limit. For both hydrochloric and sulphuric acid, the limiting concentration was found to be about 6 gram-equivalents per litre. In addition to the simple displacement of hydrogen, secondary effects resulting in the production of hydrogen sulphide and free sulphur have also been observed in the action of pure mercury on sulphuric acid solutions. These correspond with the equations: $4\text{Hg}_2 + 5\text{H}_2\text{SO}_4 = 4\text{Hg}_2\text{SO}_4 + \text{H}_2\text{S} + 4\text{H}_2\text{O}$ and $3\text{Hg}_2 + 4\text{H}_2\text{SO}_4 = 3\text{Hg}_2\text{SO}_4 + \text{S} + 4\text{H}_2\text{O}$ respectively. H. M. D.

New Process for the Preparation of Aluminium Nitride. ATH. J. SOFIANOPOULOS (*Bull. Soc. chim.*, 1909, [iv], 5, 614—616).—Aluminium powder, contained in a porcelain tube, is heated to a temperature somewhat below its melting point, and then subjected to the action of a stream of dry ammonia, until the latter passes over unchanged. The resulting *nitride*, Al_2N_2 , is an amorphous, grey, spongy product, which is quite stable when dry, and decomposes water slowly at the ordinary temperature and rapidly at 100° , yielding ammonia and aluminium hydroxide. The nitride is not affected by oxygen even when warmed in an atmosphere of this gas, but is readily attacked by halogens, yielding nitrogen and the corresponding salt of aluminium. With solutions of alkali hydroxides, it yields ammonia and alkali aluminates. The nitride can also be prepared by using the vapour of hydrazine or azoimide in place of ammonia.

T. A. H.

The Weathering of Clays. II. JAKOB M. VAN BEMMELN (*Zeitsch. anorg. Chem.*, 1909, 62, 221—236. Compare Abstr., 1905, ii, 89).—The white efflorescence on the surface of many volcanic clays in Java consists mainly of silica (diatoms), and not of calcium sulphate. Extraction with sodium hydroxide and hydrochloric acid of different strengths shows that the volcanic clay of Pasoeroean contains silica (as diatoms and as opal), a readily decomposable silicate, $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$, and a stable silicate, kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. The latter compound occurs in larger quantity in the loess and alluvial clays. Clays of the laterite type contain silicates in which the ratio of silica to alumina falls below 2. The kaolinite is probably microcrystalline, the lower silicates representing a further stage in the weathering.

It is impossible to determine how much of the ferric oxide, magnesia, lime, and alkalis is present as microcrystalline silicates, and how much as adsorption compounds of the hydrogels of silica, alumina, and ferric oxide. Crystalline pseudomorphs are certainly present.

C. H. D.

Labile Forms of Tetrahydrated Manganese Bromide and Chloride. P. I. KUSNETZOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 353—367).—Tetrahydrated manganese bromide exists in two forms:

(1) the ordinary stable α -modification, which has a pale red colour and crystallises in large, monoclinic prisms, six-sided plates, or drusy or rosette-like masses, and (2) the less stable β -form, which separates in thin, almost colourless plates. As is the case with other unstable forms (compare Lehmann, *Molekularphysik*, I, 194), the β -tetrahydrate exhibits a lower decomposition temperature and a greater solubility than the α -form. The β -modification changes into the red form at 57—58°.

Two similar modifications of the tetrahydrate of manganese chloride have been prepared. T. H. P.

Nature of the Cast Irons. GEORGE B. UPTON (*J. Physical Chem.*, 1909, 13, 388—416).—The properties of iron carbon alloys are examined from the point of view of a modified Roozeboom diagram which the author has given in a previous paper (Abstr., 1908, ii, 1042). It is shown that this is in much better agreement with observed facts than the metastable equilibrium diagrams, which have been put forward by various observers.

In regard to the metallographic nature of the cast irons, the author arrives at the conclusion that grey cast iron contains crystalline graphite mechanically mixed with a metallic matrix, which is a solution of silicon and carbon in γ -iron. White cast iron is a supersaturated solution of carbon and silicon in γ -iron. Malleable cast iron contains temper graphite mechanically mixed with a metallic matrix, which is α -iron, ferrite, and a larger or smaller quantity of pearlite.

H. M. D.

Iron Sulphide. III. HANS MALFATTI (*Zeitsch. anal. Chem.*, 1909, 48, 352—356. Compare Abstr., 1908, ii, 192).—Double compounds are described containing iron, sulphur, and potassium or calcium, formed by precipitating ferric chloride with excess of potassium or calcium sulphide. Ammonium sulphide also yields a precipitate containing ammonium.

These precipitates, which may be considered as thioferrites, are not very stable, and suffer decomposition to a large extent when treated with water. L. DE K.

The Fusion of Ferric Oxide. ERNST J. KOHLMAYER (*Metallurgie*, 1909, 6, 323—325).—Ferric oxide may be melted by introducing it into a platinum crucible previously heated to 1600°. The platinum crucible is enclosed in an outer crucible of spinel ($2\text{MgO}, \text{Al}_2\text{O}_3$) and heated by a granular carbon resistance. A current of oxygen is led through the furnace during the operation. After heating to 1600°, the crucible is allowed to cool, and a cooling curve taken. The freezing point of ferric oxide is found to be 1562—1565°. On cooling, there is a slight development of heat at 1350—1250°, and a more marked one at about 1030°. In spite of the presence of an atmosphere of oxygen, some loss of oxygen takes place, but this does not largely affect the freezing point. Pure ferrosferric oxide, Fe_3O_4 , freezes at 1527°.

Ferric oxide crystallises in tabular, rhombohedral scales with steely lustre. The edges are transparent, and ruby-red in colour; D 5·187—5·193. C. H. D.

Artificial Preparation of Rinneite on the Basis of its Solubility Diagram. H. E. BOEKE (*Sitzungsber. K. Akad. Berlin.*, 1909, 24, 632—638. Compare this vol., ii, 153).—The relationship between rinneite ($\text{FeCl}_2 \cdot 3\text{KCl} \cdot \text{NaCl}$) and its component salts has been investigated.

According to dilatometric observations, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ is transformed into $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ at 72.6° . The double salt, $\text{FeCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$ (douglasite), is formed from $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and KCl at 38.3° ; it is stable up to 85° . $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and NaCl do not yield a double salt, but in presence of sodium chloride the temperature at which $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ is transformed into $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ is lowered to 69.6° .

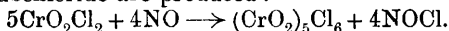
Observations with a dilatometer containing a mixture of the composition $3\text{KCl} \cdot 1\text{NaCl} \cdot 1\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ showed that rinneite is formed from its components at 26.4° . Solubility data obtained at 38° are recorded, and from these a diagram showing the relationships between rinneite and its components has been constructed. For the artificial preparation of the triple salt, a solution, obtained by dissolving 5.96 grams of sodium chloride, 20.9 grams of potassium chloride, and 123.4 grams of ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) in 55.4 grams of water, should be isothermally evaporated at 38° with the addition of a crystal of rinneite.

H. M. D.

The Hydrosol of Chromium Oxide. H. W. WOODSTRA (*Chem. Weekblad*, 1909, 6, 375—377 *).—The author has prepared a hydrosol of chromium oxide by precipitating the nitrate with potassium hydroxide, dissolving the precipitated oxide in acetic acid, evaporating to dryness, and dialysing. The colloidal solution is reddish-brown by transmitted light, and green by reflected light. It is quite different from that described by Biltz (*Abstr.*, 1903, ii, 153).

A. J. W.

Chromyl Subchloride. P. PASCAL (*Compt. rend.*, 1909, 148, 1463—1465).—When pure dry nitric oxide is passed into chromyl chloride, which is kept cool in a bath of water, nitrosyl chloride and a new chromyl subchloride are produced:



The liquid chromyl chloride is transformed with development of heat into a crystalline paste, which, when the remaining chromyl chloride is removed in a vacuum at 100° , yields chromyl subchloride as a brown, crystalline powder of density 2.51. Carbon monoxide aided by sunlight can effect the same reduction as nitric oxide.

Chromyl subchloride, unlike chromyl chloride, is strongly magnetic, so that the functions of chromium in chromyl, CrO'_2 , and in the compound radicle, $(\text{CrO}_2)'_5$, appear to be different. In fact, chlorine, which only acts above 150° , converts the subchloride back to chromyl chloride but very slowly.

Chromyl subchloride is deliquescent, and readily dissolves in water to a dark brown solution with an odour of chlorine and the reactions of chromium salts, chromic acid, and hydrochloric acid. If slowly heated to 150° , chromyl chloride is evolved, and if quickly heated, chlorine only, the solid product in both cases being Thorpe's chloride, $(\text{ClO}_2)_3\text{Cl}_2$. Above 180° oxygen is evolved, leaving an insoluble

* and *Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 33.

brownish-black residue of $\text{Cr}_6\text{O}_9\text{Cl}_4$. Towards hydrogen, hydrogen sulphide, etc., chromyl subchloride acts as a chlorinating agent at low temperatures, whilst above 200° its action is generally an oxidising as well as chlorinating one. Moist gaseous ammonia acts very violently, the products being ammonium chloride, oxygen, and the oxides CrO_2 and Cr_2O_3 . Generally speaking, however, chromyl subchloride is less reactive than chromyl chloride.

When chromyl subchloride is suspended in dry ether, and a current of slightly moist ammonia is passed through, nitrogen is evolved, and ammonium chloride and a brown, amorphous precipitate remain. Ammonium chromate and chromium chromate are removed from the precipitate by washing, and the pale brown, insoluble residue when dried at 90° has the composition $(\text{CrO}_2)_5(\text{NH}_4\text{O})_6$. This compound is explosive.

R. J. C.

Complex Tungstates : Borotungstates and Metatungstates.

HIPPOLYTE COPAUX (*Ann. Chim. Phys.*, 1909, [viii], 17, 217—267).—A résumé of work already published (compare this vol., ii, 148, 318). G. S.

Oxides of Uranium. WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1909, 148, 1462).—Uranic sulphate solution, when treated with an equivalent of barium nitrate, filtered, and evaporated almost to dryness on the water-bath, yields a mixture of the hydroxide, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ (pale yellow) with a little $\text{UO}_3 \cdot \text{H}_2\text{O}$ (orange-yellow), but not uranic nitrate. The two hydrates can be separated by hand. A mixture of uranous and uranic sulphates similarly treated gives a mixture of hydroxides, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{UO}_2 \cdot \text{H}_2\text{O}$ (reddish-brown). The latter is in a form spontaneously oxidisable by air to the orange-yellow hydroxide, $\text{UO}_3 \cdot \text{H}_2\text{O}$.

R. J. C.

Anhydrous Compounds of Thorium Chloride with Alkali Chlorides. EDUARD CHAUVENET (*Compt. rend.*, 1909, 148, 1267—1270).—Although hydrated compounds of thorium chloride (ThCl_4) with potassium, ammonium, and caesium chlorides are known, they invariably yield oxychlorides on attempting to remove the water by heat. The author prepares anhydrous double chlorides by fusing anhydrous thorium chloride and alkali chloride together in the exact proportions. The heat of solution of the mass in water, where differing from the total heat of solution of its constituents, is held to indicate the formation of a compound. The following were prepared: $\text{ThCl}_4 \cdot 2\text{LiCl}$ (heat of formation, 4.67 Cal.); $\text{ThCl}_4 \cdot 2\text{NaCl}$ (4.3 Cal.); $\text{ThCl}_4 \cdot 2\text{KCl}$ (9.14 Cal.); $\text{ThCl}_4 \cdot 2\text{RbCl}$ (19.3 Cal.); $\text{ThCl}_4 \cdot 2\text{CsCl}$ (14.9 Cal.); $\text{ThCl}_4 \cdot 4\text{RbCl}$ (26.3 Cal.); $\text{ThCl}_4 \cdot 4\text{CsCl}$ (18.11 Cal.); $\text{ThCl}_4 \cdot \text{NH}_4\text{Cl}$ (13.12 Cal.). These appear to be all the possible anhydrous compounds of thorium chloride with alkali chlorides.

The compound $\text{ThCl}_4 \cdot \text{NH}_4\text{Cl}$ is not prepared by fusion as the others are, but by heating the hydrate $\text{ThCl}_4 \cdot 2\text{NH}_4\text{Cl} \cdot 10\text{H}_2\text{O}$ at 150° , when water and ammonium chloride are given off. At 500° the remaining molecule of ammonium chloride is also lost; thus it is possible to dehydrate thorium chloride, like magnesium chloride, through the intermediation of its ammonium chloride compound.

R. J. C.

Hydrated Compounds of Thorium Chloride with Alkali Chlorides. EDUARD CHAUVENET (*Compt. rend.*, 1909, 148, 1519—1522. Compare preceding abstract).—The following compounds have been prepared by evaporating solutions of thorium chloride with three equivalents of alkali chloride: $\text{ThCl}_4 \cdot \text{LiCl} \cdot 8\text{H}_2\text{O}$; $\text{ThCl}_4 \cdot \text{NaCl} \cdot 10\text{H}_2\text{O}$; $\text{ThCl}_4 \cdot \text{KCl} \cdot 9\text{H}_2\text{O}$; $\text{ThCl}_4 \cdot 2\text{RbCl} \cdot 9\text{H}_2\text{O}$; $\text{ThCl}_4 \cdot 2\text{CsCl} \cdot 8\text{H}_2\text{O}$;

$\text{ThCl}_4 \cdot 2\text{NH}_4\text{Cl} \cdot 10\text{H}_2\text{O}$. Since the anhydrous compounds of Li, Rb, and Cs are known, it is possible to determine the heats of addition of each molecule of solid water to the hydrate. These are 3.27, 1.55, and 2.30 Cal. respectively. The heat of hydration in the case of KCl and NaCl compounds is estimated from thermal data for the known compounds $\text{ThCl}_4 \cdot 2\text{NaCl}$ and $\text{ThCl}_4 \cdot 2\text{KCl}$ to be of the same order as that of the lithium compound.

On heating these hydrates in a current of dry hydrogen chloride at 150° , the rubidium and caesium compounds with low heats of hydration are dehydrated, whereas the lithium, sodium, and potassium compounds are converted into anhydrous oxychlorides of the type $\text{ThOCl}_3 \cdot \text{MCl}$.

$\text{ThCl}_4 \cdot \text{LiCl} \cdot 8\text{H}_2\text{O}$ at 200° gives $\text{ThOCl}_3 \cdot \text{LiCl}$, which at 400° yields $\text{ThOCl}_3 \cdot \text{LiCl}$. At 800° thorium tetrachloride and lithium chloride volatilise, leaving a residue of thorium dioxide.

The metallic thorium of Berzelius and Nilson was doubtless contaminated with thorium oxide, as it was prepared from the chloride, $\text{ThCl}_4 \cdot \text{KCl} \cdot 9\text{H}_2\text{O}$. The same applies to the metallic thorium of Moissan, as the mixture he employed (ThCl_4 , MCl , and M) is hygroscopic. It should, however, be possible to prepare pure thorium from its double chloride with rubidium or caesium.

R. J. C.

Fusibility of Mixtures of Gold and Tellurium. HENRI PÉLABON (*Compt. rend.*, 1909, 148, 1176—1177).—On heating a mixture of gold and tellurium in a vacuum sealed tube, the gold readily dissolves in the tellurium as soon as the melting point of the latter element has been attained. If the proportion of gold is more than 60%, it is necessary to raise the temperature above the melting point of tellurium in order to dissolve the metal, and the mixtures become more and more pasty as the percentage of gold increases.

The fusion curve of such mixtures consists of a rectilinear portion extending from the melting point of tellurium (452°) to the eutectic temperature, 415° (16.5% Au). It then rises to a maximum at 472° , corresponding with 41—45% Au, namely, with the compound Au_2Te_4 , which occurs naturally as calaverite. Mixtures containing more than 56% Au always show only one arrest at 452° , the melting point of tellurium; they are pasty masses, which solidify to heterogeneous solids in which gold and tellurium can be readily distinguished. The fusion curve gives no evidence of the existence of a compound Au_2Te .

T. S. P.

Melting Point of Platinum. CHARLES W. WADNER and GEORGE H. BURGESS (*Compt. rend.*, 1909, 148, 1177—1179).—The authors (*Abstr.*, 1907, ii, 882) have previously found temperatures varying from 1706° to 1753° for the melting point of platinum, and Féry

and Chéneveau (Abstr., 1909, ii, 321) have attributed the discrepancies to the influence of the gaseous atmosphere in which the platinum was melted, since they found that the temperature, as measured by the optical pyrometer, varied as much as 30° to 50°, according as the metal was melted in the electric furnace or by means of a flame. The authors do not agree with this explanation, and incline to the view that the discrepancies are due to the fact that the constant C_2 in Wien's equation: $I = C_1 \lambda^{-5} e^{-C_2/\lambda\theta}$ is not known with sufficient accuracy. They also point out that, although the empirical equation: $E = -a + bt + ct^2$, which is used to calibrate a platinum-platinum-iridium thermocouple, holds between 300° and 1100°, there is no proof that it holds up to 1800°, that is, for an extrapolation of 700°. T. S. P.

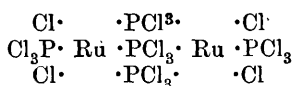
Atomic Weight of Palladium. Part II. The Analysis of Palladosammine Bromide. ALEXANDER GUTBIER, P. HAAS, and H. GEBHARDT (*J. pr. Chem.*, 1909, [ii], 79, 457—474).—Pure palladium was dissolved in a mixture of hydrobromic and nitric acids. The latter acid was expelled by repeated evaporation with hydrobromic acid, the residue dissolved in a small quantity of hydrobromic acid, and filtered into excess of ammonium hydroxide. A brown precipitate of the salt $\text{Pd}(\text{NH}_3)_4\text{Br}_2 \cdot \text{PdBr}_2$ was produced, but on prolonged digestion with ammonium hydroxide it dissolved, with the formation of palladosammine bromide, $\text{Pd}(\text{NH}_3)_2\text{Br}_2$. The solution was filtered into excess of hydrobromic acid, whereby the palladosammine bromide was obtained as a yellow, finely crystalline precipitate. The precipitate was washed free from ammonium bromide, again dissolved in ammonium hydroxide, and precipitated with hydrobromic acid, the process being repeated three times. The pure bromide thus obtained was dried at 105—110° to constant weight.

The percentage of palladium in the salt was determined by reducing it with hydrogen, and heating the hydrogenised metal so obtained to a temperature of 150° in a current of dry carbon dioxide in order to obtain the pure metal (this vol., ii, 407). Two different sets of experiments were carried out, the materials used in each set being of different origin. As a result of the first set of nine experiments it was found that 18.76375 grams of palladosammine bromide contained 6.65983 grams of palladium; in the second set of nine experiments, 21.56275 grams of palladosammine bromide gave 7.65308 grams of palladium. The mean result of these experiments gives 106.689 as the atomic weight of palladium, whereas the atomic weight deduced from experiments on palladosammine chloride (Abstr., 1909, ii, 407), after being corrected for the alteration of the atomic weight of chlorine from 35.45 to 35.46, gave the number 106.655. T. S. P.

The Action of Phosphorus Haloids on Platinum Metals. WILHELM STRECKER and M. SCHURIGIN (*Ber.*, 1909, 42, 1767—1776).—Geisenheimer (*Ann. Chim. Phys.*, 1891, [vi], 23, 231) states that phosphorus pentachloride has practically no action on metallic iridium, but the present authors find that when spongy iridium is heated with phosphorus pentachloride for five to six hours at 300—350° an unstable compound is produced, which cannot be isolated, and also a

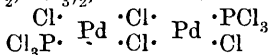
second compound, which is best obtained by adding some phosphorus trichloride to the reaction product and heating for five hours more at 250°. This substance, *tripphosphorus trichloride iridochloride*, $\text{IrCl}_3 \cdot 3\text{PCl}_3$, crystallises from chloroform in aggregates of white needles, and decomposes without melting at 230°. Using phosphorus pentabromide and tribromide in place of the corresponding chloro-derivatives, the authors obtained *tripphosphorus tribromide iridobromide*, $\text{IrBr}_3 \cdot 3\text{PBr}_3$, in the form of stable, ruby-red crystals; a substance of the same composition prepared by Geisenheimer (Abstr., 1891, 1383) is described by him as forming unstable, reddish-brown crystals which fume in the air.

Using ruthenium sponge in place of iridium, *tetrachlorodiruthenium pentaphosphorus trichloride*, $\text{Ru}_2\text{Cl}_{19}\text{P}_5$, was obtained, which separates from chloroform in dark reddish-yellow crystals. The composition of this substance may be expressed in accordance with Werner's theory by the annexed formula.



from chloroform in dark reddish-yellow crystals. The composition of this substance may be expressed in accordance with Werner's theory by the annexed formula.

The corresponding *tetrabromodiruthenium pentaphosphorus tribromide*, $\text{Ru}_2\text{Br}_{19}\text{P}_5$, was also prepared, but could not be obtained quite free from metal, owing to its insolubility. The phosphorus trichloride palladochloride, previously described by Fink (Abstr., 1892, 1285) as having the formula $\text{PdCl}_2 \cdot \text{PCl}_3$, is shown by a molecular-weight determination in chloroform solution to have the double formula $(\text{PdCl}_2 \cdot \text{PCl}_3)_2$, and its constitution may, therefore, be expressed as follows:



The corresponding *phosphorus tribromide palladobromide*, $(\text{PdBr}_2 \cdot \text{PBr}_3)_2$, forms reddish-brown, deliquescent crystals. No analogous compounds could be obtained from the metals rhodium and osmium. P. H.

Mineralogical Chemistry.

Optical Activity of Mineral Oils in an Optically Transparent State. MICHAEL A. RAKUSIN (*Ber.*, 1909, 42, 1640—1647. Compare Abstr., 1904, i, 641).—The majority of mineral oils when distilled yield dextrorotatory derivatives, a few give inactive distillates, and two from Java and Borneo give feebly lævorotatory distillates. The question arises whether the crude oils themselves possess activity, and if so, what is the magnitude and sense. The author finds that crude mineral oils from Binagady and Bibi-Eybat, after being clarified by fuller's earth, are dextrorotatory, and the rotation increases with the density.

Mineral oils do not racemise when distilled, and the active constituents are concentrated in the less volatile fractions. The sign of the rotation is unchanged by distillation. C. S.

Optical Investigation of Bibi-Eybat Naphtha. MICHAEL A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 483—500. Compare Abstr., 1907, ii, 883; 1908, ii, 115).—The percentage yields obtained

within similar limits of temperature during the fractional distillation of corresponding naphthas are inversely proportional to the densities and, consequently, also to the depths of the layers.

Natural naphthas are dextrorotatory, the amount of the rotation increasing with the density, and hence with the depth of the layer.

The questions of racemisation, carbonisation, and influence of high temperatures on the decomposition of naphtha are discussed, together with the influence of the earth's magnetism on the rotation of natural naphtha and the content of paraffins in a naphtha as a criterion of its geological age.

T. H. P.

Composition of Bauxite. H. ARSANDAUX (*Compt. rend.*, 1909, 148, 1115—1118. Compare this vol., ii, 490).—The author has made complete analyses of sixteen French bauxites containing different proportions of silica in order to determine the nature of the silicate in them. Bauxite is mainly insoluble in concentrated hydrochloric acid, but all the iron and a variable proportion of the alumina are dissolved. Traces of titanium and silica are also found in the solution. The insoluble portion consists mainly of alumina, water, silica, and titanium oxide. If the silica which cannot be boiled out with sodium carbonate solution is supposed to be all combined in the form of kaolinite ($H_4Al_2Si_2O_9$), the remaining water is slightly in excess of the ratio $H_2O : (Al_2O_3 + TiO_2)$. In two samples, however, the ratio is nearer $2H_2O : Al_2O_3$. It is supposed that in presence of silica, alumina may form a higher hydrate than $Al_2O_3 \cdot H_2O$.

R. J. C.

Constitution and Genesis of Natural Ferric Sulphates. VII. Ihleite, Janosite, Copiapite. RUDOLF SCHARIZER (*Zeitsch. Kryst. Min.*, 1909, 46, 427—453. Compare Abstr., 1907, ii, 482).—The mineral janosite ($Fe_2(SO_4)_3 \cdot 9H_2O$), recently described by H. Böckh and K. Emszt (Abstr., 1905, ii, 536) has been asserted by E. Weinschenk and by Z. Toborffy (Abstr., 1907, ii, 629) to be identical with copiapite. The present author had previously suggested (Abstr., 1907, ii, 482) that material having this composition consists of a mixture of copiapite ($Fe_4S_5O_{21} \cdot 18H_2O$) and ferric tetrasulphate ($Fe_2S_4O_{15} \cdot 9H_2O$), and new experiments support this conclusion. It also appears that a compound having the composition given for ihleite has no existence.

Ordinary copiapite ($Fe_4S_5O_{21} \cdot 18H_2O$ or $[HO]_2Fe_4[SO_4]_5 \cdot 17H_2O$) is called α -copiapite to distinguish it from a similar substance with the composition $(HO)Fe_3(SO_4)_4 \cdot 13H_2O$; the latter is called β -copiapite, and is probably identical with Rammelsberg's misy. The various ferric sulphates are differently soluble in alcohol, and they can be purified with the help of this. Experiments with acetone suggest that even concentrated solutions are hydrolytically dissociated into various components.

L. J. S.

Adamite from Monte Valerio, Tuscany. PIERO ALOISI (*Zeitsch. Kryst. Min.*, 1909, 46, 478—479; from *Proc. verb. Soc. Toscana Sci. Nat.*, 1907, 17, 4—9).—Cavities in a specimen of zinciferous limonite contained brilliant sulphur-yellow crystals of adamite. These are

orthorhombic, with $a : b : c = 0.9736 : 1 : 0.7013$. The following analysis closely agrees with the usual formula, $\text{Zn}(\text{ZnOH})\text{AsO}_4$.

As_2O_5 .	ZnO .	Fe.	H_2O .
40.75	55.79	trace	[3.46]

L. J. S.

Does Thorium Exist as Thorium Silicate in Monazite?
O. KRESS and FLOYD J. METZGER (*J. Amer. Chem. Soc.*, 1909, 31, 640—652).—Some authorities state that thorium is present in monazite as a silicate, either as orangite or thorite, whilst others claim that it is present as a phosphate, either replacing a part of the cerium earths or being present as a normal phosphate; still others claim that it is present both as phosphate and silicate.

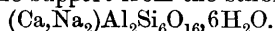
The authors have analysed a number of different specimens of monazite, determining in each case the percentages of thorium, total silica, quartz, and of silicate silica. In no case was silica absent; the percentage generally increased with an increase in thorium content, but it did not do so invariably. Out of fifty analyses in which the silicate silica was separately determined, forty-five showed insufficient silica to combine with the thorium to form thorium silicate. Thirty-nine analyses showed insufficient total silica to combine with the thorium found. Out of a total of sixty-four analyses, fifty-five indicate that the thorium is not present as a silicate.

A microscopic examination was also made of monazite, and, for the sake of comparison, of thorite. The optical characteristics of the silicate present in monazite were quite different from those of thorite, and indicated that the silicate is probably a feldspar.

The microscopic and chemical investigations thus both lead to the same conclusion, namely, that thorium is not present in monazite in the form of thorium silicate.

T. S. P.

Calcium in Potash-feldspar, and the Formation of Myrmekite.
ARTHUR SCHWANTKE (*Centr. Min.*, 1909, 311—316).—The small amount of calcium (1—2% CaO) frequently present in orthoclase has usually been assumed to be due to the isomorphous intermixture of the anorthite molecule, $\text{CaAl}_2\text{Si}_2\text{O}_8$, with the orthoclase molecule, $\text{K}_2\text{Al}_2\text{Si}_6\text{O}_{16}$. Some of the published analyses agree with this supposition, whilst others are better explained by the assumption that the hypothetical molecule, $\text{CaAl}_2\text{Si}_6\text{O}_{16}$, is present. The existence of such a molecule receives some support from the stilbite formula:



Again, the existence of the intimate intergrowth of plagioclase and quartz, known as myrmekite (which has probably been derived from the alteration of orthoclase), suggests that there may have been a change from $\text{CaAl}_2\text{Si}_6\text{O}_{16}$ to $\text{CaAl}_2\text{Si}_2\text{O}_8$ with a separation of free silica.

L. J. S.

[A Mineral Associated with Turquoise in New Mexico.]
E. R. ZALINSKI (*Zeitsch. Kryst. Min.*, 1909, 46, 388; from *Economic Geol.*, 1907, 2, 464—492).—An account is given of the occurrence of

turquoise in the Burro Mountains, New Mexico. It occurs in decomposed granite, and is associated with kaolinite, quartz, halloysite, and a pale greenish-yellow mineral of doubtful nature. The following analysis, by K. Adams, indicates that the last is related to halloysite.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	P ₂ O ₅ .	TiO ₂ .	Cu.	Total.
42.59	19.70	2.46	0.06	0.63	2.71	0.53	0.20	25.36	0.89	0.11	3.89	99.13

L. J. S.

Constitution of Zeolites. ENNIO BASCHIERI (*Zeitsch. Kryst. Min.*, 1909, **46**, 479—480; from *Proc. verb. Soc. Toscana Sci. Nat.*, 1907, **16**, 34—42).—Tschemmak's method (Abstr., 1907, ii, 771) of isolating silicic acids is extended. Natrolite (the so-called savite) from Montecatini, Tuscany, gave a silica jelly, the composition of which at the first alteration point is SiO₂ 62.32, H₂O 37.68, corresponding with orthosilicic acid. Natrolite is therefore considered to be an orthosilicate with water of constitution, the formula being H₄Na₂Al₂(SiO₄)₃.

Laumontite ("caporcianite") from the same locality has the following composition, agreeing with the formula, CaAl₂Si₄O₁₄·4H₂O, of fresh laumontite (and thus disproving the idea that caporcianite is a partly dehydrated laumontite).

SiO ₂ .	Al ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
50.10	21.50	12.02	1.17	0.20	15.06	100.05

The silica jelly obtained from this mineral is also orthosilicic acid, and the formula of laumontite is therefore written as H₈CaAl₂(SiO₄)₄.

L. J. S.

Constitution of Ilvaite. ENNIO BASCHIERI (*Zeitsch. Kryst. Min.*, 1909, **46**, 480; from *Proc. verb. Soc. Toscana Sci. Nat.*, 1907, **16**, 49—52).—Ilvaite from Elba was also examined by Tschemmak's method. The silicic acid obtained contained 30.67 H₂O, corresponding with diorthosilicic acid, H₆Si₂O₇. The formula of ilvaite is therefore written as [FeO]₂Fe₂[FeOH]₂[Si₂O₇]₂.

L. J. S.

A Nephelinic Syenite with Sodalite from the Transvaal. H. A. BROUWER (*Compt. rend.*, 1909, **148**, 1274—1277).—The mineral contains:

SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O	Cl ₂ .	Total.
48.35	0.45	23.10	2.48	2.51	0.89	13.20	3.58	2.91	1.49	100.85

In the cooling of the rock, syenite appears to have separated first, followed by ægyrine, felspar, and nepheline. The rock is very similar mineralogically and chemically to one from Greenland and one from Tavajokthai described by Rosenbusch and Ramsay respectively.

R. J. C.

[Garnet from Idaho.] JAMES FURMAN KEMP and C. G. GUNTHER (*Zeitsch. Kryst. Min.*, 1909, **46**, 389; from *Trans. Amer. Inst. Min. Engin.*, 1907, **38**, 269—296).—A garnet-rock occurs in association with copper ores at the contact of limestone with quartz-porphry

near Mackay in Idaho. Analysis I is of pale amber-yellow material, and II, of massive garnet :

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	H ₂ O.	Total.
I.	37·07	17·42	10·81	0·68	—	32·77	0·51	0·53	99·79
II.	37·79	11·97	15·77	1·31	0·31	32·57	0·37	—	100·18

L. J. S.

Sanidine from the Leilenkopf, Lake Laach. RHEINHARD BRAUNS (*Jahrb. Min.*, 1909, i, 43—57).—A description is given of the sanidine bombs found in volcanic tuff at the Leilenkopf near Niederlützingen. Analysis by M. Lubinski gave :

SiO ₂ .	Al ₂ O ₃ .	BaO.	Na ₂ O.	K ₂ O.	Fe.	Total.	Sp. gr.
63·89	20·66	0·94	2·22	12·60	trace	100·31	2·57

L. J. S.

Fused Mixtures of Oligoclase with Enstatite and Augite. MARG. SCHMIDT (*Jahrb. Min. Beil.-Bd.*, 1909, 27, 604—641. Compare Doelter, Abstr., 1906, ii, 665).—Mixtures of oligoclase and enstatite and of oligoclase and augite in various proportions (every 10%) were fused, and determinations made of the intervals of the melting points of the quickly-cooled glassy material and of the slowly-cooled crystalline product, and also of the temperature during the interval of crystallisation. The results are plotted on curves, and the microscopic structure of the crystalline products is described.

L. J. S.

Laterite from Brazil. ALBERT ATTERBERG (*Centr. Min.*, 1909, 361—366).—Three samples of laterite from the neighbourhood of Rio de Janeiro were examined : I, from Santa Teresa ; II, from Corcovado, and III, from Serra de Itatiaya. The material from the first two localities has been derived by the weathering of gneiss, whilst that from the third locality owes its origin to nepheline-syenite. A preliminary sieving of the material separated 38·2, 37·5, and 8·0% respectively of gravel and coarse sand. The finer material was then digested with hydrochloric acid, and afterwards with sodium hydroxide ; the soluble portions gave the results under Ia, IIa, IIIa respectively (calculated to 100% of the laterite). The insoluble residue was then separated by sedimentation in water into a finer clayey portion (16·7, 12·4, and 29·8%), coarser clay, and a fine sandy portion. The finer clayey portions gave on analysis the results under Ib, IIb, IIIb ; and the fine sandy portion of I (10·6% of the whole) gave Ic.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	Loss on ignition.	Moisture.	Total.
Ia.	6·30	—	5·91	6·68	nil	0·16	0·23	0·64	—	—	19·92
IIa.	5·00	—	7·93	6·16	0·07	0·21	0·06	0·08	—	—	19·51
IIIa.	1·54	—	11·92	4·51	nil	0·02	0·33	0·04	—	—	18·36
Ib.	[39·44]	3·68	36·18*	—	„	0·20	0·60	0·50	15·00	4·40	100·00
IIb.	[40·87]	3·03	37·93*	—	„	trace	0·79	0·88	13·60	2·90	100·00
IIIb.	[42·61]	3·64	36·61*	—	„	0·12	0·40	0·30	14·30	2·02	100·00
Ic.	[39·87]	5·60	33·50	1·71	trace	0·27	2·80	0·91	13·01	2·33	100·00

* Including a little Fe₂O₃.

From these analyses it will be seen that, besides quartz and iron hydroxide, the material consists largely of kaolin (or of the soluble form nacrite), and that only in III is there any appreciable amount (21%) of hydrargillite. It thus appears that while some laterites consist largely of hydrargillite, others consist largely of kaolin.

L. J. S.

French Sub-alpine Tertiary Basalts. ALBERT M. LEVY (*Compt. rend.*, 1909, 148, 1528—1531).—The degree of acidity of an igneous rock is represented by the symbol $\phi = S/(2K + 3Na)$, where, S , K , and Na are the percentages of silica, potassium, and sodium in the colourless constituents of the rock. In neutral rocks, where $\phi = 1.9$, albite and orthoclase predominate. When ϕ is less than 1.9, the rock is of the eleolitic or leucite (basic) type; when ϕ is greater than 1.9, the rock is of the acidic granite, syenite, or tonalite type. Most French tertiary and quaternary rocks are of the acidic type ($\phi > 1.9$), but towards the east in sub-alpine districts, as well as in Germany and Bohemia, the rocks with but few exceptions are neutral or basic. The French nephelinitic basalts analysed by the author are distinctly basic. The general classification of igneous rocks into Atlantic (basic) and Pacific (acidic) types according to chemical and geographical characteristics appears to be invalidated by numerous exceptions.

R. J. C.

Rocks from the Eastern Border of the Armorican Massif. L. VANDERNOTTE (*Compt. rend.*, 1909, 148, 1202—1205).—A description is given of the different rock types met with in the Massif of Ernée, near Laval (dep. Mayenne). Analyses are given of: I, normal gabbro; II, olivine-gabbro; III, gabbro-norite.

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O	Total
I.	51.30	0.32	18.20	1.28	5.10	9.35	12.79	1.80	0.25	0.31	100.70
II.	48.70	1.18	17.95	0.76	6.48	8.20	13.36	1.90	0.47	0.70	99.70
III.	53.50	1.63	15.01	—	9.45	7.05	10.30	2.50	0.52	0.50	100.46

L. J. S.

Meteorites of Cañon Diablo. GEORGE P. MERRILL and WIRT TASSIN (*Zeitsch. Kryst. Min.*, 1909, 46, 386; from *Smithsonian Miscell. Collections*, 1907, 50, 203—214).—Meteorites of a new type from Cañon Diablo consist of a nucleus of iron surrounded by iron shale. The former contains schreibersite (anal. I and II), cohenite (III), some kamacite, taenite (IV), and a small amount of olivine (V):

	Fe.	Ni.	Co.	Cu.	P.	C.
I.	63.04	23.07	0.03	—	13.80	—
II.	58.54	26.08	0.05	trace	15.37	—
III.	91.29	2.48	0.10	—	0.01	5.96
IV.	72.16	27.75	0.02	—	0.04	0.12
	SiO ₂	MgO.	FeO.	NiO.		
V.	41.51	52.70	5.89	0.29		

L. J. S.

The Supposed Meteorite ("Leucite-uranolith") of Schafstätt, near Merseburg. MAX BELOWSKY (*Centr. Min.*, 1909, 289—293).—This supposed meteoric stone described by C. Klein (*Abstr.*, 1904, ii, 351) as the representative of a new "leucite-uranolith" group of meteorites, and unique (amongst meteorites) in containing leucite, is nothing more than a piece of leucite-basanite lava from Vesuvius.

L. J. S.

Physiological Chemistry.

An Apparatus for Studying the Respiratory Exchange.

FRANCIS G. BENEDICT (*Amer. J. Physiol.*, 1909, 24, 345—374).—The apparatus used in the respiration calorimeter is modified for use in a movable form of apparatus. The same main principles are employed, and the apparatus was found to give good results. It is described in full with drawings and diagrams.

W. D. H.

Cheyne-Stokes Breathing. Regulation of Breathing. C.

GORDON DOUGLAS and JOHN S. HALDANE (*J. Physiol.*, 1909, 38, 401—419, 420—440).—Periodic or Cheyne-Stokes breathing can be easily produced in normal people, and comes on after the apnoea which follows forced breathing. It is produced by the periodic occurrence and disappearance of the indirect excitatory effects of want of oxygen on the respiratory centre. The want of oxygen may be due to abnormal deficiency in the alveolar oxygen pressure, or to the effects on the circulation of changes in the breathing, or to both causes.

The second paper is a discussion of the part played by various chemical factors in the regulation of normal breathing. It is shown that the respiratory centre acts smoothly, because some time is needed for it to become saturated or desaturated to the carbon dioxide capacity of the circulating blood. But for this, the centre would undoubtedly "hunt" like the governor of an engine without a fly-wheel. When the excitation of the centre depends partly or wholly on want of oxygen, this fly-wheel action is absent, and periodic breathing is the result.

W. D. H.

Blood-coagulation. P. MORAWITZ (*Biochem. Zeitsch.*, 1909, 18, 30—33).—Polemical against Mellanby (compare this vol., ii, 158).

W. D. H.

Oxidative Processes in the Blood. P. MORAWITZ (*Arch. exp. Path. Pharm.*, 1909, 60, 298—311).—*In vitro*, the blood of rabbits suffering from sub-chronic experimental anæmia uses up oxygen and gives rise to carbon dioxide, especially at body temperature. This appears to be related to the formed elements, and the question whether it is specially connected with the regenerative process is to be further investigated.

W. D. H.

Action of Salts of Unsaturated Fatty Acids in Hæmolysis.

BENJAMIN MOORE, FRED P. WILSON, and LANCELOT HUTCHINSON (*Proc. physiol. Soc.*, 1909, lxxiii—lxxiv; *J. Physiol.*, 38).—Bile salts dissolve free fatty acids, soaps, lecithin, and cholesterol at body temperature. The solubility of saturated fatty acids and soaps is increased by the presence of oleic acid or oleates. Lecithin also increases the solubility of soaps and cholesterol. Recent work on hæmolysis, and on sodium oleate as an anti-complement, gives a new aspect to these solubilities. All substances not acting as solvents which have marked hæmolytic properties (such as saponins and bile salts) are all unsaturated with doubly linked carbon atoms. Sodium stearate and palmitate have no laking power, but sodium erucate, oleate, and linoleate have. The linoleate has the greatest number of doubly linked carbon atoms, and the strongest action on the corpuscles.

W. D. H.

Quinine and Blood-pigment. LOUIS LEWIN (*Arch. exp. Path.*

Pharm., 1909, 60, 325—327).—The brown pigment which has been described as the specific result of the action of quinine on the blood is merely methæmoglobin, the spontaneous formation of which in the blood, especially in old blood, is somewhat hastened by the presence of quinine and certain other alkaloids (morphine and cocaine).

W. D. H.

Vasodilatin. The Active Substance of Extracts of All Parts of the Digestive Canal, Brain, Pancreas, and Peptone.

LEO POPIELSKI and K. PANEK (*Pflüger's Archiv*, 1909, 128, 222—225).—Vasodilatin is the name given to a substance in extracts of the alimentary canal, brain, pancreas, and Witte's peptone, which is believed to produce the lowering of blood-pressure. It is not precipitated by lead acetate, but it is precipitated by phosphotungstic acid. It is soluble in absolute alcohol; it is not choline or any other alkaloid; it is not a protein. Its identification is uncertain.

W. D. H.

Digestion in the Animal Body. XXVIII. E. S. LONDON.

XXIX. E. S. LONDON and A. SIVRÉ. XXX. E. S. LONDON.

XXXI. E. S. LONDON and N. A. DOBROWOLSKAJA. XXXII.

E. S. LONDON and F. J. RIWOSCH-SANDBERG (*Zeitsch. physiol. Chem.*, 1909, 60, 191—193, 194—266, 267—269, 270—273, 274—283.

Compare Abstr., 1908, ii, 1050).—XXVIII deals with further variations in the poly-fistula method in dogs. XXIX works out further details concerning the digestion and absorption of fat, starch, and flesh, given either alone, in pairs, or all three at once, so as to ascertain the influence exerted on the rate of digestion and absorption of each by the other two on the lines of the author's previous researches. XXX deals with the digestion and absorption of elastin, which are much slower than for other proteins. XXXI shows that the author's laws of digestion and absorption previously worked out for protein hold good also for carbohydrates. XXXII deals with the absorption of certain amino-acids; *D*-alanine given alone is somewhat better

absorbed than when in a digested mixture; it is absorbed better than L-alanine, and also better than glycine. The amino-acids given produce a large flow of intestinal juice.

W. D. H.

The Effects of Bone Ash on Digestion and Metabolism.

ALFRED PEIRCE LOTHROP (*Amer. J. Physiol.*, 1909, 24, 297—324).—In metabolism experiments on dogs, a convenient method of separating the faeces consists in the administration of bone ash at given intervals. It is therefore necessary to determine what changes, if any, are produced by the bone ash itself. Beyond an increase in bulk, and frequency of elimination of the faeces, it was found to produce no effect on the digestive, absorptive, or metabolic processes of the body.

W. D. H.

Can Nitrogenous Equilibrium be Maintained on Diets Containing Zein or Gliadin as the only Nitrogenous Constituents? VALDEMAR HENRIQUES (*Zeitsch. physiol. Chem.*, 1909, 60, 105—118).—It has been already shown by Hopkins and Wilcock that nitrogenous equilibrium cannot be maintained on a diet containing zein, which does not yield tryptophan as a product of hydrolysis. These experiments have been extended by the author, who has also carried out similar researches with gliadin, which yields tryptophan on hydrolysis and large quantities of glutamic acid, but not lysine. Rats were employed as the subjects of the experiments, and the intake and output of nitrogen were estimated, definite quantities of the nitrogenous food being in each case added to standard diets containing carbohydrates, fats, and salts. It was found that whilst nitrogenous equilibrium cannot be maintained on a diet containing zein as the only nitrogenous component, the loss of nitrogen was appreciably less than when the diet was quite nitrogen-free. With gliadin, if given in sufficient quantity, on the other hand, not only can nitrogenous equilibrium be maintained, but a storage of nitrogen in the organism can take place.

S. B. S.

Nuclein Metabolism, and its Relationship to the Nuclein Ferments in the Human Organism.

MILTON C. WINTERNITZ and WALTER JONES (*Zeitsch. physiol. Chem.*, 1909, 60, 180—190).—Nuclease hydrolyses nucleic acid with the formation of guanine and adenine; amidases (guanase and adenase) decompose guanine and adenine, with scission of ammonia into xanthine and hypoxanthine, and lastly, xantho-oxydase oxidises hypoxanthine into xanthine and uric acid. Little is known as to the distribution of these various ferments in the human body, and their distribution was therefore investigated in the organs taken from subjects who had suffered from two widely different diseases, namely, typhus and aneurism. In both cases similar results were obtained, and these may be regarded as typical of the normal distribution. The liver and spleen were found to be incapable of changing adenine into hypoxanthine. The liver, on the other hand, can convert guanine into xanthine, and oxidise the latter substance into uric acid. The results differ from those obtained from corresponding organs of the pig.

S. B. S.

The Absorption of Purine Substances. JOH. BIBERFELD and JULIUS SCHMID (*Zeitsch. physiol. Chem.*, 1909, 60, 292—297).—The lymph of dogs and cats after feeding on milk and meat contains no purine substances; the same is true after abundant feeding on nucleic acid. The excretion of the catabolic products of nucleic acid begins early, and is completed within twenty-four hours, as the ratio between uric acid and total nitrogen in the urine shows. W. D. H.

The Origin and Destiny of Cholesterol in the Animal Organism. Part V. On the Inhibitory Action of the Sera of Rabbits Fed on Diets Containing Varying Amounts of Cholesterol on the Hæmolysis of Blood by Saponin. MARY T. FRASER and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1909, B, 81, 230—247).—Cholesterol combines with saponin and thus inhibits its hæmolytic action on blood corpuscles. The esters do not possess similar action. The anti-hæmolytic action of sera when suspensions of corpuscles are treated with saponin was therefore investigated in order to determine whether cholesterol was present in these sera taken from rabbits which had been receiving diets containing in some cases cholesterol and in others none; in these cases the quantities are too small for estimation of chemical methods. It was found that when cholesterol is in the food of rabbits, some is absorbed and finds its way into the blood-stream as free cholesterol, only a portion of the total ingested being absorbed, the rest being excreted unchanged. The amount of cholesterol which finds its way to the blood-stream is not increased by increasing the amount given in food, and the animals appear to take up only such amounts as they can utilise. When ingested in the form of esters, the latter undergo hydrolysis in part during digestion, and cholesterol appears free in the blood-stream. Phytosterol appears to act like cholesterol, in that it is absorbed, but it is not yet known whether it appears in the blood-stream as such, or is converted into cholesterol. S. B. S.

Cerebro-spinal Fluid. Nature of the Reducing Substance. Analysis of Fluid from a Hydrocephalous Case. W. MESTREZAT (*J. Pharm. Chim.*, 1909, [vi], 29, 472—481).—Analyses of cerebro-spinal fluid taken from a hydrocephalous infant during life and after death gave the following results, expressed in parts per 1000: (1) *Fluid withdrawn during life*.—Extract dried at 110°, 10.6, ash 8.2, chlorides (as NaCl) 6.95, protein 0.35, dextrose 0.48—0.51, organic matter, other than dextrose, 1.92, Δ 0.55°. The fluid was limpid, colourless, and slightly alkaline to litmus. (2) *Fluid withdrawn after death*.—Extract dried at 110°, 10.93, ash 9.00, chlorides (as NaCl) 7.66, CaO 0.087, Na₂O 4.13, K₂O 0.37, Cl 4.64, SO₃ 0.080, P₂O₅ 0.012, carbonic acid and organic acids (expressed as lactic acid) 2.09, protein 0.17, organic matter 1.93, water 989.07, Δ 0.60°. There were also traces of dextrose, iron, nitrates, and nitrites (due to reduction of nitrates) present, but no albumoses, peptones, amylase, urea, or uric acid could be detected. The fluid was limpid and slightly alkaline to litmus.

Both specimens were normal in their content of mineral matter, although the "dry extract" was a little low, and also the lime and phosphoric oxide, as is generally found in hydrocephalous cases. The protein consisted of a mixture of serin and globulin. Dextrose was identified by the preparation of its phenylosazone. The conflict of opinion as to whether the reducing power of cerebro-spinal fluid is due to dextrose or to some other substance is explained by the observation that these specimens contained dextrose and a second reducing substance, which is precipitated in the defecation of the fluid by mercuric nitrate. This substance does not appear to be catechol, since it gives no coloration with ferric chloride, but it may be glycuronic acid or a derivative of this. It does not always occur in cerebro-spinal fluid, but is usually found when there is little dextrose present. The original contains numerous references to previous work on this and associated subjects.

T. A. H.

Lecithins and Cholesterols Contained in the Sperma and Ovary of Tunny Fish. SERAFINO DEZANI (*Giorn. R. Accad. Med. Torino*, 1909, 15).—The lecithin extracted by alcohol from the testicles and ovary had practically the same composition, and yielded 30—33% of oleic acid and 67—70% of palmitic and stearic acids. Ethereal extracts yielded lecithins containing much more oleic acid (45 and 48% respectively).

Cholesterol from sperma gave results agreeing with the formula $C_{27}H_{44}O.H_2O$, and has the properties of cholesterol obtained from other animals; m. p. 138—145°. The substance obtained from the ovary has the same composition, but gives no coloration with sulphuric acid. When treated with chloroform and sulphuric acid, a coloration appears in about an hour, and in twelve hours the chloroform layer has a reddish-violet colour, whilst the sulphuric acid shows a green fluorescence. M. p. 100—104°. It is doubtful whether the substance is a distinct compound, or whether its different behaviour is due to impurities.

N. H. J. M.

Action of Salts on Autolysis. LUIGI PRETI (*Zeitsch. physiol. Chem.*, 1909, 60, 317—340).—Ferric chloride, sulphate, and oxalate, manganese chloride, sulphate, and lactate, aluminium chloride and sulphate, and cobalt nitrate added to the liver in small quantities during autolysis increase the amount of non-coagulable nitrogen; this increase is progressive as more salt is added. Manganese acetate and cobalt chloride act in the same way at first, until the amount of salt reaches a certain height, beyond which they produce the opposite result. Platinum chloride beyond a certain point gives variable results. Sodium chloride and sulphate and copper sulphate at first produce no effect, but beyond a certain concentration lessen the non-coagulable nitrogen. Palladium chloride, calcium chloride, barium chloride, and strontium chloride and bromide have no effect. Cadmium chloride, nickel chloride and nitrate, magnesium chloride, and zinc sulphate lessen the non-coagulable nitrogen; this, however, occurs before it can affect the autolytic process.

W. D. H.

Influence of Narcotics of the Fatty Series on Autolysis. RICHARD CHIARI (*Arch. exp. Path. Pharm.*, 1909, 60, 256—264).—Narcotics at first accelerate autolysis, because they dissolve lipoids and so allow free entry of the enzymes to the protoplasm of cells.

W. D. H.

The Fat of the Liver, Kidney, and Heart. II. PERCIVAL HARTLEY (*J. Physiol.*, 1909, 38, 353—374).—The following higher fatty acids are present in the liver: palmitic, stearic, oleic, linoleic, and one with the formula $C_{20}H_{32}O_2$. The double linking in liver-oleic acid lies between the sixth and seventh carbon atoms reckoning from the methyl-group end of the chain, whereas that from adipose tissue is exactly in the middle of the chain. Some evidence was obtained of the presence of two linoleic acids in the liver. The occurrence of the acid $C_{20}H_{32}O_2$ is shown by the formation of octabromoarachidic acid on bromination, and of its hydroxy-derivative on oxidation. The unsaturated acids account for approximately one-half of the acids present. The acid $C_{20}H_{32}O_2$ occurs to the extent of about 10% of the total fatty acids, and linoleic is more abundant than oleic acid. The high iodine value and the ease with which atmospheric oxygen is taken up are due to the presence of linoleic acid and the acid $C_{20}H_{32}O_2$. The unsaturated acids are present to a large extent in lecithin and similar substances.

W. D. H.

Occurrence of Mixed Glycerides in Natural Fats. ISIDOR KLIMONT and E. MEISELS (*Monatsh.*, 1909, 30, 341—346).—To the list of fats containing mixed glycerides is to be added the fat of the domestic goose and of the domestic duck. Goose fat (D^{15} 0.9270, saponification number 193.3, iodine number 70.1), when crystallised from acetone containing a little chloroform, gives a *substance*, m. p. 59°, saponification number 203.0, the mixture of fatty acids from which has m. p. 56.5° and acid number 209.3. These numbers agree with those of a mixture of palmitic acid (2 mols.) and stearic acid (1 mol.), m. p. 55.1°. Duck fat (D^{18} 0.912, m. p. 27—28°, saponification number 193.6, iodine number 71.7), when crystallised from acetone and chloroform, gives a *substance*, m. p. 59—60°, saponification number 203.9, the fatty acids from which have m. p. 54—55° and acid number 209.7. The *substances* are probably identical with Guth's α -stearyldipalmitin or β -stearyldipalmitin (*Abstr.*, 1903, i, 225). Repeated crystallisation of a mixture of tristearin and tripalmitin yields finally a mixture of constant m. p., 66°, containing 70% tristearin and 30% tripalmitin.

C. S.

The Milk of a Woman Sixty-two Years Old. SIGMUND FRÄNKEL (*Biochem. Zeitsch.*, 1909, 18, 34—36).—The milk obtained differs in no chemical way from that of normally lactating women.

W. D. H.

The Parent Substance which is the Cause of the Cammidge Reaction in Urine. K. SMOLENSKI (*Zeitsch. physiol. Chem.*, 1909, 60, 119—130).—Cammidge has shown that in many cases of acute

diseases of the pancreas, urine is excreted, which, after boiling with acids (and only after boiling), gives a reaction with phenylhydrazine, and readily reduces Fehling's solution. These reactions have been shown by the author to be due to the presence of sucrose, by the investigation of the optical properties of the urine, both before and after hydrolysis with acids (inversion), by the identification of the phenylhydrazine precipitate obtained by Cammidge's method, and by the isolation of the disaccharide from urine in the form of its strontium compound. The output of sucrose in the urine could be markedly increased if larger quantities of this sugar were ingested. It is suggested that the phenomenon of sucrose excretion in urine should be termed "saccharosuria." The case investigated by the author was shown by subsequent post-mortem examination to be one of cancer of the stomach. The pancreas was, however, normal.

S. B. S.

The Biological Action of Salts. I. ERNST SCHLOSS (*Biochem. Zeitsch.*, 1909, 18, 14—21).—The special point investigated was the influence of salts on the body temperature of children. The univalent cations sodium and potassium appear to be the carriers (Träger) of the temperature-elevating function, and the bivalent cation calcium that of the temperature depressing function.

W. D. H.

Action of Alkali Salts on Ciliated Epithelium. RUDOLF HÖBER [with M. IWASCHKIEWITSCH] (*Biochem. Zeitsch.*, 1909, 17, 518—542).—The tissue employed was the mucous membrane from the frog's throat. The action of ions and cations was investigated separately. The anions can be arranged in the following order: I, Br, NO_3 , Cl, SO_4 , the ciliary movement being arrested most rapidly in iodides, and least rapidly in chlorides and sulphates. The action of the cations is more complex; they can be arranged, however, in the following order: Li, Cs, Na, NH_4 , Rb, K. Lithium and caesium have the strongest action, and rubidium and potassium the weakest. This order of anions and cations is similar to that which has been found in other physiological phenomena, and in the precipitation of certain colloids.

S. B. S.

The Action of Salts on Toxin and on Toxin-antitoxin Combinations in Presence of Serum Proteins. ERNST P. PICK and OSWALD SCHWARZ (*Biochem. Zeitsch.*, 1909, 17, 491—517).—The toxicity and the effect of toxin-antitoxin combination was tested in the usual way by injecting the mixtures into mice. It was found that salts with monad cation, such as sodium chloride, sodium sulphate, ammonium sulphate, thiocyanate, and bromide, which have no action on diphtheria or tetanus toxin, exert no influence on the combination between the toxins and antitoxins in relatively high concentration; nor is the combination toxin-antitoxin destroyed by these salts. Calcium and aluminium ions act on the tetanus toxin, which, however, can be protected from the destructive action by the presence of an immune serum; they also act on the toxin-antitoxin combination; the more stable the latter is the more energetic the action of the metallic ions. Magnesium salts act in the reverse way, namely, the magnesium

ion exerts its action when the toxin is added to the serum-salt mixture; it acts but little on the toxin-antitoxin combination. The authors offer an explanation of the phenomena, in which they assume that the neutralisation phenomena of toxin by antitoxin proceeds in two phases, namely, the phase of colloidal adsorption and the phase of the specific saturation of the toxin. Salts of univalent and bivalent metals in the concentrations investigated act neither on the toxin nor antitoxin, nor on the combination of the two, in the case of the diphtheria toxin.

S. B. S.

Action of the Digitalin Group on the Heart. N. WERSCHININ (*Arch. exp. Path. Pharm.*, 1909, 60, 328—339).—Frogs' hearts perfused with Ringer's solution containing 0.5 mg. of strophanthin or digitoxin are brought into a condition of systolic standstill, whereas weaker concentrations stop the heart in diastole. The action is greater if the perfusing fluid contains about one-third of rabbit's blood or rabbit's serum; then doses which ordinarily govern diastole bring about systolic stoppage.

W. D. H.

Action of Picrotoxin on the Autonomic Nervous System. HERMANN FRIEDRICH GRÜNWALD (*Arch. exp. Path. Pharm.*, 1909, 60, 249—255).—The investigations show that picrotoxin acts in a toxic manner on the central portion of the autonomic nervous system. Related substances, such as toxiresin and digitalresin, have probably a similar action.

W. D. H.

Pharmacological Investigation of Tetrahydronaphthylamine. D. JONESCU (*Arch. exp. Path. Pharm.*, 1909, 60, 345—359).—This substance produces a rise of blood-pressure, but differs from adrenaline in its action in several ways. It does not excite the vagus centre; its action on the sympathetic system is both central and peripheral; it produces mydriasis, contraction of peripheral vessels, and of other varieties of plain muscle. It has no action on glands, and does not cause glycosuria.

W. D. H.

Mechanism of the Action of Atoxyls. WILHELM ROEHL (*Chem. Zentr.*, 1909, i, 1666; from *Berlin. klin. Woch.*, 1909, 46, No. 11).—The chief process is that of reduction, which leads to the formation of *p*-aminophenylarsenious oxide. This view is in agreement with the action of arsenic trioxide, and also with all known phenomena. It is neither necessary to assume the reduction product first unites with albumin to produce a toxalbumin (Levaditi), nor that the organisms must be in some definite relationship with the body-cells (Uhlenhuth).

J. V. E.

Acid Poisoning. JULIUS POHL (*Biochem. Zeitsch.*, 1909, 18, 24—29).—Eppinger regards amino-acids and urea as substances which neutralise the toxic effects of acids, because they give rise to ammonia. The present experiments on herbivora (rabbits) lend no

support to this idea. The administration of proteins, amino-acids, and urea has no such protective action against mineral acids. W. D. H.

An Improved Method of Desiccation. L. F. SHACKELL (*Amer. J. Physiol.*, 1909, 24, 325—340).—The method of drying is improved (1) by the production of a high vacuum by the Geryk pump; (2) by freezing the material prior to desiccation, and (3) by keeping the sulphuric acid absorbent well mixed throughout. Liquids need not be frozen, but can be absorbed on dry sand. The method is very rapid, and the materials dried are not chemically altered. It ought to be specially valuable in the drying of the serums, etc., used in serum therapy. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Metallic Filter with Adjustable Uniform Interstices Reducible to Ultramicroscopic Dimensions. ÉMILE GOBBI (*Compt. rend.*, 1909, 148, 1126—1128).—The Chamberland filter and others of the same kind retain bacteria and fine particles for a certain time only. The action of the filter is to pass the liquid through long canals, which, although wide enough to pass small particles, cause them to be arrested by surface action. The author's filter aims at arresting bacteria and colloid particles by the uniform minuteness of the interstices of the filter, whilst not impeding the liquid by long canals. The filter is composed of several hundred metres of nickel ribbon 0.1 mm. thick, 1.5 mm. wide, rolled spirally on its flat face to make up a cylinder. The ribbon has a series of tiny ribs on one side of it very close together, so that when the filter is tightened by screwing up the ribbon the size of the interstices depends on the height of the ribs. Liquid friction is small, since it depends on the width of the ribbon employed—in this case 1.5 mm.

Seine water, filtered under a pressure of 30 metres, remained quite sterile even when the filter had been in continual use for several days. Solutions of neutral-red and Magdala-red were entirely decolorised by filtration, but methyl-violet was only partly retained. In presence of 2% of sodium chloride, however, the latter dye was apparently polymerised, and was retained by the filter for some hours. R. J. C.

The Influence of Glucosides on the Growth of Acid-fast Bacilli, with a New Method of Isolating Human Tubercle Bacilli Directly from Tuberculous Material Contaminated with Other Micro-organisms. F. W. TWORT (*Proc. Roy. Soc.*, 1909, B, 81, 248).—Investigations were undertaken with the object of determining the action of acid-fast bacilli on glucosides, of which forty-three were tested; no evidence was obtained of any fermentative action. One glucoside, ericolin, was found to kill a

large number of species of micro-organisms, but had little effect on acid-fast bacilli. If sputum is treated with a 2% ericolin solution at 38° for from three-quarters to one hour, most of the other organisms are killed; the tubercle bacilli are unaffected, and by sub-culturing on to Dorset's medium, and again sub-culturing from this if necessary, a pure strain of tubercle bacilli is easily obtained.

S. B. S.

Bacillus amylobacter A. M. et Bredemann. G. BREDEMANN (*Centr. Bakt. Par.*, 1909, ii, 23, 385—566).—A long treatise on this organism in its various relationships. It fixes nitrogen, decomposes carbohydrates with formation of alcohol and volatile acids, and is characterised by its property of making and storing glycogen, a property shared by few other micro-organisms. The method of examining the volatile acids was to prepare a mixed barium salt from the distillate and determine the percentage of barium in the mixture. So far as the method can be depended on, it fails to indicate any difference between the cultures obtained from different sources, and to this extent shows that the limits within which the organism is liable to variation are narrow.

A full bibliography is appended.

E. J. R.

The Growth of Bacillus tuberculosis and Other Micro-organisms in Varying Percentages of Oxygen. BENJAMIN MOORE and R. STENHOUSE WILLIAMS (*Bio-Chem. J.*, 1909, 4, 177—190).—*Bacillus tuberculosis* either does not grow at all, or grows very badly in the entire absence of oxygen or in presence of a partial pressure of oxygen amounting to 80 to 90% of an atmosphere. *Staphylococcus aureus* and *S. albus* behaved in a similar way. On the other hand, *B. coli*, *typhosus*, *diphtheriae*, and *dysenteriae* (Kruse) grew equally well both in air and oxygen; two other forms of *B. dysenteriae* make less growth in oxygen than in air, whilst *S. citreus* showed certain differences in the manner of growth.

E. J. R.

The Stereochemistry of Lactic Acid Fermentation. REGINALD O. HERZOG and F. HÜRTH (*Zeitsch. physiol. Chem.*, 1909, 60, 131—151).—The action of various bacteria capable of producing lactic acid was investigated, and a bouillon medium containing different sugars was employed. The amount of lactic acid, its optical properties, and the amount of unchanged sugars after bacterial action were determined. It was found that both aldehyde and ketone alcohols, as well as substances containing alcohol groups alone (such as mannitol), formed satisfactory substrates for lactic acid fermentation; also, in some cases, pentoses, hexoses, disaccharides, and methylglucoside. Glycerol, erythritol, and dulcitol were unattacked. In some cases the quantity of lactic acid formed corresponded with the amount of sugar which had disappeared from the substrate after fermentation; in other cases there was a loss. The lactic acid formed was in most cases optically active. The form of the lactic acid appears to depend on the nature of the ferment rather than on the configuration of the substrate.

S. B. S.

Citric Acid Fermentation by Citromycetes. EDUARD BUCHNER and HERMANN WÜSTENFELD (*Biochem. Zeitsch.*, 1909, 17, 395—442).—The conditions under which the micro-organisms of various origin will develop from dextrose the maximum amount of citric acid were investigated. As source of nitrogen, inorganic salts, decoction of white beans, and beer-wort were employed. The most favourable results were obtained from the organic sources of nitrogen. Good yields of the acid were obtained only in the presence of calcium carbonate; if this were absent, the citric acid appeared to be to a great extent destroyed by the micro-organism. The largest yield of citric acid from dextrose was obtained by *Citromycetes citricus* from a solution poor in nitrogen and containing 13% dextrose; in this case the yield of citric acid was 55% of the weight of sugar employed. Investigations were also undertaken with a view to throwing light on the chemical mechanism of the reaction. It is conceivable that citric acid could be derived from a condensation of two molecules of acetic acid and one molecule of oxalic acid, which could be formed as intermediate products from the sugar. No citric acid was obtained, however, when the micro-organism was grown on media containing the two above-mentioned acids. Negative results were also obtained when attempts were made to produce alcohols by the deamidisation of amino-acids. The expressed juice of the organisms was incapable of producing citric acid. S. B. S.

Effect of Different Bases on the Changes of Ammonia and Nitrate Nitrogen. OTTO LEMMERMANN, H. FISCHER, and B. HUSEK (*Landw. Versuchs-Stat.*, 1909, 70, 317—334). **Effect of Lime on Soil Bacteria.** H. FISCHER (*ibid.*, 335—342).—The results of experiments with liquid cultures showed that nitrogen in the forms of ammonia and nitrates is to a considerable extent converted into proteins by soil organisms. The conversion is greater in the case of ammonium salts than with nitrates. The proteins thus formed are soon decomposed.

Calcium carbonate distinctly increases the production of protein from ammonia, but has very slight, if any, effect on the conversion of nitrates. Barium carbonate considerably increases protein formation from ammonium salts, and has a retarding effect in the case of nitrates. Magnesium carbonate and ferric hydroxide diminish the conversion of ammonium salts into protein, and ferric hydroxide acts similarly with nitrates.

The lower manurial effect of ammonium salts as compared with nitrates may be due, in part, to the greater readiness with which ammonia is converted into proteins; loss of ammonia due to the presence of calcium carbonate in the soil is too slight to account for the difference.

Calcium hydroxide has a much greater influence on soil organisms than calcium carbonate. N. H. J. M.

Presence of Indole-producing Substances in Culture Bouillon. CHARLES PORCHER and L. PANISSET (*Compt. rend.*, 1909, 148, 1336—1338).—Liquid bacterial cultures which have been freed

from indole by extraction with ether yield a further quantity of this substance when distilled in steam. This arises from the decomposition of certain indole-derivatives, such as indolecarboxylic acid, which are formed in the bacterial decomposition of tryptophan.

W. O. W.

The Chemical Permeability of Living Algæ and Protozoa to Inorganic Salts and the Specific Action of the Latter. MARGHERITA TRAUBE-MENGARINI and ALBERTO SCALA (*Biochem. Zeitsch.*, 1909, 17, 443—490).—The majority of the experiments were made with *Cladophora* and *Spirogyra*, and the authors describe the morphological changes when these organisms are immersed in various salt solutions. It was found that sodium chloride in 0.7% solution in pure distilled water was less injurious to the organism than the corresponding isoelectric solution of potassium chloride, and the latter salt was less injurious than magnesium chloride. In the presence of small quantities of carbonates of the alkaline earths, the injurious action was in the order $MgCl_2 < NaCl < KCl$. The injurious action was manifested in a different way with each of these salts. With more concentrated solutions (2—4%) of sodium chloride in distilled water, the same phenomena take place in a half-hour as take place in the weaker solutions after several days. In this case a marked formation of free mineral acids takes place within the cells. The place of permeability of salts has been localised in the various organisms. A hypothesis is suggested to explain the action of salts, based on the assumption that certain salt-protein compounds can be formed.

S. B. S.

Respiratory Gaseous Exchanges in Aerial Vegetal Organs of Vascular Plants. G. NICOLAS (*Compt. rend.*, 1909, 148, 1333—1336).—The leaves of vascular plants are distinguished from the stalks by the rapidity with which gaseous interchange takes place at their surface. With respect to gaseous transpiration and circulation, the difference between the leaves and stalk is comparable with that shown to exist between leaves in their normal state and those which have been coated with vaselin or glycerol.

W. O. W.

Permeability of the Plasma Membrane for Dissolved Substances. W. W. LEPESCHKIN (*Ber. Deut. bot. Ges.*, 1909, 27, 129—142).—The author measures the increase in size of the *Spirogyra* cells when placed in the solution under investigation, and deduces therefrom the isotonic coefficient. It is pointed out that the method has only a limited application, and breaks down if the cells have to remain so long in the solution that the permeability of the membrane alters, or if substances entering the cell react to form new substances exerting osmotic pressure. A series of measurements with sugar solution and glycerol solution are given.

E. J. R.

Direct Absorption of Nitrites by Plants. F. PERCIABOSCO and V. ROSO (*Chem. Zentr.*, 1909, i, 1497; from *Stazz. sper. agrar. ital.*, 1908, 42, 5—36).—Whilst dilute solutions of sodium nitrite have no

retarding effect on the growth of plants, stronger solutions act very injuriously.

Maize plants absorb sodium nitrite in dilute solutions without previous conversion into nitrate. N. H. J. M.

The Changes Undergone by the Nucleo-protein Phosphorus in Plants. W. ZALESKI (*Ber. Deut. bot. Ges.*, 1909, 27, 202—210).—The phosphorus compounds in plants include phosphates, phytin, phosphatides, nucleo-protein, and others. The phosphorus existing in the form of nucleic acid can be estimated by Plimmer's method; a scheme is also suggested for discriminating between other phosphorus compounds, and is applied to the growing ends of the bean plant. It is shown that the nucleic acid phosphorus does not change in amount when the plants are grown in water culture with sugar or in pure water. The statement made by Iwanoff to the contrary is incorrect.

E. J. R.

Composition of Shea Butter; Analysis of the Oil from the Seeds of *Symphonia globulifera*. JAS. E. SOUTHCORBE (*J. Soc. Chem. Ind.*, 1909, 28, 499—500).—*Shea Butter*.—A sample tested by the author showed: D^{98-99} 0.861, m. p. 29° , solidifying p. $20-21^{\circ}$, acid number 26.17, saponification number 178.7, iodine number 57.6. Hehner number 93.8, Reichert-Meissl number 1.15.

From a more extended analysis the composition of the insoluble fatty acids derived from the sample may be taken as oleic acid 60%, stearic acid 30—35%, lauric acid 3—4%.

*Oil from the seeds of *Symphonia globulifera*.*—The following data were obtained for the oil itself: D^{99-100} 0.8849, m. p. 35° , acid number 10.1, saponification number 194.6, iodine number 64.2, Hehner number 94.3, Reichert-Meissl number 1.00. The mixed fatty acids gave D^{99-100} 0.891, m. p. $48-50^{\circ}$, solidifying p. 46° , iodine number 64.8, unsaponifiable matter 1.1%. L. DE K.

Synthesis of Salicin by means of Plants. GIACOMO L. CIAMICIAN and C. RAVENNA (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 419—422. Compare Abstr., 1908, ii, 773).—The authors' previous work indicated that plants are capable of transforming saligenin, benzyl alcohol, and vanillin into glucosides, the change being a reversible one resulting in a chemical equilibrium.

A number of well-grown maize plants, as nearly equal as possible, were inoculated with saligenin. When growth was complete, it was found that the ratio of combined to free saligenin had the value 1 : 2. The same result was obtained if salicin were introduced into the plants in place of saligen. Hence, maize resembles kidney beans and hyacinths in being capable of transforming saligenin into salicin.

By means of experiments on a large number of maize plants, the authors were able to isolate the salicin formed in this way. T. H. P.

Nature of Anthocyanin. Miss M. WHELDALE (*Proc. Camb. Phil. Soc.*, 1909, 15, 137—168).—The author considers that chromogen is of the nature of the flavone and xanthone classes of natural

colouring matters, and exists in the plant as a glucoside. When acted on by peroxydase, the chromogen is converted into a red or purple pigment. The results are brought to bear on the phenomena observed in the genetics of flower colour. The two factors, chromogen and enzyme, are necessary in order that there should be colour; if either is absent an albino results. There appears also to be a third factor which can co-exist with these two, and which produces a blueing of the red pigment.

A full bibliography of the subject of chromogens and flower colours generally is appended.

E. J. R.

The Taxine in Irish Yew, *Taxus baccata* var. *Fastigiata*. RICHARD J. MOSS (*Sci. Proc. Roy. Dubl. Soc.*, 1909, 12, 92—96).—The author has applied the method of isolating taxine described by Thorpe and Stubbs (*Trans.*, 1902, 81, 874) to the leaves and seeds of female trees of the Irish yew.

In the leaves of two different trees 0.623% and 0.323% of taxine were found, whilst in the seeds of the fruit from the same trees the amounts were 0.079% and 0.082% respectively. The fleshy part of the berries is quite free from taxine. The leaves of a male specimen of the common yew gave 0.082% of the alkaloid, whilst Thorpe and Stubbs obtained 0.18% from the male and 0.12% from the female tree.

The results seem to indicate that the Irish yew contains much more taxine than the common yew. By microscopical examination the author has detected signs of softening when taxine is heated at 60°, that is, 22° below the reputed m. p.

The substance is found to be partly decomposed by dilute hydrochloric acid even in the cold, a brown, humus-like substance being produced. By using 1% oxalic acid solution for extraction in place of 1% hydrochloric acid, 0.402% of taxine was isolated instead of the 0.323% recorded above. Attempts to crystallise the alkaloid were unsuccessful.

E. H.

Choline, Betaine, and Trigonelline from Plants, and the Methods for the Preparation and Estimation of these Bases. ERNST SCHULZE (*Zeitsch. physiol. Chem.*, 1909, 60, 155—179).—The extracts of plants were first freed from the constituents precipitable by lead acetate. The liquid thus obtained could then be treated by two alternative methods. Either the excess of lead could be removed by hydrogen sulphide, the filtrate from the sulphide evaporated to dryness, the residue extracted with alcohol, and the bases precipitated from alcoholic solution by alcoholic mercuric chloride, or the bases could be precipitated by phosphotungstic acid, the precipitate thus obtained decomposed by barium or calcium hydroxide, the solution of the bases acidified by hydrochloric acid, and evaporated to dryness; from this residue the hydrochlorides were extracted by alcohol, and the bases precipitated by mercuric chloride in the way already described. When alloxuric bases and arginine were present, they could be separated, after decomposition of the phosphotungstic acid precipitate with alkalis, by means of silver nitrate, which precipitates the alloxuric bases, and by silver nitrate and baryta, which precipitate

the arginine and histidine. The filtrate from these precipitates was reprecipitated by phosphotungstic acid, and the choline, etc., isolated by the method already mentioned. The mercuric double salts were recrystallised, decomposed by hydrogen sulphide, and the solution of the hydrochlorides evaporated to dryness in a vacuum. The choline could be separated from the betaine or trigonelline (which do not occur together in the same plant) by extraction with cold alcohol, in which it alone is readily soluble.

S. B. S.

The Theobromine-content of Cocoa Beans. ADOLF KREUTZ (*Zeitsch. Nahr. Genussm.*, 1909, 17, 526—528).—The author has carried out a number of experiments, the results of which confirm his former statement that the theobromine in cocoa beans is present partly in the free state and partly combined (compare this vol., ii, 193); evidence that the theobromine is in combination as a glucoside was not, however, conclusive. About one-half of the total theobromine occurring in cocoa beans is free, and can be directly extracted with chloroform, whilst the remainder only becomes soluble after the cocoa has been subjected to hydrolysis.

W. P. S.

Effect of Different Relations of Calcium and Magnesium on the Development of Plants. LUIGI BERNARDINI and G. CORSO (*Bied. Zentr.*, 1909, 38, 304—305; from *Staz. sper. agrar. ital.*, 1908, 41, 191).—The results of water- and sand-culture experiments with rye, wheat, and beans showed that the most suitable relations of lime to magnesia are 1 : 1, 2 : 1, and 3 : 1 respectively. In the case of field experiments no definite results were obtained.

N. H. J. M.

Physiological Action and Manurial Value of the Salts of Dicyanodiamide. RENATO PEROTTI (*Chem. Zentr.*, 1909, i, 1497; from *Staz. sper. agrar. ital.*, 1908, 42, 81—88).—Dicyanodiamide sulphate (0.05%) retards the germination of cereals and also root development. With 0.025% solutions growth is normal. The conclusion is drawn that when present in small quantities, dicyanodiamide is available as source of nitrogen for plants.

N. H. J. M.

Variations in the Respective Proportions of Dextrose and Lævulose in Grape Musts. P. C. MESTRE (*Ann. Chim. anal.*, 1909, 14, 185—187).—A useful table is given, showing the respective proportions of dextrose and lævulose in a large number of grape musts of various origin.

L. DE K.

Various Destinations of Acetaldehyde in Red Wine. AUGUSTE TRILLAT (*Bull. Soc. chim.*, 1909, [iv], 5, 546—549).—Various authors have shown that acetaldehyde occurs in wine and cognac, and the present paper gives a résumé of results of investigations on the destination of this aldehyde.

The amount present, estimated by adding phosphoric acid to the wine to decompose any aldehyde additive products and then distilling, rarely exceeds 200 mgs. per litre of wine. The amount is increased by ageing, aeration, or the presence of certain micro-organisms. The free aldehyde gradually disappears by (1) forming precipitates with

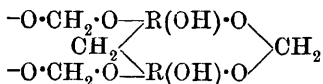
the red colouring matter of the wine; (2) combination with alcohols to form acetals, which in turn precipitate the colouring matter of the wine; (3) oxidation to acetic acid, which then esterifies and contributes to the bouquet of the wine; (4) polymerisation to form resinous matters, and (5) formation of the yellow colouring matter characteristic of old wine and cognac. In the last two changes the acetals may also take part.

T. A. H.

Influence of the Aldehyde of Red Wine on the Formation of Deposits. AUGUSTE TRILLAT (*Bull. Soc. chim.*, 1909, [iv], 5, 550—555. See preceding abstract).—On adding acetaldehyde to red wine, a deposit is formed either immediately or after a longer or shorter time, due to the combination of the aldehyde with the colouring matter. The quantity of aldehyde required to give a deposit with different wines varies very much, as does also the time taken for the deposit to form. A high alcohol content hinders the formation of a deposit, whilst the presence of much sugar or glycerol favours it. The deposits form equally well in the absence of air. These artificial deposits resemble in microscopic structure those formed naturally in wine. After being washed in water and dried at 100°, they yield acetaldehyde on distillation with water and phosphoric acid.

T. A. H.

Mechanism of the Fixation of the Aldehyde Residue on the Colouring Matter of Wine. AUGUSTE TRILLAT (*Bull. Soc. chim.*, 1909, [iv], 5, 555—558. Compare two preceding abstracts).—It has been shown by various authors that aldehydes furnish precipitates when added to solutions of phenols or amino-compounds, and the author suggests that these precipitates consist of condensation products of the aldehyde and phenol or amino-compound; thus with formaldehyde a product of the type $(\text{HO})_3\text{R}\cdot\text{CH}_2\cdot\text{R}(\text{OH})_3$ might be formed, R being an aromatic nucleus.



By the continued action of formaldehyde further condensation might take place, leading to the production of compounds of the annexed type. The author has obtained evidence of the formation of such substances by the action of formaldehyde on triphenylmethane dyes, and since the latter comport themselves in the same way towards formaldehyde as does the colouring matter of wine, he suggests that this is the mechanism of the combination of this colouring matter with aldehydes.

T. A. H.

“Tofu.” YOGORO KATO (*Mem. Col. Sci. Eng. Kyōto*, 1908, i, 325—331).—“Tofu” is prepared in Japan from a species of beans by soaking them in water, grinding, adding water, filtering the milky suspension, and coagulating with a solution containing chiefly calcium and magnesium salts, the soft, jelly-like mass being separated from the water by straining. Tofu has hitherto been regarded as mainly a compound of casein with calcium and magnesium, but this view is now regarded as improbable, because of the small amount of ash in the residue left after the extraction of tofu with water, and more particularly with

dilute hydrochloric acid. It seems probable that the calcium and magnesium exist as phosphates.

The milky suspension behaves like a typical negative colloid as regards migration of the particles with the electric current, ready coagulation on addition of salts, and microscopic appearance. Hence it is considered that the manufacture of tofu depends on the coagulation of the colloid by calcium and magnesium ions, and it is suggested that other multivalent ions might be used for the same purpose. G. S.

So-called Nitrogen-free Extract Substances in Foods.

JOSEF KÖNIG and W. SUTTHOFF (*Landw. Versuchs-Stat.*, 1909, 70, 343—403).—The not inconsiderable number of undetermined substances in the non-nitrogenous extract contain high percentages of carbon, and probably belong to the lignin group. The substances are insoluble in cold water, but dissolve when heated with water under pressure, or in dilute acids, or in glycerol-sulphuric acid (König's method). The portion dissolved by water under pressure has a lower percentage of carbon than the portion dissolved by glycerol-sulphuric acid. The latter is even higher than that of the undissolved crude fibre. The digestibility of the group dissolved by glycerol-sulphuric acid is the same as, or less than, that of crude fibre.

The amount of carbon in digested total nitrogen-free extract substance is higher than in the digested nitrogen-free crude fibre. The name "nitrogen-free extract substances," implying that the substances are readily soluble, is misleading. N. H. J. M.

Deposition of Protein from Amides. WILLI THAER (*Landw.*

Versuchs-Stat., 1909, 70, 413—444).—Results of feeding experiments with sheep showed that the amides of molasses are practically without effect as regards deposition of protein. Asparagine seems to have a greater value, but its value in feeding is very slight. Deposition of protein depends only on protein and starch value. N. H. J. M.

Action of Carbon Disulphide and Similar Substances on

Soils. K. STÖRMER (*Bied. Zentr.*, 1909, 38, 296—298; from *Jahresber. Vereinigung angew. Bot.*, 1908, 113).—Application of carbon disulphide, carbon tetrachloride, chloroform, benzene, toluene, xylene, phenol or *o*- and *m*-cresols resulted in considerably increased production of dry matter, varying from 20.2 to 110.4%, and of nitrogen taken up by the plants (from 36.3 to 144.5%). The amounts of ammonia and of total soluble nitrogen in the soil were increased, whilst the nitrates diminished.

The first effect of such applications is to kill all injurious and beneficial organisms except a few very resistant ones. These are mostly organisms which are capable of attacking such substances as chitin, horn meal, and the residues of fungi with production of ammonia. Under these conditions the soil organisms very rapidly increase in numbers, and the growth of plants is promoted by increased breaking down of soil constituents and the decomposition of the organisms killed by the poisonous substances applied. N. H. J. M.

Manurial Action of Sodium Nitrate, Calcium Nitrate, and Calcium Cyanamide with Sugar Beet. JOSEF URBAN (*Zeitsch. Zuck-erind. Böhm*, 1909, 33, 535—547).—Calcium cyanamide gives satisfactory results, especially when there is plenty of rain; it is, however, less effective than sodium nitrate. The amount of sugar was higher (0.35%) in 1906, and lower (0.18%) in 1907, when calcium cyanamide was employed than with sodium nitrate.

Calcium nitrate, as compared with sodium nitrate (in 1907), gave an increased yield of 11.3%, and the percentage of sugar was 0.16% higher than with sodium nitrate.

N. H. J. M.

Changes in Calcium Cyanamide when Stored and their Estimation. H. KAPPEN (*Landw. Versuchs-Stat.*, 1909, 70, 445—469).—No loss of nitrogen occurred when calcium cyanamide was properly stored. A slight change was observed in warm weather, probably due to the conversion of cyanamide (produced by the action of moisture and carbon dioxide) into dicyanodiamide.

Perotti's titration method, somewhat modified, yielded quantitative results with pure compounds. In some recent samples, however, there was an absence of agreement, not yet explained, between the nitrogen as cyanamide and total nitrogen.

N. H. J. M.

Rational Use of Superphosphates. J. DUMONT (*Compt. rend.*, 1909, 148, 1205—1207).—It has been known for some time that when superphosphates are employed as a manure, either in the autumn or in the spring, they rapidly undergo retrogradation in the soil, owing to the formation of more basic phosphates, or of phosphates of sesquioxides, which are not so readily assimilated. The author has previously shown (*Abstr.*, 1901, ii, 274) that when the soil is rich in humus, a portion of the phosphoric acid escapes retrogradation, being fixed by the organic matter. Experiments which have recently been carried out on the agricultural station at Grignon show that better crops are obtained when a mixture of superphosphate and ordinary manure is made some days before being applied to the ground, than when the superphosphate and manure are used in the usual way, that is, applied separately. The crops experimented on were those of beet-root, potatoes, wheat, and oats.

T. S. P.

Analytical Chemistry.

Modification of the Hempel Gas Burette. J. F. SPENCER (*Ber.*, 1909, 42, 1786—1787).—The burette is fitted with a four-way tap which has two vertical, parallel branches, *a* and *b*, and one horizontal branch, *c*. Both *a* and *b* can be connected either to the burette or to the branch, *c*, but the latter cannot be connected with the burette. This arrangement obviates the inconvenience of the air-space between

the burette and the absorbing liquid, since the latter can be driven from the pipette through *a* or *b* into the side-tube *c*, whereby all the air in the tubes is displaced; by turning the tap, the gas in the burette can then be brought directly into contact with the absorbing liquid in the branches *a* or *b*. P. H.

A New Electrical Method for the Continuous Analysis of Gas Mixtures and its Application to the Measurement of the Velocity of Gas Currents. ADOLF KOEFSSEL (*Ber. Deut. physikal. Ges.*, 1909, 237—242. Compare this vol., ii, 89).—In reference to the author's previous observation that the cooling effect exerted by a gas surrounding an electrically heated wire appears to attain a maximum value when a certain temperature is reached, it has now been found that the apparent maximum is due to a change in the heated nickel wire. New observations with silver wires do not exhibit the effect at all, the cooling produced increasing continuously as the temperature rises.

Experiments with platinum wires and a mixture of air and 5% of hydrogen show that explosion takes place when the temperature exceeds about 250°. In the case of mixtures of methane and air there is no explosive effect, but the methane undergoes combustion at temperatures below 400°. This is accompanied by a very considerable rise of temperature of the enclosed platinum wire. In the case of nickel wires no such effect is observed for temperatures up to 750°.

H. M. D.

The Centrifuge in Quantitative Analysis. HARRY G. PARKER (*J. Amer. Chem. Soc.*, 1909, 31, 549—551).—The apparatus consists essentially of a flask (that is, a flask-shaped tube open at both ends) 14 cm. long, with a diameter at the widest part of 3.5 cm.; this flask, holding about 75 c.c., is called the precipitation flask, as the solution to be analysed is precipitated in it by a suitable reagent. The neck of the flask fits into a weighed platinum crucible by means of a firm, water-tight joint, made by a short section of rubber tubing, which is held between the outside of the neck and the inside of the crucible.

The flask with the crucible is then placed in the jacket of a specially constructed centrifuge, and the space between is filled with water; the hydrostatic pressure being the same inside and outside the flask, there is no tendency to leak. A few minutes rotation at a speed of 1500—1800 revolutions per minute causes the precipitate to collect in the crucible. The flask is removed from the jacket, the water is drawn off by means of an ordinary siphon bottle, and the precipitate is washed three times with a very little water, each time repeating the process. Finally, the crucible is detached from the flask, dried, ignited, if necessary, and weighed. The chief advantage of the method appears to lie in the fact that no filter-paper is used.

L. DE K.

Preparation and Use of Asbestos for Gooch Crucibles. PHILIP A. KOBER (*Amer. Chem. J.*, 1909, 41, 430—432).—The asbestos

is first purified by digestion with nitro-hydrochloric acid for several hours, it is then washed on a Buchner funnel, transferred to a bottle with sufficient water to make a good emulsion (2—10 grams per litre), a strong current of air passed through it for some time, and finally any large fibres remaining are got rid of by filtering through a Buchner funnel. Pulp thus prepared and diluted to about 0.1% can be used to give a layer of asbestos of any desired weight in a crucible.

G. S.

Preservation of Filter-paper; its Influence on Certain Estimations. LUCIEN L. DE KONINCK (*Bull. Soc. chim. Belg.*, 1909, 23, 221—222).—Mallinckrodt and Stull (*J. Amer. Chem. Soc.*, 1904, 26, 1029) called attention to the danger of using filter-paper unduly exposed to laboratory fumes. In the author's laboratory this fact has been confirmed by Lejeune. In the case of a nickel estimation based on the amount of chlorine evolved by heating the precipitated hydrated oxide with hydrochloric acid, the results were in excess of the truth when filter-paper was used instead of asbestos. It was then shown that this was due to the filter-paper. Mallinckrodt and Stull consider it probable that this had absorbed nitric compounds. The author, however, expresses an opinion that even pure air may be the cause of this, as a combination may take place between the nitrogen and oxygen under the influence of moisture and the porosity of the paper. L. DE K.

Automatic Pipette for Sodium Hydroxide Solution. FRANCIS G. BENEDICT (*J. Amer. Chem. Soc.*, 1909, 31, 652—654).—An arrangement is described by means of which a definite volume of saturated sodium hydroxide solution can be automatically run off from a stock solution. A wide glass tube has a two-holed rubber stopper inserted in the base. In one of the holes is a glass tube leading to the reservoir of sodium hydroxide solution, and in the other a goose-neck tube, which serves as an overflow for the expelled liquid. A glass plunger works in the wide tube by means of an iron rod, cord, and pulley; attached to the iron rod is a lever which actuates the mechanism for cutting off the supply of solution from the reservoir. When the plunger is raised, the shut-off from the reservoir is simultaneously opened, and the solution is allowed to flow into the wide glass tube until it rises to a mark which can be arbitrarily adjusted. At that moment the weight is released; it descends into the liquid, simultaneously shuts off the supply, and displaces a definite amount of the solution through the overflow tube. T. S. P.

Iron-alum as a Standard in Titrations. LUCIEN L. DE KONINCK (*Bull. Soc. chim. Belg.*, 1909, 23, 222—224).—Iron-alum (crystallised ferric ammonium sulphate) is recommended for standardising purposes on account of its high equivalent, its great stability in air, and the ease with which it is purified. To obtain it in a fit state as a reagent, the commercial salt is dissolved in a little hot (not boiling) water, and 100 c.c. of *N*-sulphuric acid added for every 100 grams of the alum. Perfectly pure crystals are then gradually deposited, which are spread on filter-paper and put, whilst still

slightly moist, in a stoppered bottle. When required, a portion of it is exposed to the air for some fifteen to twenty minutes until its weight is constant, when its iron content corresponds exactly with the salt with 24 mols. of water; 100 parts of the salt = 11.6 parts of metallic iron.

When exposed to the air for weeks or months, a white powder is formed containing 6 mols. of water. L. DE K.

Detection and Estimation of Chloride in Presence of Bromide and Estimation of Iodide, Bromide, and Chloride in Mixed Solution. ROBERT M. CAVEN (*J. Soc. Chem. Ind.*, 1909, 28, 505—508).—Chlorides may be detected in presence of bromides by boiling the solution, which should be concentrated to a small volume with 10—15 c.c. of dilute nitric acid (1 vol. of acid, D 1.42; 3 vols. of water), until the bromine has been expelled and the liquid has turned colourless. The solution is then tested for chlorine as usual. The process may be rendered quantitative by heating in a flask at 80° in a current of air, then boiling for just one minute, and again passing a brisk current of air. No chlorine is then volatilised. Volhard's titration process is used. When the three halogens are present, the process may be summarised as follows. The total halides are estimated by Volhard's titration process. The iodine is titrated indirectly by estimating with standard dichromate the ferrous iron generated on boiling the solution with iron-alum. The chlorine is estimated after eliminating the iodine by means of hydrogen peroxide and acetic acid and boiling in a current of air; the bromine is then expelled by nitric acid as directed. The bromine is found by difference. L. DE K.

Detection of Chlorides in the Presence of Complex Cyanides and other Halogenides. WILHELM BÖTTGER (*Zeitech. anal. Chem.*, 1909, 48, 356—368).—The process is briefly as follows. About 0.5 gram of the cyanogen compound which has to be tested for chlorine is mixed with 3 parts of mercuric oxide and boiled for a few minutes with 10 c.c. of 2*N*-sulphuric acid diluted with 20 c.c. of water. When cold, the mercury and other heavy metals are removed with hydrogen sulphide, the excess of which is then displaced by passing a rapid current of carbon dioxide. Before testing for chlorine, any ferrous iron must be oxidised to the ferric state, and this is done most conveniently with potassium permanganate, which reagent is also suitable for the elimination of any iodine or bromine present. L. DE K.

Analyses of Mixtures of Halogen Acids. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1909, 31, 525—529).—The process is intended for solutions of halogens in an alkali hydroxide. In the case of a bromine solution ("hypobromite"), the solution is titrated for bromide by adding *N*/10-silver nitrate until silver oxide begins to separate. Sodium hydrogen carbonate is now added until the colour of the precipitate turns white or light yellow (with bromides this addition is not essential), the liquid is poured off through a Gooch funnel, and the precipitate is washed by decantation. The precipitate both in the flask and the funnel is treated with

dilute nitric acid to dissolve the excess of silver, which is then estimated by Volhard's thiocyanate method.

The *hypobromite* is estimated by boiling a known volume of the solution with ammonia until the excess of this has been expelled, or hydrogen peroxide may be added to the cold solution. A known volume of *N*/10-silver nitrate and some sodium hydrogen carbonate are then added, and the liquid is poured through an ordinary filter. The excess of silver in the precipitate is estimated as directed, and the loss incurred corresponds with the sum of the halide and hypohalite. The total bromine (including that in the state of bromate) is estimated by first reducing the hypobromite as directed, and the bromate is then reduced by means of finely divided metallic iron and a very slight excess of sulphuric acid. The solution is filtered, and treated with a known volume of *N*/10-silver nitrate. After fully oxidising the iron by boiling with nitric acid, the excess of silver is estimated as directed, and the difference represents the total bromine.

Solutions of chlorine and iodine in sodium hydroxide may be analysed in a similar manner, but in the case of iodine the addition of sodium hydrogen carbonate should be omitted.

L. DE K.

Estimation of Iodine in Iodoform and Thymol Iodide.
EUSTACE H. GANE and W. H. WEBSTER (*Zeitsch. angew. Chem.*, 1909, 22, 1059—1061, 1190—1191).—*Iodoform*.—Utz's process (*Apoth. Zeit.*, 1903, 9/12) is preferred. 0.5 Gram of the sample is dissolved in 10 c.c. of a mixture of 1 part of ether and 2 parts of alcohol. Fifty c.c. of *N*/10 silver nitrate and then 1 c.c. of cold fuming nitric acid are added, and the whole is heated on the water-bath until the odour of nitrous acid has disappeared. One hundred c.c. of water are then added, and the excess of silver is titrated with thiocyanate, using ferric alum as indicator. A second method is based on saponifying the iodoform by prolonged boiling with strong alcoholic potassium hydroxide and finally titrating the potassium iodide formed after neutralising the alkali with nitric acid, but is less practical.

Thymol Iodide.—The authors have worked out the following process. One gram of the sample is mixed with 1 gram of potassium sodium tartrate and 5 grams of dry sodium carbonate, placed in a deep porcelain crucible, and the solid mass is then covered with another portion of the soda mixture. The crucible is covered and the contents gradually heated to fusion for forty-five minutes. The mass is extracted with water, and a third part of the filtrate is carefully neutralised with 5% nitric acid, using methyl-orange test-paper as indicator. After adding a pinch of calcium carbonate, the iodine is titrated with *N*/10-silver nitrate, using potassium chromate as indicator. The liquid is now acidified with nitric acid, and the silver iodide collected and weighed as usual. Should it contain chloride, its weight will not correspond with the titration result, but the true amount of iodine and chlorine may then be found by a simple calculation. For the direct estima-

tion of both chlorine and iodine, the first and second portions of the filtrate may be used, the usual methods being employed.

Detection of Inorganic Iodine.—Two grams of the sample are dissolved in 20 c.c. of carbon disulphide, and shaken with 100 c.c. of water for thirty minutes so as to dissolve any iodides present. Seventy-five c.c. of the aqueous solution are filtered, and again shaken twice with 15 c.c. of carbon disulphide to remove the last traces of thymol iodide. The iodine is then liberated with nitric acid, and extracted with carbon disulphide as usual.

Matter insoluble in ether is best estimated by treating 2 grams of the sample in a tared beaker with 10 c.c. of ether. After carefully decanting the ether, the residue is washed thrice in succession with further portions of 10 c.c. of ether, and then dried at 100°.

L. DE K.

Fluorides in Wine. CARLO MENSIO (*Chem. Zentr.*, 1909, i, 1046; from *Staz. sperim. agrar. ital.*, 1908, 41, 819—832).—The following method is recommended for the detection of fluorides in wine. One hundred c.c. of the sample are mixed with 2—3 c.c. of 2*N*-sodium carbonate, and the liquid is heated and precipitated with calcium chloride. The washed precipitate is heated in a platinum dish with sulphuric acid; the dish is covered with a watch-glass which is coated with wax, only a small, bare spot being exposed to the fumes. The test shows the presence of as little as 0.009 gram of sodium fluoride; smaller quantities may be found by working on larger quantities of the sample.

L. DE K.

Quantitative Nitrogen Analysis for Very Small Amounts.

EILHARD A. MITSCHERLICH, PAUL HERZ, and ERNST MERRES (*Landw. Versuchs-Stat.*, 1909, 70, 405—411).—The apparatus for the first process consists of a 1-litre Kjeldahl flask provided with a Hughschhoff distilling tube, which reaches to the bottom of a second 500 c.c. Kjeldahl flask. The substance is heated with 200 c.c. of water and 3 grams of Devarda's alloy, and 50 c.c. of concentrated sodium hydroxide solution in the larger flask, and most of the water distilled over into the second flask containing 60 c.c. of strong sulphuric acid and 20 c.c. of water. When the heating is discontinued, the acid solution rises in the tube and flows into the larger flask. The latter is again heated two or three times in order to rinse out the receiver, the condensed water being allowed to flow back each time. The Kjeldahl flask is then disconnected and heated until the conversion into ammonia is complete. It is again fitted with a distilling tube, which passes through the cork of a 200 c.c. Kjeldahl flask, reaching to the bottom. This flask is provided with a quartz-glass tube, which passes to the bottom of an Erlenmeyer flask containing a suitable amount of *N*/50 sulphuric acid and 50 c.c. of distilled water. The Kjeldahl residue is dissolved in water, sodium hydroxide added, and distilled as usual for twenty minutes. The acid is titrated with *N*/50 alkali, free from carbonate, Congo-red being used as indicator.

Results obtained by the method showed that the error need not be more than ± 0.000020 gram N.

N. H. J. M.

Estimation of Ammonia without a Condenser. R. O. E. DAVIS (*J. Amer. Chem. Soc.*, 1909, 31, 556—558).—A slight modification of Kober's process (*Abstr.*, 1908, ii, 776) for urine, so as to render it fit for the estimation of nitrogen in cotton-seed meal.

The heat developed by the neutralisation of the acid in the Kjeldahl flask by the alkali drawn into it by suction from another bottle is not lasting enough, but if the flask is placed in an asbestos box it keeps warm for an hour and a-half, and the ammonia may thus be expelled fully by the air current. The best plan is to absorb the ammonia in a Folin tube supplemented with a tube filled with glass beads moistened with acid. The expulsion of the ammonia from the Kjeldahl flask may be facilitated by adding scrap aluminium, which gives off hydrogen. In the case of cotton-seed meal, 0.5 gram is digested with 30 c.c. of sulphuric acid; a little aluminium may be added instead of the usual globule of mercury. Before neutralisation, 100 c.c. of water are added, and the alkali introduced develops enough heat to make the solution boil. An illustration showing the complete apparatus is given. L. DE K.

Apparatus for the Estimation of Ammonia. HENRI VIGREUX (*Bull. Soc. chim.*, 1909, [iv], 5, 574—577).—The author has applied his special form of condenser tube (*Abstr.*, 1908, ii, 938) to the apparatus for the Kjeldahl estimation. Such a tube rises vertically from the flask, and therefore the distillation is really a fractional one, the ammonia passing over with the minimum amount of water. There is no danger of loss of acid from the receiver, as the condensing tube to which the vertical tube is in turn connected by a double right-angled bend is long enough to prevent its getting into the distilling flask should any sudden regurgitation take place. L. DE K.

Gravimetric Estimation of Nitric Acid. MAX BUSCH (*Zeitsch. anal. Chem.*, 1909, 48, 368—370).—A reply to Hes (this vol., ii, 265). The use of dried filters is open to objection. As regards the concentration, the author insists that 10—12 c.c. of 10% nitron acetate solution should be added to 80—100 c.c. of the liquid under examination; Hes uses only 5 c.c. to 250 c.c., finally to 750—1000 c.c., and this may be the reason why he did not get satisfactory results in the estimation of nitrates in waters by the nitron method. L. DE K.

Busch's Nitron Process. PETER POOTH (*Zeitsch. anal. Chem.*, 1909, 48, 375—376).—The author advises the preparation of only a small quantity of "nitron" solution at a time, and that this should be kept in the dark. The influence of hydrochloric acid on the precipitation has been studied, and it is found that for every 0.1 gram of a nitrate the hydrochloric acid should not exceed 100 c.c. normal solution. L. DE K.

Estimation of Nitrates by Grandval and Lajoux's Method. L. FARCY (*Bull. Soc. chim.*, 1909, [iv], 5, 562—563).—A reply to Lombard and Lafore (this vol., ii, 436). The author agrees that nitro-hydrochloric acid is formed in the reaction (see following abstract). L. DE K.

Influence of Bromides and Iodides on the Estimation of Nitrates in Waters. L. FARCY (*Bull. Soc. chim.*, 1909, [iv], 5, 563—566).—The author has continued his experiments (this vol., ii, 344), and investigated the influence of bromides and iodides on the estimation of nitrates in water by Grandval and Lajoux's colorimetric process. The following conclusions are arrived at: The halogen salts exercise a disturbing influence. The coefficient of decolorisation is different according to the salt present (the action of the iodide is intermediate between that of the chloride and bromide). The mechanism of the reaction is most likely the same for the three classes of halogen derivatives. It seems to be rather complex, and the investigation is being continued.

Tables are given, also a curve, by the aid of which the true amount of nitrate may be deduced if the quantities of halogens are known.

L. DE K.

Detection of Phosphorus by means of the Photographic Plate. LUIGI SABBATANI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 468—475).—The detection of phosphorus in blood, tissue, etc., can be effected conveniently by means of an ordinary silver bromide plate. Either of two methods may be employed: (1) In a dark room, a drop of the liquid or a piece of the tissue is placed on the plate, which, after ten minutes, is washed under a water tap, developed, and fixed in the ordinary way. Should there be phosphorus in the liquid or tissue, a brown or black spot will appear on the plate, the depth depending on the amount of the phosphorus. By this method a few hundred-thousandths of a mg. of phosphorus are rendered evident. (2) About 10 c.c. or 10 grams of the material to be examined, well shredded if solid, is placed in a small, cylindrical beaker with a flat, ground edge, on which rests the plate with the emulsion downwards. After an hour, the plate is washed, developed, and fixed as usual. The action of phosphorus vapour on the plate is favoured by the presence of water vapour and by a rather high temperature of the material and a rather low one of the plate.

The presence of small quantities of phosphorus in the air expired by a poisoned animal or in the surrounding air may be detected by allowing a jet of the air to impinge on a part of the photographic plate arranged in a suitable case.

Other substances which influence a sensitive plate similarly, and are of biochemical importance, are hydrogen sulphide and hydrogen peroxide. The sensitiveness of the plate to these three substances in aqueous solution at the ordinary temperature is of the same order when the aqueous solutions are placed in contact with the plate, but is very much less for hydrogen peroxide vapour than for hydrogen sulphide or phosphorus vapour. If hydrogen sulphide is present, a few drops of lead acetate solution are added before testing for phosphorus, whilst the influence of hydrogen peroxide is avoided by allowing the vapour to act on the plate as described above. T. H. P.

Microchemical Method for Phosphorus in Plants. CORRADO BONGIOVANNI (*Atti R. Istituto Veneto Sci., Lett. Arti.*, 1907—8, 67, 679—685. Compare this vol., ii, 512).—The method of Lilienfeld and

Monti (Abstr., 1893, ii, 135), modified by Pollacci (*Malpighia*, 1894, 8, 361), is unsuitable for the detection of phosphorus (compare Raciborski and Arcangeli, *Bot. Zeit.*, 1893, 145; Macallum, Abstr., 1899, ii, 232).
N. H. J. M.

Method for the Estimation of Phosphoric Acid in Urine and in Alkali Phosphate Solutions. PAUL VON LIEBERMANN (*Biochem. Zeitsch.*, 1909, 18, 44—57).—The method is similar to Volhard's estimation of halides. The phosphoric acid is precipitated by the addition of a known quantity of standard silver nitrate solution, and the excess of silver in the filtrate estimated by titration with alkali thiocyanate. In the case of urine, it is necessary to first precipitate the phosphates by means of magnesia mixture, and then wash in order to remove other substances which yield precipitates with silver salts.

Full details for using the method in the case of urine are given. With an alkali phosphate solution the following procedure is recommended.

A given volume of the solution is treated with 12.5 c.c. of pure nitric acid (1.31) and diluted to 50 c.c., the silver nitrate is added, the solution neutralised with ammonia, diluted to a given volume, filtered, and the silver estimated in 100 c.c. of the filtrate.
J. J. S.

Examination of Calcium Phosphate Food. OSKAR KELLNER (*Landw. Versuchs-Stat.*, 1909, 70, 471—480).—The following method is recommended. The finely powdered substance (2.5 grams) in a dry 400 c.c. flask is treated with 250 c.c. of Petermann's citrate solution, and shaken for half an hour in a rotatory apparatus. The solution is then passed through a dry filter into a dry vessel, and 50 c.c. of it (= 0.5 gram substance) treated with strong nitric acid (20 c.c.) and then with water (about 50 c.c.), and boiled for ten minutes. The phosphoric acid is then precipitated.
N. H. J. M.

Mercury Seal in Place of Cork or Indiarubber for Connecting the Combustion Tube with the Calcium Chloride Tube. J. MAREK (*J. pr. Chem.*, 1909, ii, 79, 510—512).—The author has simplified the mercury seal previously described by him (Abstr., 1907, ii, 909). The end of the combustion tube is drawn out and turned upwards at right angles. Over this narrow portion is fitted, by means of a cork, a wide glass tube containing mercury, which forms the seal. The side-tube of the calcium chloride tube is so modified that it fits over the narrow end of the combustion tube and dips under the mercury, thus forming an air-tight joint.
T. S. P.

Apparatus for Estimating Hydrogen Given Off on Treating Metals with Acids. ÉMILE KOHN-ABREST (*Ann. Chim. anal.*, 1909, 14, 177—182).—The apparatus consists essentially of a generating flask in which the metal is attacked by hydrochloric acid (1:10), drying tubes, a combustion tube with copper oxide heated to redness, tubes intended for absorbing the water formed, and an apparatus to supply carbon dioxide to sweep out completely any traces of hydrogen

and water vapour. For details, the illustrations of the rather complicated arrangement should be consulted. L. DE K.

Direct Estimation of Two Co-existent Substances Without Separation. ATH. J. SOFIANOPOULOS (*Bull. Soc. chim.*, 1909, [iv], 5, 632—641).—This depends on the principle that if a known weight of a mixture of salts of two metals with the same acid is wholly converted into a mixture of the salts of a second acid and the product is weighed, it is possible to calculate the composition of the original mixture. In the first part of the paper the method of obtaining the two equations necessary for this calculation is given, and in the second part the possibility of extending this method to mixtures of more than two substances is discussed. As a concrete illustration, the analysis of a Greek pyrolusite is quoted. After separating silica as usual, two-thirds of the filtrate, containing the matter soluble in hydrochloric acid, is treated with ammonia, ammonium chloride, and bromine in the usual way, and the mixed precipitate collected, dried, treated with nitric acid, ignited, and weighed as a mixture of ferric, aluminium, and manganese oxides. The mixture is then treated with hydrofluoric acid, and the mixed dry fluorides obtained weighed. A definite portion of the original filtrate is next boiled with excess of zinc oxide, and the manganese in it estimated by titration with potassium permanganate. From the three figures thus obtained, the relative proportions of manganese, iron, and aluminium in the precipitate can be calculated. The compounds most suitable for this method of working are the fluorides, silicofluorides, and oxides obtained by ignition of nitrates.

T. A. H.

Estimation of Potassium in Soils. P. DE SORNAY (*Bull. Assoc. chim. Sucr. Dist.*, 1909, 26, 976—978).—A slight modification of Ronnet's process (*Abstr.*, 1908, ii, 534). An aliquot part of the nitric acid extract of the soil (representing 20 grams of material) is evaporated with addition of a few drops of barium nitrate, and the residue is ignited for about five minutes in order to decompose the nitrates formed. The mass is then mixed with 12 to 15 grams of oxalic acid and a little water, precautions being taken against spirting. The whole is then evaporated to dryness and again calcined, so as to convert the calcium and magnesium into carbonates. Iron and aluminium remain as oxides. The residue is now boiled with water, of which 30 to 40 c.c. suffice for a complete extraction of the potassium, which is then estimated as usual as platinichloride. L. DE K.

Estimation of Potassium in Soils as Phosphomolybdate. P. DE SORNAY (*Bull. Assoc. chim. Sucr. Dist.*, 1909, 26, 978—980).—By adding to solutions of potassium chloride, nitrate, and sulphate of known potassium content a definite amount of phosphomolybdic acid, and estimating the phosphoric acid both in the precipitate and filtrate, the author has obtained results proving that the composition of potassium phosphomolybdate is not constant. L. DE K.

Double Fluorides of Sodium. W. A. R. WILKS (*Proc. Camb. Phil. Soc.*, 1909, 15, 76—77).—Experiments are described which show that sodium can be precipitated almost completely from solution in the

form of a double fluoride with aluminium. To prepare the precipitant, excess of moist aluminium hydroxide is left for two days in contact with concentrated hydrofluoric acid. To diminish the concentration of the hydrogen ions, an equal bulk of a cold saturated solution of copper acetate is added to the hydrofluoro-aluminic acid solution, which is then boiled and filtered. An equal volume of a 50% solution of ethyl alcohol is then added; this increases the sensitiveness of the reaction.

The solution to be tested for sodium is added to the hot reagent and boiled for some time. The test appears to be very delicate, one part of sodium chloride in 20,000 parts of water being readily detected. The precipitated substance has not the composition of cryolite; the atomic ratio of sodium to aluminium is 1.1 to 1. Potassium and ammonium are not precipitated by the reagent, but it yields insoluble compounds with solutions containing silver, magnesium, calcium, strontium, barium, and lead.

H. M. D.

Assay of [Burnt] Magnesite. MERCK GUANO UND PHOSPHAT WERKEN, AKTIEN-GES. (*Chem. Zeit.*, 1909, 33, 545—546).—5.05 Grams of burnt magnesite are boiled with 150 c.c. of 2*N*-sulphuric acid until foaming sets in; some water is then added, and the boiling is repeated. When cold, the whole is diluted to 500 c.c.; 100 c.c. of the solution are mixed with 50 c.c. of 20% ammonium chloride solution, and the excess of acid is then titrated with *N*/2-sodium hydroxide, using methyl-orange as indicator. This gives the joint amount of the magnesium, calcium, iron, and aluminium oxides. Another 100 c.c. are placed in a 500 c.c. flask, the requisite amount of *N*/2-alkali is added, and then 25 c.c. of 2*N*-sodium hydroxide. After diluting to the mark and thorough shaking, the liquid is filtered after a-quarter of an hour; 100 c.c. of the filtrate are now titrated with *N*/10-sulphuric acid, with phenolphthalein as indicator. The sodium hydroxide consumed represents the joint amount of magnesium and iron-aluminium oxides. The two latter are estimated in the usual manner, by a double precipitation with ammonia, in one gram of the sample after removing the soluble silica by evaporation with hydrochloric acid as usual. The calculation is as follows: The magnesium oxide content is obtained by deducting the number of c.c. of sulphuric acid (second titration) from 100. For each 1% of joint iron and aluminium oxides, 0.7 c.c. should be deducted, and to the final result 0.2 must be added; each c.c. = 1% of magnesium oxide. The calcium oxide content is calculated from the two titrations. If the number of c.c. of alkali (first titration) is deducted from 120, the amount of *N*/2-sulphuric acid consumed is obtained. The difference between this number and the number of c.c. of alkali (second titration) reckoned as decinormal gives when multiplied by 1.385 the calcium oxide content.

Burnt magnesite contains a large proportion of its silica in the soluble condition, but in the crude mineral there seems to be no soluble silica.

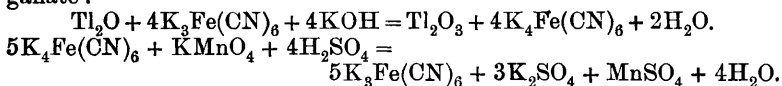
L. DE K.

The Mercury Cathode. WILHELM BOTTGER (*Ber.*, 1909, 42, 1824—1839).—An improved method is described for performing

electrolytic estimations with a mercury cathode, which requires less time and gives more concordant results than the usual methods. A fairly low current density (28 amperes per sq. dm.) is used, to avoid heating. At the end of the electrolysis, an excess of 2*N*-sodium acetate is added, the current disconnected, and the amalgam washed successively with water, alcohol, and ether. The adhering ether is removed as far as possible with filter paper, and finally by a current of dry air, led in by a capillary tube above the surface of the amalgam. No mercury is lost in this way. A helical rotating anode is used. Methyl alcohol may replace the alcohol and ether for washing. A large number of estimations of zinc are given to show the accuracy of the method. The addition of sodium acetate is shown not to cause deposition of sodium. The addition of ammonia to neutralise the acidity of the electrolyte, instead of sodium acetate, leads to loss of zinc, apparently owing to a formation of ammonium amalgam, which decomposes and emulsifies the amalgam. C. H. D.

Spectrographic Analysis of a Specimen of Commercial Thallium. JAMES H. POLLOK (*Sci. Proc. Roy. Dubl. Soc.*, 1909, 11, 338—344).—For the detection of the lines due to impurities a photograph was first taken with a pure specimen of the metal, using a long slit. The slit was then reduced to one-third of its original length, and a photograph of the commercial metal was superposed on the former. By this means the lines which are due to impurities are found in the short spectrum, and can be very quickly measured and identified. The impurities thus found in a sample of commercial thallium were lead, tin, copper, and aluminium. H. M. D.

Volumetric and Gravimetric Estimation of Thallium in Alkaline Solution by means of Potassium Ferricyanide. PHILIP E. BROWNING and HOWARD E. PALMER (*Zeitsch. anorg. Chem.*, 1909, 62, 218—220 *).—The method previously described for the estimation of cerium (*Abstr.*, 1908, ii, 736) is also applicable to thallium. Excess of potassium ferricyanide is added to a solution of a thallic salt, followed by potassium hydroxide. The brown thallic hydroxide is filtered through asbestos and washed. The filtrate is acidified with sulphuric acids, and titrated with potassium permanganate:



A small correction has to be made for the amount of permanganate required to produce a visible coloration.

The same method may be employed gravimetrically, the precipitated thallic hydroxide being washed with hot water and dried at 200°. Both methods give accurate results. C. H. D.

Volumetric Method for the Estimation of Cerium in the Presence of other Rare Earths. FLOYD J. METZGER (*J. Amer. Chem. Soc.*, 1909, 31, 523—525).—Fifty c.c. of the nitrate solution are evaporated with 20 c.c. of sulphuric acid until sulphuric fumes appear. When cold, 2 grams of ammonium sulphate are added, and the whole

* and *Amer. J. Sci.*, 1909, [iv], 27, 379—380.

is diluted with 80 c.c. of water. One gram of sodium bismuthate is added, and the mixture heated to boiling; this converts the cerium into ceric sulphate. After cooling slightly, 50 c.c. of 2% sulphuric acid are added, the solution is filtered, and the filter washed with 100—150 c.c. of the same acid. Standard ferrous ammonium sulphate is added until the colour has changed from yellow to colourless, in order to reduce the salt to the cerous state, and the excess of iron is then titrated with permanganate. The value of the permanganate in terms of iron $\times 3.08415$ = cerium dioxide.

L. DE K.

Separation of Chromium, Iron, Aluminium, and Zinc in a Mixture. M. EMMANUEL POZZI-ESCOT (*Bull. Soc. chim.*, 1909, [iv], 5, 558—559).—*Estimation of Iron.*—To the boiling solution is added an excess of sodium hypobromite (containing a large excess of alkali), and the boiling is continued for ten minutes. The precipitate is freed from aluminium and zinc by redissolving in hydrochloric acid and reprecipitating with excess of potassium hydroxide. The iron precipitate is then once more redissolved in hydrochloric acid and reprecipitated with ammonia as usual.

Estimation of Aluminium.—The alkaline liquid containing aluminium, chromium, and zinc is acidified with hydrochloric acid and boiled to expel the bromine. The aluminium is then precipitated at the boiling point with ammonia.

Estimation of the Chromium.—The filtrate from the aluminium is acidified with hydrochloric acid, and the chromic acid is reduced by boiling with alcohol; the chromium is then precipitated with excess of ammonia.

Estimation of Zinc.—The filtrate from the chromium is precipitated with ammonium sulphide, and the zinc sulphide treated as usual.

L. DE K.

Copper as a Reducing Agent for Ferric Salts previous to their Estimation Volumetrically. W. COLET BIRCH (*Chem. News*, 1909, 99, 273—275).—The author confirms the experiments of Storch (Abstr., 1893, ii, 468), who obtained satisfactory results by reducing the ferric iron with metallic copper in sulphuric acid solution, and has extended the process to hydrochloric acid solutions. The analysis is briefly as follows:

Twenty-five to thirty pieces of pure clean sheet copper, 2 by $2\frac{1}{2}$ cm., and bent at right angles in the middle, are placed in a round-bottomed flask, the acid iron solution is added, and the whole boiled gently for at least five minutes. The liquid is then poured off, the copper rinsed a few times with air-free water, and the liquid titrated with potassium dichromate solution in the usual way, a solution of potassium ferricyanide in dilute sulphuric acid serving as indicator. The dichromate must be standardised by means of a definite quantity of iron oxide dissolved in hydrochloric acid previously reduced by copper as described.

L. DE K.

Estimation of Nickel in Presence of Cobalt. JEAN A. SANCHEZ (*Bull. Soc. chim.*, 1909, [iv], 5, 641—647).—The process depends on the fact that if excess of potassium cyanide is added to a solution

containing nickel and cobalt, the latter is converted into potassium cobaltocyanide, which, if the solution is evaporated to dryness in air, changes to potassium cobaltcyanide. On re-solution in water and addition of silver nitrate, in excess, the cobalt is precipitated as silver cobaltcyanide and the nickel is left in solution as the nitrate, and can be estimated, the excess of silver being first removed by adding potassium bromide. To the filtrate, sodium hydroxide and bromine are then added, and the hydrated nickel sesquioxide ignited and weighed. As an alternative, the hydrated sesquioxide may be transferred to a flask containing a solution of potassium iodide acidified with sulphuric acid, when the action represented by the following equation takes place: $\text{Ni}_2\text{O}_3 + 2\text{KI} + \text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{NiO} + \text{I}_2$. The iodine liberated may be estimated by means of sodium thiosulphate.

If it is desired to determine cobalt as well as nickel, the mixed oxides are precipitated in the usual way with sodium hydroxide and bromine water, and weighed. This mixture is then treated as described above for the estimation of nickel, and the cobalt obtained by difference. Full details of the methods of manipulation, quantities to be used, and precautions to be taken are given in the original.

T. A. H.

Assay of Antimony Alloys. PAUL NICOLARDOT and KRELL (*Bull. Soc. chim.*, 1909, [iv], 5, 559—562).—The process is based on Deville's nitrate method (*J. Pharm. Chim.*, 1855). The alloy is attacked with nitric acid (D 1.2) and, after evaporation on the water-bath, the residue is heated for some time at 125° or a little above, and the mass is then taken up with water acidified with nitric acid. Tin and antimony remain as insoluble oxides, which are collected at the pump in a small, cylindrical tube, and finally reduced in a current of hydrogen at 400°. The metal obtained is tested quantitatively for tin and antimony by the ordinary methods. Tin may be weighed as oxide, but not the antimony, its oxide being of a somewhat variable composition.

Lead is estimated as usual in the nitric acid solution. Copper in bronzes is best deposited electrolytically from a nitric acid solution; the tin and antimony oxides should not be removed.

L. DE K.

Analysis of Tantalum Ores. EDWARD S. SIMPSON (*Chem. News*, 1909, 99, 243—244).—A reply to Giles, who objects to fusion with alkali hydroxide (this vol., ii, 352). Potassium hydroxide is the most suitable substance for opening up the tantalum ores, using 6 parts to 1 part of finely powdered sample. Nickel, or in some cases silver, crucibles may be used, covered with a lid slightly convex on the under-side; the fusion is continued for fifteen to sixty minutes.

In order to prevent creeping of the alkali during fusion, a small sheet of asbestos millboard is taken, and in it is cut a circular hole of such a size that when the crucible is pressed tightly into it the bottom only projects a quarter of an inch. By means of a bunsen burner the lower part of the crucible is thus heated to redness, whilst the upper part remains comparatively cold.

It appears that when a dilute solution of mixed potassium tantalate,

niobate, and titanate is slightly acidified with hydrochloric acid, only a portion of the niobium is precipitated as hydroxide, the remainder being present in the form of a soluble double chloride of titanium and neobium.

L. DE K.

Detection of Wood Spirit in Galenical Tinctures. HENRI CARETTE (*J. Pharm. Chim.*, 1909, [vi], 29, 481—484).—Gay's test, which depends on the formation of nitrogen iodide when ammonia is added to a solution of iodine in presence of acetone (which always occurs in wood spirit of commerce), is modified with a view to increasing its delicacy.

Ten c.c. of the tincture are distilled, and 5 c.c. of distillate collected. To this are added 5 c.c. of water, 5 c.c. of ammonia (D 0.930), and 1 c.c. of tincture of iodine (Codex Français, 1884). The mixture is shaken during fifteen minutes, and exposed to diffused daylight. A black precipitate of nitrogen iodide is formed on adding the iodine solution, and if acetone is present, on remaining at 18° in the light, this precipitate gradually changes into iodoform. If very little acetone is present, the tube should be warmed at 55° until the precipitate disappears, and then the liquid shaken with ether. The latter dissolves out the iodoform, which can be recovered by allowing the solvent to evaporate. In the absence of acetone, the nitrogen iodide persists in daylight for at least twelve hours at 18°, but only for about fifteen minutes at 65°.

T. A. H.

Schmitt's Process for the Estimation of the Total Esters in Wine. FRANCESCO SCURTI and G. DE PLATO (*Chem. Zentr.*, 1909, i, 1045—1046; from *Staz. sperim. agrar. ital.*, 1908, 41, 681—688).—A solution is prepared containing the same amount of dextrose, lævulose, and onotannin as the sample to be tested, and its neutralising power when boiled with alcoholic potassium hydroxide is ascertained. The alkali absorbed is then deducted from the amount of alkali neutralised on saponification of the sample, and the result, after allowing for the acidity of the wine, represents the esters. One c.c. of *N*/10-potassium hydroxide = 0.010275 gram of esters calculated as diethyl tartrate. A number of results are given in a table.

L. DE K.

Estimation of Essences in Liqueurs. L. VANDAM (*Ann. Chim. anal.*, 1909, 14, 174—179).—One hundred c.c. of the sample are placed in a distilling flask, a little fine pumice stone is added, and 70 c.c. are collected in a 100 c.c. receiver. After taking the alcoholic strength, the liquid is diluted with a calculated amount of water and alcohol in such a manner that there shall be exactly 100 c.c. of alcohol of 50°. If the solution is still turbid at 17—18°, it must be diluted with an equal volume of alcohol (of 50°). It contains all the essence present in the sample.

Twenty-five c.c. of the solution, are placed in a test-tube, and water is added from a burette until a permanent turbidity is noticed (temp. from 16° to 18°). Reference is then made to empirical tables constructed for various kinds of essences.

L. DE K.

A General Reagent for Phenols. JEAN PUGNET (*Chem. Zentr.*, 1909, i, 1508; from *Bull. Sci. Pharm.*, 1909, 16, 142—145).—The reagent consists of 20 drops of 40% formaldehyde per 10 c.c. of water, to which before use an equal volume of sulphuric acid is added. On adding this to phenols or substances containing at least one phenolic group, characteristic precipitates or colorations are obtained. The test is applied as follows: about 0.02 gram of the substance is placed in a test-tube, 1 c.c. of the reagent is added, and then 1 c.c. of sulphuric acid. If the substance is a liquid, 1 c.c. is mixed with 1 c.c. of sulphuric acid, and 2 drops of formaldehyde are added. The author has tried the test with thirty-four substances. The reagent, in which the formaldehyde had been replaced by acetaldehyde, paraldehyde, anisaldehyde, acetone, and benzaldehyde, was also tried with resorcinol and morphine.

L. DE K.

Methylglyoxal as a General Colour Reagent in Analysis. GEORGES DENIGÈS (*Bull. Soc. chim.*, 1909, [iv], 5, 649—651).—Methylglyoxal is found to give characteristic colour reactions with many phenols, alkaloids, etc., and consequently it is proposed to employ it as a general reagent. The solution used is prepared by adding to 20 c.c. of a 5% aqueous solution of glycerol, 100 c.c. of water and 0.6 c.c. of bromine, and, after the halogen has dissolved, heating the solution during twenty minutes at 100°. It is then concentrated to 100 c.c., 20 c.c. of sulphuric acid added, and 50 c.c. of distillate, which is to be used as the reagent, collected.

This in presence of sulphuric acid gives the following colorations with the substances named: pyrogallol (brown), resorcinol (orange), catechol (red), apomorphine (violet-red), morphine (yellow to yellowish-brown), codeine (yellow, changing to green). In presence of sulphuric and acetic acids it gives the following reactions with the substances named: indole (strawberry-red), scatole (orange), pyrrole (brown). With potassium bromide and sulphuric acid the following colours are obtained: phenol (carmine-red, changing to orange), salicylic acid (violet), gallic acid (blue, changing to violet), benzene homologues (red), naphthalene (green), santonin (reddish-violet, changing to blue, and finally to green), and thiophen (red, changing to violet and blue). Traces of thiophen may be detected in benzene by this reagent.

Slight variations in applying the test are necessary in some cases, and these are given in detail in the original. Glyoxal gives reactions of a similar kind, but is less easy to use.

T. A. H.

Detection of Inositol in Natural Wines. G. PERRIN (*Ann. Chim. anal.*, 1909, 14, 182—183).—Two hundred c.c. of the sample are mixed with 20 c.c. of basic lead acetate and a few drops of alcoholic tannic acid. The filtrate is freed from lead by means of hydrogen sulphide, and after decolorising the filtrate with animal charcoal, if necessary, the colourless liquid is evaporated in a porcelain dish on the water-bath until 10—20 c.c. of a syrupy mass are left. Two drops of this are placed on a platinum foil with a drop of 10% silver nitrate solution, and the whole is evaporated and heated until the mass is carbonised;

on further incineration, a fine rose coloration, slightly violet, is noticed, which disappears on cooling, but returns on heating. L. DE K.

Seliwanoff's Reaction. WILLIAM OECHSNER DE CONINCK (*Bull. Soc. chim.*, 1909, [iv], 5, 569).—A reply to Pieraerts (this vol., ii, 272). The author states that the colorations obtained by heating with hydrochloric acid certain urines to which resorcinol has been added, are not characteristic of diabetes. These colorations, as far as diabetic urines are concerned, may be due to dextrose as well as lævulose. The Seliwanoff-Borchardt test is not at all an absolute one, and is no criterion of true lævulosuria. L. DE K.

Analysis of Galactose. ALBERT FERNAU (*Zeitsch. physiol. Chem.*, 1909, 60, 284—288).—The following modification of Tollens' method is recommended: 60 c.c. of nitric acid (1.15) are poured into 5 grams of galactose in a 150 c.c. beaker, and the mixture evaporated to 15—16 c.c. on a water-bath. When cold, 40 c.c. of water are added, and the mixture left for twelve hours at the ordinary temperature. The precipitate of mucic acid is then removed to a Gooch crucible, washed with 50 c.c. of water, dried in a steam-oven, and weighed. By this method, pure galactose invariably yields more than 70% of mucic acid. If smaller amounts of water are used, other acids are retained by the mucic acid and affect the result.

Any specimen which gives 70% of mucic acid may be regarded as fairly pure. J. J. S.

Defecation of Milks for the Estimation of the Lactose by Copper Solutions. CYRILLE CARREZ (*Ann. Chim. anal.*, 1909, 14, 187—188).—When dealing with human milk, most of the defecation reagents are unsuitable. The following process, however, gives satisfactory results: In a 100 c.c. flask are introduced the following substances in the order indicated; after each addition the contents are well mixed. Milk, 10 c.c.; water, 40—60 c.c.; ferrocyanide solution (150 grams per litre), 2 c.c.; zinc acetate solution (300 grams per litre), 2 c.c.; phenolphthalein (1% solution), 1 drop; aqueous sodium hydroxide, a sufficiency to get a slight coloration; water, up to mark. The filtrate, which represents the milk ten times diluted, may then be titrated with alkaline copper solution for lactose as usual. The method is, of course, also applicable to milks from other sources.

L. DE K.

The Estimation of Mannose, Arabinose, Xylose, and Hydrolysed Milk Sugar. REGINALD O. HERZOG and F. HÖRTH (*Zeitsch. physiol. Chem.*, 1909, 60, 152—154).—Tables are given showing the amount of cuprous oxide produced by different quantities of the sugars when treated with Fehling's solution according to Kjeldahl's method. S. B. S.

New Method of Estimating Starch in Grains and Meal. L. M. LJALIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 472—476).—The refraction of a starch solution is not altered by saccharifying the

starch, so that, in the estimation of starch by the refractometer, it is only necessary to effect complete liquefaction of the starch. Experiments with starches of various sources show that 1 gram of starch per 100 c.c. of solution corresponds with four scale-divisions of the Zeiss immersion refractometer. The diastase used by the author is precipitated from an aqueous infusion of a well-grown malt rich in protein by addition of ammonium sulphate, the method of estimation being as follows.

Two to three grams of the finely-ground cereal is pounded in a mortar with a little water, and introduced quantitatively into a 100 c.c. flask, the volume being made up to about 80 c.c. 0.2 c.c. of a 1% diastase solution is then added, the flask heated for five minutes on a boiling water-bath, and subsequently cooled to the ordinary temperature. A further 0.2—0.3 c.c. of the 1% diastase solution is then added, and the flask kept at 55—60° for half an hour, the liquid being then cooled, made up to 100 c.c., well shaken, filtered, and examined in the refractometer at 17.5°. In order to correct for the refraction of the soluble substances in the cereal, 2 to 3 grams of the latter are pounded with water in a mortar, made up to 100 c.c., and filtered, the refraction of the filtrate being measured at 17.5°.

This method gives results in good agreement with those yielded by Lintner's polarimetric method (Abstr., 1908, ii, 1077). T. H. P.

Estimation of Starch [in Potatoes, etc.]. M. BUISSON (*Bull. Assoc. chim. Sucr. Dist.*, 1909, 26, 980—983).—5.41 Grams (the normal weight of the French saccharimeter) of the potato pulp are introduced into a 200 c.c. flask, and 100 c.c. of water and 25 c.c. of cold saturated picric acid solution are added. The whole is heated in a calcium chloride bath (115°) and boiled for forty-five minutes, counting from the time it starts boiling. The flask is removed from the bath and 80 c.c. of water are added, and when the whole has cooled down to 15°, water is added up to the mark. The filtrate, which should be perfectly clear and fluid, is then polarised as usual. For farinas the picric acid may be reduced to 15 c.c. and the time of boiling to thirty minutes. L. DE K.

Reaction for Acetone. BRUNO BARDACH (*Chem. Zeit.*, 1909, 33, 570. Compare Abstr., 1908, ii, 332).—To 5 c.c. of the clear, nearly neutral solution to be tested are added 1 c.c. of a 3% solution of peptone, then Lugol's solution (made by dissolving 4 grams of iodine and 6 grams of potassium iodide in 100 c.c. of water) until the liquid turns dark reddish-brown, and finally 3 c.c. of ammonia. The liquid should remain dark brown for some ten minutes, and, if necessary, a little more iodine solution may be added. After an hour, the liquid is decanted from the precipitate formed, and the remaining portion is acidified with hydrochloric acid. If everything dissolves, there is no acetone present, but if a deposit remains, it is examined microscopically. It may be freed from any free iodine by a few drops of sodium thiosulphate, and if present in any quantity its characteristic appearance may be recognised by the naked eye. L. DE K.

Detection of Free Mineral Acids in Wine and Vinegar. LUIGI MEDRI (*Boll. Chim. Farm.*, 1909, 48, 331—337).—In place of decolorising wine or vinegar by means of animal charcoal before testing for mineral acids by methyl-violet, the author recommends dialysis of the liquid. The apparatus employed consists of a small beaker with widened upper part, the ledge serving as support for a capsule made from a parchment disk by turning the edge up. Water (50 c.c.) is placed in the lower part of the beaker, and the wine or vinegar (50 c.c.) into the capsule, which is pressed down into the water by the weight of the liquid in it. After an hour, 10 c.c. of the dialysate are removed and tested with 10—12 drops of a 0.1% solution of metanil-yellow; in presence of free mineral acid, the colour is changed to orange-yellow or red, according to the amount of the acid.

T. H. P.

Sensitive Reactions for Lactic and Glycollic Acids. GEORGES DENIGES (*Bull. Soc. chim.*, 1909, [iv], 5, 647—649).—The reactions depend on the fact that lactic and glycollic acids, when warmed with sulphuric acid, yield acetaldehyde and formaldehyde respectively, and that these aldehydes can be recognised by one of their characteristic colour reactions.

In practice not more than 0.2 c.c. of a solution of lactic acid (up to 2% strength) is warmed with 2 c.c. of sulphuric acid (D 1.84) at 100° during two minutes. To the cold mixture a drop of an alconal solution of guaiacol or codeine is added, when with the former a rose-red tint is produced, and with the latter, an orange-red coloration.

A similar method is used for glycollic acid, but in this case a higher temperature is required. With the cold solution, codeine gives a yellow coloration changing to an intense violet. Guaiacol gives a violet coloration changing to brown on dilution with alcohol, and *p*-cresol, a green tint. In using the two latter phenols, the mixture of glycollic acid, sulphuric acid, and phenol is slightly diluted with acetic acid, and the whole heated together.

T. A. H.

Detection of Benzoic Acid in Foodstuffs. Mlle. ANNA JONESCU (*J. Pharm. Chim.*, 1909, [vi], 29, 523—525).—When a solution of ferric chloride is added to one of benzoic acid, followed by a few drops of hydrogen peroxide solution, the liquid assumes a yellow tint, which changes gradually to deep violet, due to the conversion of the benzoic acid into salicylic acid by the action of the peroxide. It is proposed to apply this test to the detection of benzoic acid, or its salts, in such foods as butter and milk, the benzoic acid being separated by steam distillation. The colour reaction is also given by "saccharin."

T. A. H.

Estimation of Uric Acid in Urine. FERRUCCIO SICURIANI (*Chem. Zentr.*, 1909, 1, 1782; from *Arch. Farm. sperim.*, 1909, 8, 55—62).—One hundred and fifty c.c. of the sample are heated, and 5 grams of ammonium chloride are added. After one hour and a-half, the precipitate is collected and washed with 96% alcohol. The precipitate is then dissolved on the filter with 50 c.c. of *N*/10-potassium

hydroxide, and the filtrate plus the washings is boiled until no more ammonia is given off. When cold, the solution is titrated with *N*/10-sulphuric acid, using phenolphthalein as indicator. The number of c.c. of alkali consumed $\times 0.056$ = the amount of uric acid per litre.

L. DE K.

Estimation of Fats in Pork and Other Products Containing Water. GUSTAVE PERRIER (*Bull. Soc. chim.*, 1909, [iv], 5, 569—571).—The process described avoids the difficulties experienced in extracting fat from moist products with ether, and secures that the fat as isolated will not have become oxidised or otherwise changed. Ten grams of the material are triturated thoroughly in a mortar with 3 or 4 grams of washed and dried sand, and to this mixture is gradually added from 20 to 25 grams of anhydrous sodium sulphate, and the whole mixed completely. After half an hour, the mixture is transferred to a paper thimble, and extracted in a Soxhlet or other apparatus in the usual manner with ether; the extraction occupies about two hours, and yields a limpid solution.

T. A. H.

A New Reaction Characteristic of Adrenaline. SIGMUND FRÄNKEL and RUDOLF ALLERS (*Biochem. Zeitsch.*, 1909, 18, 40—43).—Most of the chemical reactions of adrenaline are also given by related substances; the following new and sensitive one is not. Iodic acid or potassium iodate and dilute phosphoric acid are warmed with a solution of adrenaline, when a red coloration is produced, which is believed to be due to the formation of an iodo- or iodoso-compound of adrenaline.

W. D. H.

Detection of Adrenaline in Blood-serum. G. COMESATTI (*Chem. Zentr.*, 1909, 1, 1609; from *Berl. Klin. Woch.*, 1909, 46, 8).—Six c.c. of fresh blood-serum, transudation, exudation, or extracts of organs prepared with physiological sodium chloride solution are shaken and then centrifugalised with double the volume of a solution made by dissolving 10 grams of mercuric chloride in 200 c.c. 95% alcohol. After twelve to twenty-four hours a diffused red colour is visible in the supernatant liquid should adrenaline be present.

L. DE K.

Detection of Adrenaline. KURT BOAS (*Chem. Zentr.*, 1909, 1, 1609; from *Zentr. Physiol.*, 1909, 22, 825—826).—The author having tried Comesatti's process (compare preceding abstract), obtained negative results, but on heating the mixture, the characteristic red coloration was obtained. In presence of a large excess of hydrochloric acid, adrenaline causes a violet coloration.

L. DE K.

General and Physical Chemistry.

Change in Refractive Index with Temperature. II. K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1909, 31, 806—821).—In an earlier paper (this vol., ii, 197) an account was given of measurements of the refractive indices of several liquids for the *C*, *D*, *F*, and *G'* lines at temperatures varying from 15° to 75°. The work has now been extended, and the results obtained for the *D*-line are given by the following equations: *iso*Butyl acetate, $n_D/1.40013 + t/2963.17 = 1$; ethyl butyrate, $n_D/1.40196 + t/2911.77 = 1$; *iso*amyl acetate, $n_D/1.40973 + t/3101.40 = 1$; methyl hexyl ketone, $n_D/1.42437 + t/3308.23 = 1$; nitrobenzene, $n_D/1.56146 + t/3339.79 = 1$; methylaniline, $n_D/1.58104 + t/3236.85 = 1$; benzyl cyanide, $n_D/1.53281 + t/3623.00 = 1$; benzaldehyde, $n_D/1.55439 + t/3404.86 = 1$. The densities of these liquids at different temperatures and the dispersions at 10° and 80° are recorded.

The refractive indices are plotted as curves, which show that in each case the index is a linear function of the temperature. The refractive powers were calculated for temperatures from 10° to 80°; the expression $(n_2 - 1)/d$ gave decreasing values as the temperature increased, $(n^2 - 1)/(n^2 + 2)d$ gave increasing values, whilst $(n - 1)d$ gave increasing values in some cases and decreasing values in others.

It is shown that the molecular refractions, calculated by using Brühl's values for atomic refractions, gave results agreeing with the experimental values as well at high as at low temperatures.

An attempt was made to study the state of equilibrium between the two forms of tautomeric substances, such as acetylacetone and ethyl acetoacetate, by means of the refractive indices, but it was found that only qualitative results could be obtained. E. G.

Flame Spectra of Certain Metalloids. CHARLES DE WATTEVILLE (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1909, 7, 279—285).—The solutions to be examined were sprayed into the gas or air supply of a Bunsen flame, which was photographed through a quartz spectrometer on Lumière plates or films.

Solutions of ammonia, ammonium nitrate, or nitric acid gave the same band spectrum, which was ascribed to ammonia by Eder and Valenta, but must be the spectrum of nitrogen itself. Phosphoric acid and ammonium phosphate give a regular spectrum of six groups of bands, which were noticed, among others, by Geuther in the arc spectrum of phosphorus, where they were the faintest bands present. Arsenic solutions give a spectrum of 15 lines and 4 groups of bands which is extremely similar to the alternating spark spectrum of arsenic, and is only seen in the hottest region of the flame. Antimony solutions or vapour of antimony pentachloride give a spectrum of forty-four known lines and a number of bands intermingled with the bands of the water vapour spectrum as described by Hartley.

The spectra described are all in the ultra-violet region beyond the range of the solar spectrum. R. J. C.

Ultra-red Line Spectra. II. Spectra of Thallium, Aluminium, Zinc, Cadmium, Magnesium, and Calcium. FRIEDRICH PASCHEN (*Ann. Physik*, 1909, [iv], 29, 625—663. Compare this vol., ii, 3).—The author has investigated in detail the ultra-red spectrum of the above metals. The representation of the various lines by means of series formulæ is considered.
H. M. D.

Influence of Pressure on the Absorption of Ultra-red Radiation by Gases. EVA VON BAHR (*Ann. Physik*, 1909, [iv], 29, 780—796).—The dependence of the ultra-red absorption on the pressure has been investigated for a number of different gases. In the case of carbon dioxide, carbon monoxide, nitrous oxide, carbon disulphide, methane, ethylene, acetylene, ammonia, and water vapour, the absorption increases with the pressure. The change in the absorption as the pressure is increased to one atmosphere is in general the same whether the increased pressure is brought about by the introduction of a foreign gas or by increase in the density of the absorbing gas. At low pressures the absorption increases rapidly with the pressure, but the rate of increase soon falls off, and the absorption approximates to a constant maximum value. In the case of carbon disulphide this condition is reached at 400—500 mm., in that of nitrous oxide at about 760 mm. On the other hand, for methane and carbon monoxide, the absorption increases with the pressure even at five atmospheres.

For a given gas the change of absorption with pressure is in general the same for the different absorption bands. In certain cases, increase in the density of the absorbing gas results in a widening of certain absorption bands, a phenomenon which is not brought about by increase in the total pressure as the result of admixture with a foreign gas.

The behaviour of methyl and ethyl ether is quite different from that of the above-mentioned gases, in that the ultra-red absorption of these vapours is independent of the pressure between 1 and 760 mm.

H. M. D.

Absorption of Ethereal Oils in the Ultra-violet. AL. PFLÜGER (*Physikal. Zeitsch.*, 1909, 10, 406).—The ultra-violet absorption of a number of ethereal oils and synthetic organic substances has been examined. A mercury lamp was used as radiator, a thermopile as indicator, and the substances were examined in thin layers between quartz plates. The percentage absorption values for various lines are tabulated.
H. M. D.

Phosphorescence at very low Temperatures. HENRI BECQUEREL, JEAN BECQUEREL, and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 76—88).—The authors have investigated the phosphorescence spectra of uranyl salts at the temperatures of liquid air and liquid hydrogen. The bands, which are characteristic of the uranyl salts at the ordinary temperature and undergo subdivision at the temperature of liquid air, are transformed into groups of much finer lines at the temperature of liquid hydrogen. At the same time the emission maxima are displaced towards the

smaller wave-lengths. Since the displacement is relatively small when the temperature falls from that of liquid air to that of liquid hydrogen, it is possible that the bands approach asymptotically a limiting position as the temperature is lowered.

From a comparison of the frequencies of the low temperature bands, the conclusion is drawn that the difference between the frequencies of two successive homologous bands is practically constant, and this holds for all series of homologous bands of the same salt. For different uranyl salts the values of this constant differ but slightly from one another. In structure, the uranyl salt bands resemble the band spectra of gases. At the temperature of solid hydrogen, a strong magnetic field has no influence even on the narrow bands.

The collective observations indicate that the phosphorescence of the uranyl salts is quite different in character from that of other classes of phosphorescent substances, and in no way depends on the presence of traces of impurities. The transfer of electrons under the photo-electric influence of the absorbed light appears to be a process which is entirely confined to the uranium atom, or at least to the uranyl group.

H. M. D.

Anomalous Rotatory Dispersion. LEO TSCHUGAEFF (*Ber.*, 1909, 42, 2244—2247).—Anomalous rotatory dispersion in the neighbourhood of absorption bands has been observed by Cotton (*Ann. Chim. Phys.*, 1896, [vii], 8, 347). The author has investigated three coloured substances, *l*-menthyldixanthogenide, $S_2(CS \cdot O \cdot C_{10}H_{19})_2$, thioanhydride of *l*-menthyl hydrogen xanthate, $S(CS \cdot O \cdot C_{10}H_{19})_2$, and *l*-bornyldixanthogenide, $S_2(CS \cdot O \cdot C_{10}H_{17})_2$, in toluene solution. The rotatory power in each case rises with diminishing wave-length, reaches a maximum, and then falls rapidly, the last two substances even showing a reversal of sign. The maximum lies nearer to the red end of the spectrum the more orange the colour of the compound examined. The position of the maximum varies with the solvent, obeying Kundt's rule.

C. H. D.

Isodynamic Change Revealed by Magnetic Rotatory Power. PAUL TH. MULLER and M. THOUVENOT (*Compt. rend.*, 1909, 149, 32—34).—Magnetic rotatory power has been shown by Becquerel to be quantitatively related to refractivity, which has been of great use in revealing tautomerism. Measurements here described of the magnetic rotatory power of substances well known to exist in tautomeric forms show that this property is also a trustworthy criterion of tautomerism. Methyl cyanoacetate dissolved in methyl alcohol has the magnetic rotatory power, $R = 4.371$, whereas its sodium derivative has $R = 7.312$ under like conditions. Ethyl acetoacetate and ethyl sodioacetoacetate in ethyl alcohol have $R = 6.580$ and $R = 11.25$ respectively. The difference, due to the substitution of sodium for hydrogen in these cases (2.94 and 4.67) being in excess of the normal difference on substituting sodium for hydrogen (between 1 and 2), is held to demonstrate the tautomeric difference in constitution between each sodium derivative and its parent substance.

On the other hand, methyl cyanoacetate or ethyl acetoacetate, whether as pure liquid or dissolved in alcohol, has practically the same magnetic rotatory power.
R. J. C.

Electrochemistry of Light VII. WILDER D. BANCROFT (*J. Physical Chem.*, 1909, 13, 449—468. Compare this vol., ii, 454).—A paper dealing with the theory of solarisation, in which the views of Abney, Trivelli, and others are discussed at length. Abney's view that the substance forming the latent reversed image is a silver oxybromide of the general type AgBr_xO_y is untenable, as hypobromous acid does not give satisfactory reversals even when the concentration is varied over fairly wide limits. The author's theory is based on the assumptions (1) that the action of light on a silver halide corresponds with that of a direct current (Grothaus), causing the silver halide to pass through all the possible stages; (2) a developer does not cause the silver halide to pass through all the possible stages, and reduces certain silver halogen solid solutions or subhalides faster than others which contain less halogen. Abney's statement that oxidising agents facilitate reversal is not strictly true. Experiments with potassium nitrite and potassium permanganate indicate that when no oxidising agent is used, the finished plate contains a more intense reversed image and a less intense normal silver image, and that the effect of depolarisers in causing a reduction to silver is diminished in the presence of an oxidising agent, so that the finished plate contains less of the normal silver image, and therefore gives a clearer reversed image.

The antagonistic effect of different lights and a number of other phenomena are also considered.
G. S.

De-accelerating Action of Bromides in the Photographic Developers. SAMUEL E. SHEPPARD (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 43—44).—In opposition to Lüppo-Cramer's view that the influence of bromides in diminishing the velocity of development is to be attributed to a colloido-chemical process, the author points out that the reaction is reversible, and can be explained completely from the molecular-kinetic standpoint as a consequence of the diminution of the concentration of the silver ions which are formed from the silver bromide.
H. M. D.

Photopolymerisation of Anthracene. ALFRED BYK (*Zeitsch. physikal. Chem.*, 1909, 67, 64—77).—Weigert has recently stated (Abstr., 1908, ii, 748) that the author's electrochemical addition to the thermodynamic theory of photochemical processes (Abstr., 1908, ii, 339) is unnecessary, but it is now shown that this is not the case. In connexion with the experimental basis of the theory, it is shown that the molecular weight of anthracene in phenetole is approximately normal, and up to a concentration of 0.37 mol. per litre does not tend to increase with the concentration.
G. S.

Quantitative Study of the Photochemical Reaction between Quinine and Chromic Acid. ROBERT LUTHER and GEORGE SHANNON FORBES (*J. Amer. Chem. Soc.*, 1909, 31, 770—783).—A study of the reaction between chromic acid and quinine in light has been made

by Goldberg (Abstr., 1906, ii, 514), whose results seemed to indicate that the velocity was dependent on the quantity of light absorbed by the chromic acid.

It has now been found, however, by means of monochromatic light, that the quinine is the substance which is sensitive to light, whilst the chromic acid only acts as an indifferent light filter, absorbing a part of the light and converting it into heat. Determinations of the initial velocities of the reactions induced in solutions by monochromatic light have been made, and the quantities of light absorbed by the quinine and chromic acid have been calculated from measurements of extinction coefficients. The concentrations of the reacting substances, the intensity of the incident light, and the wave-length of the light were varied, one at a time, in successive experiments. The apparatus is described with the aid of a diagram. The source of light was a uviol mercury vapour lamp, and a series of light filters were employed. It was found in preliminary experiments that the total reaction velocity was proportional to the concentration of the hydrogen ion. In order to make this velocity large enough for convenient measurement, sulphuric acid (2.7 mols. per litre) was added to the reaction mixtures.

It has been found that the photochemical reaction is exactly the difference between the total reaction and the spontaneous reaction of the same mixture in the dark, and that the combined effect of two rays is additive. The speed of the photochemical reaction is proportional to the quantity of light of given wave-length absorbed by the quinine alone unless the concentration of the chromic acid is very small. It is probable that the reaction takes place in two stages: (1) the formation of sensitised quinine with a velocity proportional only to the light absorption, and (2) a reaction, in the ordinary sense, between this product and chromic acid with a velocity proportional to the concentration of the chromic and sulphuric acids. Formulæ have been deduced from which the velocity can be calculated of the reaction produced by the incidence of known amounts of light of various wave-lengths on any mixture of quinine and chromic acid under the conditions of the investigation. The photochemical efficiency of a given amount of absolute light-energy decreases as the wave-length of maximum absorption is approached. The effect of varying the thickness of the layer has been studied, and it is found that for given light absorption the velocity induced is inversely proportional to the thickness. The relative effect of two rays of different wave-length depends entirely on the thickness of the layer. E. G.

Amount of Radium Present in Sea-water. A. S. EVE (*Phil. Mag.*, 1909, [vi], 18, 102—107).—The examination of six samples of sea-water from the North Atlantic indicates the average radium content to be 9×10^{-16} gram per gram of sea-water. This is about one-seventeenth of the value found by Joly.

In the course of the measurements, it was observed that radium emanation may be collected either over water or mercury without any appreciable difference in the results obtained. H. M. D.

Expulsion of Radio-active Matter in the Transformations of Radium. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1909, 10, 422).—In reference to a recent publication of Russ and Makower (this vol., ii, 455), the authors point out that they have already explained certain observations as being due to the recoil of the atomic residues which result from the emission of α - and β -particles.

H. M. D.

α -Rays from Radium-*B*. HOWARD L. BRONSON (*Physikal. Zeitsch.*, 1909, 10, 393—395).—The author has examined the influence of the air-pressure on the ionisation due to the active deposit on a wire exposed to radium emanation. The ionisation values are proportional to the pressure between 3 and 76 cms. of mercury, and from this the author draws the conclusion that no α -particles with a range between 0.5 and 5 mm. are emitted by the active deposit. These observations contradict the conclusion drawn by Harvey (this vol., ii, 203) that small range α -particles are emitted by radium-*B*.

H. M. D.

Condensation of Radium Emanation. A. LABORDE (*Compt. rend.*, 1909, 148, 1591—1593).—Rutherford and Soddy (Abstr., 1903, ii, 462) found that when radium emanation is condensed in a copper tube by means of liquid air, it became gaseous once more when the temperature rose to about -150° . The author has used tubes of different materials in order to see if this temperature varied with the material of the tube. The emanation was condensed in the tube, and then a current of dry air, free from carbon dioxide, drawn through it, the air being tested for emanation from time to time as the temperature of the tube rose. With tubes of copper, iron, tin, and silver, the temperature at which the emanation became gaseous was -153° to -155° , whereas, with glass and silvered glass, it was -177° . This difference in temperature is possibly due to the absorption of the emanation by the metals, and consequently the effects of cocoanut charcoal, meerschaum, platinum-black, and spongy platinum were studied. With these substances, spongy platinum excepted, the liberation of the emanation took place slowly, and not rapidly as in the case of the metal tubes, and was not complete in an hour even when the temperature was raised considerably.

The conclusion is drawn that the temperature at which radium emanation is condensed depends on the physical nature of the containing vessel.

T. S. P.

Comparison of the α -Rays Produced by Different Radio active Substances. MLE. BLANQUIES (*Compt. rend.*, 1909, 148, 1753—1756).—If the α -particles emitted by different radio-active substances differ only in their velocity of projection, then, at one and the same distance from the end of their course, they should have the same properties, independent of the substance from which they are emitted. In order to test this, the author has made experiments with polonium, radium-*C*, and actinium-*B*. To obtain a homogeneous radiation, it was necessary to use an extremely thin layer of the radio-active substance, since the velocity of particles emitted from the interior of a

thick layer is diminished by passage through the layer. The polonium was deposited electrolytically on a sheet of metal, and the other two substances were obtained by exposing sheets of metal for some hours to the emanations from radium and actinium. The ionisations produced by these substances at different distances were then measured, and curves plotted, showing the relation between ionisation and distance. These curves, after making corrections for the unequal activities of the three substances, should be superposable. This was found to be the case for polonium and radium-*C*, but not for actinium, the rate of decrease of activity with distance being less for actinium than for the two other substances.

The explanation put forward is that the α -particles emitted by the three substances are identical, except in so far as their velocities of projection are concerned, but that the radiation from actinium-*B* is complex. Actinium-*B* is supposed to be transformed, with the emission of α -particles, into another substance with a very short period of decay, which also emits α -rays. T. S. P.

Radioactivity of Potassium Salts. ÉMILE HENRIOT and G. VAVON (*Compt. rend.*, 1909, 149, 30—32. Compare Henriot, this vol., ii, 458).—The authors find it impossible to concentrate the radioactivity of potassium by fractional crystallisation of potassium chloride, or its precipitation by gaseous hydrogen chloride, or by repeated precipitations of barium sulphate in potassium sulphate solutions. The various products obtained differed in radioactivity by less than 1%.

The radiation, which must be assumed to come from the potassium atom, possesses the penetrative power of β -rays, and is deviable by a magnetic field (compare Campbell, *Abstr.*, 1907, ii, 597). The authors show that the rays are deviated as a negative flux would be, and can produce ionisation after passing through a sheet of tinfoil. This is held to prove definitely that potassium emits β -rays. R. J. C.

[**The Radioactivity of Pitchblende from St. Joachimsthal.**] JOSEF ŠTĚP (*Oesterr. Zeitsch. Berg. Huttenwesen*, 1909, 57, 155).—A description of the apparatus and calculations employed for estimating the radioactivity in the raw, intermediate, and final products of the St. Joachimsthal uranium factory. The author was led to conduct this research from the work of H. Mache and S. Meyer, who demonstrated that a larger yield of radium chloride might be obtained from a given quantity of pitchblende than Curie had obtained.

F. M. G. M.

Induced Activity on the High Sea. H. SIEVEKING (*Physikal. Zeitsch.*, 1909, 10, 398—399).—The rate of decay of the induced activity collected on a negatively-charged wire exposed for two hours during a journey from Alexandria to Naples has been examined. The observed rate of decay agrees with that obtained for the disintegration products of radium, and no evidence of thorium activity was found. In the author's opinion, the radium emanation is carried by air currents from the land. H. M. D.

Ionisation in the Atmosphere. A. S. EVE (*Le Radium*, 1909, 6, 88).—The apparatus for this estimation is described, and the following results deduced. If the value of the charge of an ion be taken as 3.4×10^{-10} U E S, and if it be supposed that an ion carries a single elementary charge, the following numbers are indicated.

Series.	Number of + ions per cm. ³ .	Number of - ions per cm. ³ .	Relation.
1	37,570	34,300	1.09
2	19,900	10,100	1.99
3	22,320	16,820	1.33
4	14,330	11,850	1.21
5	7,280	5,800	1.25
		average	1.39
without radium	1,280	1,050	1.22

The variations in results are due to changes in hygrometric conditions, or to the presence of water vapour. One point is well marked, namely, that although the γ -rays of radium produce equal quantities of positive or negative electricity, the ionisation of a gas in a closed vessel leads to the production of a large excess of positive electricity.

F. M. G. M.

Effect of Temperature on Ionisation. J. ARNOLD CROWTHER (*Proc. Roy. Soc.*, 1909, 82, A, 351—357).—The ionisation produced by Röntgen rays has been measured in air at the temperature of liquid air, and in ethyl bromide and methyl iodide at various temperatures up to 184°. In every case the ionisation produced was found to be independent of the temperature if the density of the gas remained constant.

G. S.

Ionisation [Produced] in Various Gases by Secondary γ -Rays. R. D. KLEEMAN (*Proc. Roy. Soc.*, 1909, 82, A, 358—377).—The ionisation produced in various gases and vapours by secondary γ -rays has been measured by the usual method. Zinc, carbon, and lead were used as radiators. The results are given in tabular form, and are compared with those obtained for α -, β -, and primary γ -rays, and for soft and hard X-rays by previous observers.

The results can be divided into three sets. The first set consists of gases the molecules of which are composed of atoms of hydrogen, carbon, nitrogen, oxygen, sulphur, chlorine; in these the ionisation is much the same for α -, β -, and primary and secondary γ -rays, and does not vary much with the nature of the radiator. The second set consists of gases the molecules of which contain at least one atom of greater mass than the chlorine atom; for these the ionisation is greater for secondary than for primary γ -rays, and the ionisation for different rays varies considerably with the nature of the radiator. The third class consists of hydrogen, which shows several peculiarities.

The ionisation for the various gases, with the exception of hydrogen, is approximately additive, being made up of the sum of the atomic ionisations. The atomic ionisations for the primary and secondary γ -rays are plotted as ordinates against the atomic weights as abscissae, and it is shown that, whereas the upward slope of the curve for the

secondary rays increases with increase of atomic weight, the curve for the primary rays shows no increase in slope.

The degree of ionisation depends somewhat on the direction of propagation of the secondary rays with respect to that of the primary.
G. S.

Heat Developed by Polonium. WILLIAM DUANE (*Compt. rend.*, 1909, 148, 1665—1667).—The heat liberated by 0.2 gram of a salt rich in polonium, but free from radium and radiothorium, has been measured by the method previously described (this vol., ii, 534). In order to absorb in the thermo-junction the heat disengaged by the polonium, a current of 0.00143 ampere was required, corresponding with a liberation of 0.0117 cal. per hour. The ionisation produced in air by the α -rays from the same quantity of polonium was found to give a saturation current of 1.3×10^{-7} amperes. According to Rutherford the same saturation current is obtained with 0.749 mg. of radium bromide free from emanation and induced activity. This quantity of radium bromide disengages 0.011 cal. per hour (Duane, *loc. cit.*), a value very near that now found for the polonium (0.0117 cal. per hour).

Polonium and radium emit α -particles only, and these have approximately the same range (38.6 mm. and 35 mm. respectively), that is, the same kinetic energy. Since quantities of polonium and radium producing the same ionisation effect develop almost the same amounts of heat, it appears probable that the heat given out by these two substances is derived from the kinetic energy of the α -particles emitted.
R. J. C.

Effect of Temperature on the Rate of Production of Uranium-X. R. W. FORSYTH (*Phil. Mag.*, 1909, [vi], 18, 207—209).—Uranium nitrate, freed from uranium-X by Crookes's method, was ignited, and the resulting oxide divided into two equal portions. These were enclosed in quartz tubes, one being kept at the temperature of the laboratory, the other heated at 1000°. The rate of formation of uranium-X in the two specimens was followed by measurements of the β -ray activity. The results indicate that the rate of production of the β -ray substance at 1000° is not sensibly different from that at the ordinary temperature.
H. M. D.

Distribution of Thorium in the Earth's Surface Materials. JOHN JOLY (*Phil. Mag.*, 1909, [vi], 18, 140—145. Compare this vol., ii, 458).—The values previously recorded for the thorium content of various minerals are reduced by one-third as a result of a re-standardisation of the author's electroscope. New data for the rocks of the St. Gothard Tunnel have been obtained, and for these it appears that the thorium content is roughly proportional to the quantity of uranium present.
H. M. D.

Physical Origin of the Liberation of Electricity in Chemical Reactions. MAURICE DE BROGLIE and L. BROZARD (*Compt. rend.*, 1909, 148, 1596—1598; this vol., ii, 535).—The liberation of electricity in chemical reactions is not due to any chemical causes; it

is a physical phenomenon caused by the rupture either of a liquid surface or of the surface of a crystal.

If crystalline salts are heated to such a temperature that they decrepitate without, at the same time, undergoing decomposition, electrically charged powders are obtained, owing to the breaking of the crystal surfaces; if the salts have been fused previously and are heated to the same temperature, there is no electrical charge. On the other hand, when amorphous powders, such as lead carbonate, are decomposed by heat, there is no liberation of electricity, silver oxide being, however, an exception.

When gases are prepared in the wet way, their electrical charge is solely due to the splashing of the bubbles of gas in the liquid. This explains the charged fumes which are formed when such substances as sulphur trioxide or phosphorus pentachloride are thrown into water; if these substances are simply exposed to moist air, the fumes are not charged. Certain liquids, for example, benzene, do not become charged when agitated (splashed), and in these cases the fumes evolved when they are submitted to the vigorous action of nitric acid are not charged.

In chemical reactions which give rise to a charged powder, and, at the same time, a high temperature, the electrical charge may be due to a physical cause, although the experiments of Garrett and Willows (Abstr., 1907, ii, 524) indicate that there is a chemical expulsion of electrons, and the charge acquired by heated salts has been studied by J. J. Thomson (Abstr., 1907, ii, 221).

T. S. P.

Measurement of the Intensity of the Field along the Axis of a Coil of Wire by Weighing, and its Application to the Deduction of Absolute Values of the Verdet Constant of Certain Liquids. N. STOYANOFF (*Physikal. Zeitsch.*, 1909, 10, 430—438).—Measurements of the electromagnetic rotation of the plane of polarisation have been made for light of various wave-lengths. From these the Verdet constants for carbon disulphide, benzene, and nitrobenzene have been deduced.

H. M. D.

Molecular Condition of Salts Dissolved in a Fused Salt. II. The Electrical Conductivity of Salts in Fused Mercuric Chloride. H. W. FOOTE and N. A. MARTIN (*Amer. Chem. J.*, 1909, 41, 451—457. Compare Abstr., 1907, ii, 440).—Beckmann (Abstr., 1907, ii, 739) has recently found that the molecular weights, as determined by the freezing-point method, of the alkali chlorides and of mercurous and cuprous chlorides in fused mercuric chloride agree very closely with those calculated in every case except that of cuprous chloride, in which the values found lie between those necessary for CuCl and Cu_2Cl_2 . The authors have now investigated the conductivities at 282° of such solutions, using platinum electrodes in a special apparatus. It is found that the molecular conductivities are high, and that they decrease with the dilution in every case. The salts used were cuprous chloride and the chlorides of caesium, potassium, sodium, and ammonium. Chlorides of bivalent metals were nearly all insoluble.

The explanation given of the results is that a complex salt is

formed, which then dissociates in solution: $2MCl + HgCl_2 \rightarrow Mg_2HgCl_4 \rightarrow \overset{+}{M} + M\overset{-}{Hg}Cl_4$. Two molecules of alkali chloride give two ions, so that the depression due to the ions would be the same as that due to the original salt. The dissociation expressed by the above equation should be independent of the dilution; the increase in conductivity with the concentration is probably due to the formation of some other complex salt in solution.

Solutions of mercurous chloride do not conduct electricity, in marked contrast to those of cuprous chloride. T. S. P.

Absolute Zero of Potential. JEAN BILLITER (*Zeitsch. Elektrochem.*, 1909, 15, 439—440).—In reply to Freundlich and Mäkel (this vol., ii, 368), the author upholds the accuracy of his views, and thinks that the exceptional behaviour of ammonia which they observed is not a sufficient reason for rejecting the evidence in very different directions which he has accumulated. T. E.

Ionisation of Air by High Tension Electric Cables. LOUIS HOULLEVIGUE (*Compt. rend.*, 1909, 148, 1668—1670).—It has been suggested that high tension aerial transmission lines give off swarms of ions which bear enormous electric charges into the air and may give rise to storms. The author estimates the ions in a volume of air by drawing it slowly through a cylindrical condenser connected to a charged electroscope. The number of ions deposited in the condenser is proportional to the discharge of the electroscope.

Air collected 3 cm. from the spark of a Ruhmkorff coil contained 2.8×10^5 negative ions per c.c., the charge per ion being taken as 3.4×10^{-10} coulomb. The same air after passing through 5 metres of rubber tube contained only 0.44×10^5 negative ions per c.c. The air in a Marseilles street contained 0.16×10^5 negative, and 0.20×10^5 positive, ions per c.c.

Measurements were taken of the air at 200 metres and 10 metres from an aerial line conveying 3-phase current at 50,000 volts. As these showed no appreciable ionisation, experiments were continued in the receiving chamber, where, owing to the lightning conductors, continuous discharges occur with formation of ozone. Air was also examined in the transforming station at 30 cm. from the cables with a rubber tube, or at 1 metre distance without rubber tube. In all cases the ions were fewer in the neighbourhood of the high tension cables than in the air of the surrounding country, and considerably less than in Marseilles. R. J. C.

Cathodic Volatilisation of Metals in Dilute Gases. V. VOLKMAR KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1909, 15, 316—328).—The author's previous results (Abstr., 1908, ii, 457, 799, 800, 925) were obtained with the fluctuating current of an induction coil, and the electrical conditions were therefore ill-defined. The experiments described in this paper are made with the direct current of a Töpler electrical machine, and the cathode fall of potential and the current passing are measured. The cathode used is a wire sealed into a glass

tube and placed in the centre of a glass globe so that the discharge is not influenced by the walls of the vessel. The discharge is prevented from taking place from the glass tube carrying the cathode by means of a disc of mica which is fitted at the base of the wire. The results confirm those obtained by Holborn and Austin (*Wiss. Abhand. Phys.-Techn. Reichsanstalt*, 4, 101) in air. In nitrogen, volatilisation begins at a certain value of the cathode fall, which is the same for all metals (570 volts), and then increases in proportion to it. It is also proportional to the equivalent of the metal if the valencies of the metals are taken as follows: silver, 1; gold, 2; platinum, 3; palladium, 2; copper, 2, and nickel, 4. The magnitude of the volatilisation is in the order given. In argon, gold is more volatile than silver, the order being otherwise the same. Silver and platinum begin to volatilise when the cathode fall of potential is 420 volts; the other metals begin at 570 volts as in nitrogen. The valencies found in argon are also different; gold, silver, palladium, and copper are univalent, and platinum and nickel bivalent.

In hydrogen the volatilisation is always small, and the quantities volatilised instead of increasing regularly with the cathode fall appear very quickly to reach a maximum or become constant.

Calling P the quantity volatilised ($\text{mg.} \times 10^{-1}$) by a current of 7×10^{-4} ampere in thirty minutes, V the cathode fall in volts, A the atomic weight, and n the valency, $P = k.A(V - S)/n$, where S is the cathode fall at which volatilisation begins. The mean values of $n.k/A$ are in nitrogen 0.000396, and in argon, 0.000371.

With the same current and the same cathode fall the volatilisation is always greatest in argon, and least in hydrogen.

The quantity volatilised is proportional to the current. T. E.

Thermo-elements. O. KNOPP (*Physikal. Zeitsch.*, 1909, 10, 439—445).—The dependence of the thermo-electric force on the resistance of the junction, on the nature of the juxtaposed metals or alloys and on the percentage composition of the alloys, on the thickness of the wires, and the influence of temperature and gas pressure, has been experimentally examined. H. M. D.

Oxide Theory of the Oxygen Electrode. IV and V. RICHARD LORENZ and PERCY E. SPIELMANN (*Zeitsch. Elektrochem.*, 1909, 15, 293—297, 349—355. Compare this vol., ii, 15, 371, and 463).—In the first part of the paper the *E.M.F.*'s of a platinum oxide electrode and a hydrogen electrode are measured by the compensation method, that is, with no current flowing. The platinum oxide electrode was made by surrounding a platinum wire with a paste of the oxide in *N*-sulphuric acid, or sometimes acetic acid. Some salts of platinum are also examined in saturated solution. The mean values found are: $\text{PtO}_2 \cdot 4\text{H}_2\text{O}$, (0.829) volt; $\text{PtO}_2 \cdot 3\text{H}_2\text{O}$, 0.982 (0.736) volt; $\text{PtO}_2 \cdot 2\text{H}_2\text{O}$, 0.965 (0.722) volt; $\text{PtO} \cdot 2\text{H}_2\text{O}$, 0.949 (0.647) volt; K_2PtCl_6 , 0.740; PtCl_4 , 0.936; K_2PtCl_6 , 0.720; PtCl_2 , 0.875, and $\text{BaPt}(\text{CN})_6$, 0.604. The numbers in brackets refer to acetic acid solutions. Among the oxides, the greater the content of oxygen and water the greater is the *E.M.F.*, but the values lie so near each other that the authors suspected some error. It is known, for example, that

platinous oxide decomposes into platinum dioxide and platinum. Another method was therefore tried in which the cell was allowed to discharge through a high resistance. The *E.M.F.* time curve then shows a number of arrests, each of which corresponds with some definite compound. From the study of a very large number of such curves, the following *E.M.F.*'s (in *N*-sulphuric acid) are taken as corresponding with the known oxides.

$\text{PtO}_2, 4\text{H}_2\text{O}$, 0.93 volt ; $\text{PtO}_2, 3\text{H}_2\text{O}$, 0.86 volt ; $\text{PtO}_2, 2\text{H}_2\text{O}$, 0.74 volt ; $\text{PtO}, 2\text{H}_2\text{O}$, 0.45 volt. In addition to these four arrests, six others were observed ; these are provisionally ascribed to the following compounds : $\text{PtO}_2, \text{H}_2\text{O}$, 0.63 ; PtO_2 , 0.53 ; $\text{PtO}, \text{H}_2\text{O}$, 0.34 ; PtO , 0.25 ; PtSO_4 , 0.15, and Pt , 0.05.

These *E.M.F.*'s agree with those found by Lorenz and Lauber in the discharge curves of polarised platinum electrodes. The three highest points observed by these authors are not, however, as yet identified.
T. E.

Graphite Cathode Dish. J. W. TURRENTINE (*J. Physical Chem.*, 1909, 13, 438—448).—A graphite cathode dish which can take the place of the Classen platinum dish as cathode in many electro-chemical operations is described. The dish was turned on a lathe, and, after treatment with paraffin, it no longer rubbed off on the finger or absorbed solutions placed in it. It could not be dried after an experiment by treatment with alcohol like a platinum dish, but satisfactory results were obtained by drying directly over the smokeless flame of a Bunsen burner. The electrolytic estimation of solutions of copper sulphate, using the graphite cathode and a copper anode, gave satisfactory results when compared directly with a coulometer containing a copper cathode. A graphite anode has been designed for use with the dish, and the efficiency of the apparatus is being further tested.
G. S.

Piezoechemical Studies. ERNST COHEN and L. R. SINNIGE (*Zeitsch. physikal. Chem.*, 1909, 67, 1—47).—A detailed account of work already published (compare this vol., ii, 291).
G. S.

Magnetic Transformation of Lead. LUTSHINSKY (*Compt. rend.*, 1909, 148, 1759—1760).—The coefficient of magnetisation of lead crystals obtained from the fused substance is about ten times greater than that for lead which has been mechanically treated by hammering or drawing into wire. The coefficient varies with the treatment.

Similar results have been obtained with a lead-tin alloy containing 30% of tin, but not with pure zinc, tin, ammonium nitrate, or potassium chloride. The compound Zn_{10}Fe is not magnetic until fused ; the magnetic properties are then due to the partial separation of iron.
T. S. P.

Magnetic Dichroism of the Rare Earths. GEORGES MESLIN (*Compt. rend.*, 1909, 148, 1598—1599).—In the group of the rare earths the magnetic properties of neighbouring elements differ considerably, although the solubilities of their salts are almost identical

and their atomic weights only slightly different (compare Urbain, Abstr., 1909, ii, 116).

The author has studied the magnetic dichroism and the dichroism of the oxalates of lanthanum, samarium, gadolinium, and dysprosium in five different liquids. The magnetic dichroism of lanthanum and dysprosium is more marked than that of samarium and gadolinium, gadolinium being inactive in four out of the five liquids. Gadolinium and dysprosium do not show ordinary dichroism. T. S. P.

Metronome Interrupters for Electromagnetic Stirrers in Freezing-point Apparatus. ERNST BECKMANN (*Zeitsch. Elektrochem.*, 1909, 15, 355—357).—When a metronome is used to make and break the electrical circuit of an electromagnet, sparks are apt to spoil the contact. A detailed description with figures is given of two arrangements which have been found satisfactory; the contact piece is simply made movable, so that a clean surface can be brought into action. T. E.

Ebullioscopic and Cryoscopic Measurement of Molecular Weights in Iodine. ERNST BECKMANN (*Zeitsch. anorg. Chem.*, 1909, 63, 63—64).—Iodine, like chlorine and bromine (Abstr., 1903, ii, 235; 1906, ii, 845; this vol., ii, 137), is a good solvent. Ebullioscopic measurements give the molecular weights corresponding with Al_2I_6 and Fe_2I_6 ; sulphur gives S_8 , and selenium, S_2 . The ebullioscopic constant, determined by means of Sn, Bi, and SbSnI_4 , is 110° . The cryoscopic constant, from experiments with Sn, SnI_4 , HgI_2 , Sb, and CH_3I , is 210 (253.5° : Timmermanns, Abstr., 1906, ii, 429). Sulphur and selenium give the same results as on boiling. Since at 860° selenium still has a molecular weight in excess of Se_2 , the temperature of the iodine does not appear sufficiently high to cause dissociation of the Se_{10} and Se_8 molecules. Violet solutions of iodine in carbon disulphide or carbon tetrachloride become brown on shaking with selenium, and combination thus appears to occur. The iodine-selenium freezing-point curve, however, does not indicate the formation of a compound (Pellini and Pedrina, Abstr., 1908, ii, 833). C. H. D.

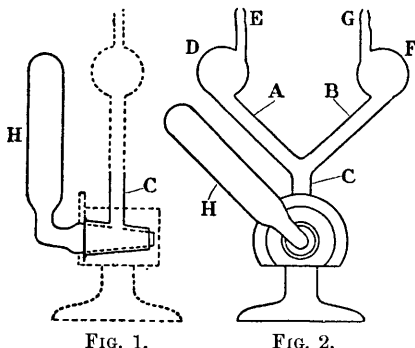


FIG. 1.

FIG. 2.

Pressure Regulator for Vacuum Distillation. HERMANN J. REIFF (*Zeitsch. angew. Chem.*, 1909, 22, 1360—1361).—The apparatus described is an improved form of Bertrand's pressure regulator (Abstr., 1903, ii, 643). It consists of a Y-shaped tube

A , B , C , into the lower limb of which a closed tube, H , is ground so as to be capable of rotation vertically. The other limbs, A and B , each carry a bulb and a short tube, indicated respectively by D E and F G .

Tube *H* and part of *C* are filled with mercury, *D* and *F* are filled with glass beads to arrest mercury spray, and *E* is connected to the pump and *G* to the distillation apparatus. When the pressure is reduced to a certain point, the mercury will sink in *H* and rise in *C* sufficiently to close the passage through *A B*. The pressure at which this occurs is regulated by rotation of the mercury tube *H*, the vertical position indicated in Fig. 1 being that of maximum pressure, Fig. 2 a position of decreased pressure.

J. V. E.

Measurement of the Saturation Pressure of Water Vapour below 0°. KARL SCHEEL and WILHELM HEUSE (*Ann. Physik*, 1909, [iv], 29, 723—737).—Measurements have been made of the vapour pressure of supercooled water between 0° and -15.3°, and of ice between 0° and -68°. The pressures were recorded by means of a Rayleigh manometer. As the sum of several determinations, the vapour pressure at 0° is 4.5788 ± 0.0006 mm. The variation of pressure with temperature cannot be satisfactorily represented by the formula of Hertz or that of Thiesen. On the other hand, the experimental data show a maximum difference in the vapour pressures of water and ice at -11.7°, and this is the temperature indicated by Thiesen's formula.

H. M. D.

Simple Method for Determining Vapour Densities. IX and X. PHILIP BLACKMAN (*J. Physical Chem.*, 1909, 13, 426—432. Compare this vol., ii, 298).—A modified method for determining the vapour density of liquids is described. In a long capillary tube is placed a thread of mercury, and at some distance from the latter a thread of the liquid in question, the tube is sealed, heated to a temperature at which the liquid is completely vaporised, and the density calculated as in the method already described. Further practical details in connexion with the previous methods are given.

G. S.

New Method for Determining Vapour Densities. VII and VIII. PHILIP BLACKMAN (*J. Physical Chem.*, 1909, 13, 433—435. Compare this vol., ii, 298).—A method for determining vapour densities is described, in which the increase of pressure produced when a known weight of liquid is vaporised at constant volume is determined.

G. S.

Simple Method for Determining Vapour Densities and for Analysing Binary Mixtures. PHILIP BLACKMAN (*Chem. News*, 1909, 100, 13—14).—A method for determining vapour densities, very similar to that already given by the author, is described in detail. The apparatus may also be used for analysing binary mixtures when the respective vapour densities of the components are known.

G. S.

Calculation of Critical Densities. REGINALD O. HERZOG (*Zeitsch. Elektrochem.*, 1909, 15, 345—348).—If Avenarius' equation: $v = a - b \log(T_k - T)$, where v is the specific volume of a substance at

the absolute temperature T , T_k its critical temperature, and a and b are constants which depend on the nature of the substance, is divided all through by the critical volume, the quantities a/v_k and b/v_k are found to be constants for all non-associated substances. The critical density may, therefore, be calculated for such compounds from the formula $d_k = d[0.906 - 0.233 \log(T_k - T)]$. The calculated values (for 40 substances) differ occasionally as much as 10% from those observed, but the agreement is in most cases much better.

T. E.

New Form of Characteristic Equation of Gases. ANATOLE LEDUC (*Compt. rend.*, 1909, 148, 1670—1673. Compare this vol., ii, 298, 381, 382).—Since Van der Waals' and other equations do not satisfactorily represent deviations from Boyle's law between 0 and 3 atmospheres pressure, the author endeavours to formulate an equation of the Clausius type which shall do so.

The equation given is $(P + F/v^2)(v - h) = k\theta$, where h and k are constants, and F is a somewhat complicated function of the temperature θ . To h is assigned the value $3/8 \sqrt{2} = 0.265$ calculated by O. E. Meyer. Employing the known values of the specific volume and critical density of carbon dioxide, nitrous oxide, and sulphur dioxide, k is found to be about 3.6. By the use of these constants, the critical densities and internal pressures of sixteen gases are approximately calculated. There appears to be a systematic error, however, which may necessitate a further term in the characteristic equation.

R. J. C.

Heat of Formation of Titanium Dioxide and Heat of Combination of Acidic Oxides with Sodium Oxide. WILLIAM G. MIXTER (*Amer. J. Sci.*, 1909, [iv], 27, 393—397).—The heat developed in the oxidation of metallic titanium by sodium peroxide corresponds with the equation $\text{Ti} + \text{O}_2 = \text{TiO}_2$ (amorphous) + 215,600 cal. From measurements of the heat developed in the action of sodium peroxide on titanium dioxide, lead peroxide, zirconium dioxide, and ceric oxide, the following data are obtained: $\text{Na}_2\text{O} + \text{TiO}_2 + \text{O} = \text{Na}_2\text{TiO}_4 + 69,700$ cal.; $\text{Na}_2\text{O} + \text{PbO}_2 = \text{Na}_2\text{PbO}_3 + 38,700$ cal. With zirconium dioxide the fusions obtained were not satisfactory, but the results indicate that the union of the acid and basic oxide is attended by only a small development of heat. In the case of cerium the thermal data indicate that sodium oxide does not combine with the acid oxide.

H. M. D.

Comparisons between Nitriles and Carbylamines. PAUL LEMOULT (*Compt. rend.*, 1909, 148, 1602—1604. Compare Abstr., 1907, ii, 10).—The author compares the experimental values obtained by Guillemard (*Thesis*, Paris, 1908) for the heats of combustion of methyl-, ethyl-, propyl-, isobutyl-, isoamyl-, benzyl-, and allyl-carbylamines with the theoretical values calculated from his own formula (Abstr., 1904, ii, 382), adopting 17 Cal. as the thermal equivalent of the carbylamine grouping. The results are found to be in close agreement. The heats of combustion of the following nitriles have

also been determined : acetonitrile, 304 Cal. ; propionitrile, 458.5 Cal. ; *n*-butyronitrile, 616.3 Cal. ; isovaleronitrile, 775.7 Cal. ; α -naphthonitrile, 1333.2 Cal. ; β -naphthonitrile, 1327.3 Cal. These values also accord closely with the calculated numbers.

W. O. W.

Absorption of Carbon Dioxide by Charcoal. ALEXANDER E. M. GEDDES (*Ann. Physik*, 1909, [iv], 29, 797—808).—The amount of carbon dioxide absorbed by cocoanut charcoal at different pressures has been determined for 14°, 31°, and 35°. The observations, which extend up to approximately one atmosphere, are in satisfactory agreement with the equation $v = ap^n$, in which v is the volume of carbon dioxide absorbed by unit volume of charcoal, p the pressure, and a and n are constants. The values of the constants vary with the temperature.

The absorption process is not reversible, so that when the pressure is reduced to a lower value, the amount of carbon dioxide retained by the charcoal is greater than that which would be absorbed at this lower pressure. The process of gas evolution does not appear to be regulated by any simple law.

H. M. D.

Hydraulic Viscosity of Liquids. EMIL BOSE and DIETRICH RAUERT (*Physikal. Zeitsch.*, 1909, 10, 406—409).—With the object of obtaining information in regard to the constants which determine the "hydraulic" flow of liquids through a capillary tube, the times required for the efflux of a given volume of liquid have been determined for pressures ranging from about 0.005 to about 2 kilo. per sq. cm. For the lower pressures the motion of the liquid is that required by Poiseuille's equation, whereas for the higher pressures the flow is hydraulic in character. The substances examined were water, ethyl alcohol, ethyl acetate, benzene, toluene, acetone, chloroform, bromoform, and mercury. The tabulated data indicate that the relative rates of flow of two liquids frequently change, so that the one which is more viscous at the lower pressures is apparently less viscous at higher pressures.

H. M. D.

Determination of a Constant in Capillarity. R. D. KLEEMAN (*Phil. Mag.*, 1909, [vi], 18, 39—44).—A relationship has been deduced between the surface energy and the internal latent heat of vaporisation at a given temperature and the molecular weight, critical temperature, and critical density. It is shown that the experimental data for ethyl ether, methyl formate, carbon tetrachloride, benzene, and chlorobenzene are in satisfactory agreement with the relationship.

H. M. D.

Diffusion-Velocity and Size of Particles in Disperse Systems. THEODOR SVEDBERG (*Zeitsch. physikal. Chem.*, 1909, 67, 105—111).—Einstein (*Ann. Physik*, 1905, [iv], 17, 549 ; 1906, 19, 371) has deduced the formula $D = RT/6\pi\eta PN$ (where D = diffusion-coefficient, η = viscosity of medium, N = number of molecules in a mol. of substance, P = radius of the particles, and the other symbols have the usual significance) for the relationship between the rate of

diffusion and the size of the particles in a colloidal solution, and in the present paper the formula is proved to be valid.

In the first place, two solutions of colloidal gold, containing particles of magnitude 1—3 $\mu\mu$ and 20—30 $\mu\mu$ respectively, have been prepared by methods described by Zsigmondy, and, from observations on the relative rates of diffusion through parchment paper, it is shown that $D_1/D_2 = P_2/P_1$, as the theory requires.

Further, a solution of colloidal gold containing still smaller particles has been prepared, and its coefficient of diffusion into water determined by Scheffer's method; $D^{117} = 0.27$. Substituting this value in Einstein's formula, and putting $N = 7 \times 10^{23}$, the value $P = 0.94 \mu\mu$ is obtained for the diameter of the particles, in almost exact agreement with the value determined ultramicroscopically by Zsigmondy for solutions of this type. G. S.

Dependence of the Gas Diffusion Coefficient on the Mixture Ratio. ANTON LONIUS (*Ann. Physik*, 1909, [iv], 29, 664—678).—An examination of the data obtained in recent experimental work on the diffusion of gases into one another shows that in all cases the coefficient of diffusion depends on the relative proportions of the mixed gases, that is to say, on the density gradient. This result is opposed to the requirements of the diffusion theory of Stefan-Maxwell. H. M. D.

Classification and Nomenclature of Disperse Systems. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 44—46).—A further scheme for the classification of the different types of disperse systems is described. H. M. D.

Rate of Solution of Gases in Water. W. A. ROTH (*Zeitsch. Elektrochem.*, 1909, 15, 328—331. Compare J. Meyer, this vol., ii, 471; Luther and MacDougall, *Abstr.*, 1908, ii, 361).—The rate of absorption of nitrous oxide and of carbon dioxide in water, and also the rate at which they are removed from solution by a current of hydrogen, are measured by means of the heat evolved or absorbed, or by measuring the freezing point of the solutions. The rate is proportional to the difference between the concentration of the gas in the saturated solution and that in the solution at the moment of measurement. T. E.

Apparatus for the Determination of Solubilities at the Boiling Point of the Solvent. JOHANNES SCHROEDER (*Zeitsch. anal. Chem.*, 1909, 48, 349—350).—The apparatus consists of a graduated boiling tube, which is connected by ground-glass joints with a vertical reflux condenser. A narrow tube, which is sealed through the wall of the boiling tube and reaches almost to the base of the latter, permits of the removal of the saturated solution for analysis. The solute is added in successive portions until the boiling point registered by a thermometer, divided into tenths of a degree, has attained a maximum value. H. M. D.

Simple Apparatus for Extraction in the Cold and for the Determination of Solubility at Room Temperature. JOHANNES SCHROEDER (*Zeitsch. anal. Chem.*, 1909, 48, 351—352).—The apparatus is designed to prevent the evaporation of volatile liquids during the process of filtration from admixed solid substances. It consists of a graduated, cylindrical, separating tap funnel, the lower end of which fits into the cover of a funnel, the lower end of which fits in turn into the mouth of a graduated cylinder. The cover and the funnel proper are connected by a ground-glass joint. To eliminate pressure differences, the upper parts of the separating funnel and the lower cylinder are connected by a side-tube. By means of this arrangement a saturated solution contained in the upper cylinder can be filtered without appreciable loss of the volatile solvent by evaporation.

H. M. D.

Solubility of Salts in Concentrated Acids. ARTHUR E. HILL and JOHN P. SIMMONS (*J. Amer. Chem. Soc.*, 1909, 31, 821—839).—Investigations dealing with the influence of the common ion in reducing the solubility of compounds and with the action of strong acids in increasing the solubility of salts of weak acids have hitherto been chiefly carried out with dilute solutions. The work now described has been performed with the object of obtaining data on solubility relations in concentrated solutions, and of testing the applicability to such solutions of the laws relating to dilute solutions.

Experiments have been made to determine the increase of solubility of several salts on addition of nitric acid of varying concentration (usually up to 5*N* and, in some cases, up to 10*N*) to their aqueous solutions. The salts studied were silver acetate, chloroacetate, oxalate, iodate, and sulphate, and thallous chloride. The results are tabulated and plotted as curves. A mathematical solution of the known laws bearing on solubility relations has been developed.

On comparing the experimental and calculated results, it is found that the laws for dilute solutions are valid for highly concentrated solutions of a salt of a weak acid in a strong acid, whilst, under the same conditions, the solubility of a salt of a strong acid is greatly depressed by some factor probably connected with the neutral salt effect, but not yet capable of quantitative expression.

E. G.

Diminution of the Cohesion Pressures and of the Solubilities of Salts by Non-Electrolytes. ISIDOR TRAUBE (*Ber.*, 1909, 42, 2185—2188. Compare this vol., ii, 216).—The following generalisation is given: Substances with appreciable cohesion pressures in water (for example, salts) diminish the solubilities of substances with small cohesion pressures (for example, organic compounds). The greater the difference in the cohesion pressures the greater is the diminution of the solubility.

The effects of the addition of non-electrolytes on the solubilities of salts in water have been investigated. The salts used were lithium carbonate, silver sulphate, and potassium bromate, and various organic compounds were used as the non-electrolytes. The values $100/n \log l_0/l$

have been calculated, where l_0 is the solubility of the salt in water, l is the solubility in the presence of the non-electrolyte, and n is the molecular concentration of the latter.

The author claims that the results prove that the cohesion pressure of the non-electrolyte determines the solubility of the salt.

J. J. S.

Properties of Colloidal Solutions. I. The Osmotic Pressure of Congo-Red and of some other Dyes. WILLIAM M. BAYLISS (*Proc. Roy. Soc.*, 1909, 81, B, 269—286).—The nature of solutions of Congo-red has been investigated. Although Congo-red is unable to diffuse through parchment paper and exhibits other colloidal properties, it exerts an osmotic pressure equal to that which would be expected if it were present in true solution in the form of simple molecules. The theoretical osmotic pressure is only attainable in the complete absence of extraneous electrolytes. Small quantities of acid, alkali, or neutral salts cause a marked diminution in the observed osmotic pressure, and even the carbonic acid present in ordinary distilled water is sufficient to produce a considerable effect. The electrolytes are supposed to act by causing the aggregation of molecules to particles. Stable colloids, such as serum-albumin, exert a protective action on Congo-red and also on arsenious sulphide, and this is due to the formation of minute aggregates, which result in a fall of the osmotic pressure, but the aggregates are not of sufficient size to precipitate.

By dialysis, a blue colloidal solution of the free acid of Congo-red can be obtained. This is easily resolved under the ultra-microscope, but it shows a definite, although small, osmotic pressure, which for a 1% solution amounts to about 14 mm. of mercury. On the basis of the kinetic theory this corresponds with the formation of aggregates which contain, on the average, twenty molecules. The entire observations are capable of explanation on the assumption that colloidal particles possess the kinetic energy of molecules, but they are opposed to the view according to which foreign electrolytes are necessary for the development of the phenomena.

H. M. D.

Fractional Precipitation from Solution. PHILIP BLACKMAN (*J. Physical Chem.*, 1909, 13, 436—437).—An algebraic proof of the well-known result that if a substance is dissolved in a liquid and another used to precipitate it, more can be precipitated by using the latter liquid in portions than in one operation.

G. S.

Spontaneous Crystallisation of Drops of Solutions as Spherulites. JACQUES CHEVALIER (*Min. Mag.*, 1909, 15, 224—231).—Drops of solutions of lithium sulphate, ammonium sulphate, lithium phosphate, iron sodium sulphate, manganese potassium sulphate, potash alum, and lithium sodium sulphate, were examined under the microscope. Spherulites and spherocrystals are in most cases the results of spontaneous crystallisation. When other crystals grow first, it is probably because they have been introduced, the drop in that case appearing to be metastable. The spherulites mark the

passage of the solution to the labile state (Trans., 1906, 89, 413). Spherulites would appear to be generally a modification of the substance with a lower degree of hydration than the ordinary crystals, and to be more stable and less soluble.
L. J. S.

Crystallisation through Membranes. JAMES H. WALTON, jun. (*J. Physical Chem.*, 1909, 13, 490—500).—The experiments were made by putting a supersaturated solution, or supercooled liquid, in a test-tube, closing the tube by a membrane, and placing it in a beaker containing more of the supersaturated solution in such a way that the membrane and the solution in the beaker were in contact. Crystallisation was then started, preferably in the beaker, and it was observed whether it extended to the contents of the tube. Parchment, collodion, goldbeaters' skin, and rubber, 0.005 inch thick, were used as membranes.

With all the solutions used, crystallisation was propagated sooner or later through the first three membranes, but not in general through the rubber. In the case of certain supercooled liquids, however, such as acetophenone and salol, crystallisation was propagated through the rubber membrane, but not in the case of supercooled water or of phenol containing a little water.
G. S.

Kinetics of the Reaction between Alkyl Sulphates and Inorganic Salts. PAUL WALDEN and MIECZYSLAW CENTNERSZWER (*Zeitsch. Elektrochem.*, 1909, 15, 310—316).—The velocities of the reactions between methyl sulphate and sodium, cadmium and stannic iodides, potassium bromide and sodium, potassium, ammonium, and cobalt thiocyanates are measured in methyl alcohol and, in a few cases, in acetone solutions. Only one methyl group reacts, and in all cases the reaction is incomplete, an equilibrium being attained. The equation of the bimolecular reaction applies very well when equivalent quantities of the reagents are used, or when the salt is present in excess, an excess of the methyl sulphate, however, causes the constants to diminish as the reaction proceeds. The temperature-coefficients of the reactions lie between 2.56 and 4.14. The velocity in acetone solution is about one hundred times greater than it is in methyl alcohol. The velocity depends on the nature of both the cation and anion of the salt used, and the more completely the reaction takes place the greater is its velocity.
T. E.

Sulphonic Acids and Ostwald's Dilution Law. RUDOLF WEGSCHEIDER and PAUL LUX (*Monatsh.*, 1909, 30, 411—445; Wegscheider, Abstr., 1902, i, 617).—The conductivity at 25° of aqueous solutions of β -naphthalenesulphonic acid, *p*-toluenesulphonic acid, and their sodium and potassium salts has been determined.

The conductivity values of β -naphthalenesulphonic acid may be represented approximately by the formula $\mu = A + Bv^{-\frac{1}{2}} - Cv^{-1}$, and for solutions having a dilution greater than 80 litres, also by the Kohlrausch-Maltby formula, $(\mu_{\infty} - \mu) : \mu^p = Cv^{-\frac{1}{2}}$; in both cases, however, regular deviations from the observed values are noticeable. The values derived from the formula $(\mu_{\infty} - \mu)^p \log V = C$ agree remarkably well with the observed values for solutions up to 0.003*N*.

The mol. conductivity of the acids at infinite dilution, μ_{∞} , derived by extrapolation from interpolation formula for the conductivity values, differs according to the formula employed. In the case of the acids examined, van't Hoff's formula is applicable when a higher value for μ_{∞} is chosen.

Ostwald's dilution law is in close agreement with the observations for solutions up to 0.006*N* when the value μ_{∞} derived from the conductivity of the salts is employed; it also applies to solutions up to 0.016*N* when a smaller value for μ_{∞} is used. W. H. G.

[Formation of Esters.] HEINRICH GOLDSCHMIDT (*Zeitsch. Elektrochem.*, 1909, 15, 305—310. Compare this vol., ii, 129, 305).—Mainly polemical. A reply to R. Wegscheider and to A. Kailan. Details of older experiments and several new ones on the rate of esterification of 1:3:5-dinitrobenzoic acid in presence of hydrochloric acid are given. T. E.

The Alcoholysis or Esterification of Acid Amides. E. EMMET REID (*Amer. Chem. J.*, 1909, 41, 483—510).—The rates of esterification at 50° of benzamide and *m*- and *p*-nitrobenzamides in aqueous-alcoholic solution have been measured, using hydrochloric acid as a catalytic agent. The course of the reaction was followed by determining the amount of ammonia formed after different intervals of time. The reaction is found to be bimolecular, and this is accounted for mathematically by assuming that the amide forms a salt with the hydrochloric acid, and that the complex cation is the reactive substance; the reaction equation holds for a range of decomposition from 2 to 75%. Using 99.5% alcohol as solvent, it is found that the velocity constant (K_p) for *p*-nitrobenzamide is 1.17 times that (K_m) for the meta-amide; moreover, K_p and K_m are directly proportional to the molecular conductivity of the hydrochloric acid in the alcohol used as solvent. The velocity constant (K_b) for benzamide is less than K_m . It is not proportional to the molecular conductivity of the hydrochloric acid, probably because benzamide is a comparatively strong base, and consequently an increase in the concentration of the acid will not produce a proportionate increase in the concentration of the complex ion, as it does with the very weak bases *m*- and *p*-nitrobenzamides.

The addition of water considerably retards the velocity of reaction, the effect being greater with *m*-nitrobenzamide than with benzamide. For small additions of water to alcohol, or vice-versa, the changes in viscosity seem able to account very largely for the observed changes in reaction velocities; the greater the viscosity the less the velocity of reaction.

The remainder of the paper is not suitable for abstraction. It consists of a mathematical discussion of the mechanism of the reaction, and is based on the assumption that the hydrions of the catalysing acid form complex ions with the solvent (water or alcohol, or both), and these further combine with the amide, forming more complex ions, which are the reactive substances. It is also shown how the relative rates of hydrolysis and alcoholysis in aqueous-alcoholic solution may be calculated. T. S. P.

Dependence of the Reaction Velocity on the Temperature in Homogeneous Gaseous Systems. HANS GOLDSCHMIDT (*Physikal. Zeitsch.*, 1909, 10, 421—422. Compare this vol., ii, 390).—Nernst's conception of a "chemical resistance" which opposes the progress of a reaction is not inconsistent with the view of Arrhenius, that only a certain proportion of the gas molecules are in a chemically active state.
H. M. D.

Relation between the Rate of a Chemical Reaction and those of its Intermediate Changes. GERHARD JUST and W. BEREZOWSKY (*Zeitsch. Elektrochem.*, 1909, 15, 297—305. Compare Abstr., 1908, ii, 825).—The polarisation of electrodes immersed in a solution containing ferro- and ferri-cyanide is studied in great detail. Using gold electrodes, the rate of stirring the solution was found to affect the polarisation; this source of error was eliminated by using constant, very violent agitation. The polarisation was then found to depend on the previous history of the electrode; a freshly polished electrode is almost unpolarisable, whilst one which has been exposed to the air is polarisable. The polarisable or unpolarisable condition can be produced at will by long immersion in a ferrocyanide solution or short exposure to a ferricyanide solution, so that it appears that an oxidised surface is polarisable. Quite similar results are obtained with platinum, except that it is much less polarisable than gold. Chromium, on the other hand, is practically unaffected by any treatment, and is equally strongly polarisable under all circumstances. It follows that platinum accelerates the reaction $\text{FeCy}_6''' + F = \text{FeCy}_6''''$ very markedly, gold accelerates somewhat less strongly, and chromium not at all. This conclusion is confirmed by allowing a mixture of potassium ferri-cyanide and iodide and sodium thiosulphate to react in presence of the metals. Iodine appears in five minutes with no metal, in forty-five to fifty-five seconds in presence of platinum, in 2.5 minutes in presence of gold, and in 5 minutes with chromium.
T. E.

Temperature-Coefficient of Chemical Reaction Velocities.
III. **Physical Meaning of the Velocity Constant, and its Replacement by Thermal Data and the Time Unit for Dilute Solutions.** MAX TRAUTZ (*Zeitsch. physikal. Chem.*, 1909, 67, 93—104. Compare Abstr., 1908, ii, 824; this vol., ii, 557).—By a thermodynamical method, a complicated expression is deduced for the velocity constant in dilute solution in terms of the thermal data for the reacting substances and the time. Similarly, the equilibrium constant for solutions has been determined, and its dependence on the properties of the solvent is discussed. Further, an expression for the temperature-coefficient of the velocity constant has been obtained.

The maximum in the temperature-coefficient of the velocity of ester saponification, described in a former paper, is probably due to a diminution of the molecular heat of the solvent or the reacting substances with increase of temperature.
G. S.

Catalysis. X. Formation of Esters from Amides and Alcohols. SALOMON F. ACREE (*Amer. Chem. J.*, 1909, 41, 457—483; Abstr., 1908, ii, 1022).—The greater part of this paper is occupied by a recapitulation of the author's views on catalysis.

Acree and Johnson (Abstr., 1907, i, 506; ii, 855) have shown that hydrochloric acid causes a catalysis of acetylbromo(chloro)aminobenzene into *p*-bromo(chloro)acetanilide in proportion to the square of the concentration of the hydrochloric acid, and have explained this by assuming that the reactive substance is an intermediate product formed by the combination of the acetylbromo(chloro)aminobenzene with both the hydrions and chloridions. The experimental data were not completely satisfactory, owing to the high concentrations of the solutions used. It is now found, however, that the action of hydrobromic acid on acetylchloroaminobenzene in 10% acetic acid solution at 3° proceeds rapidly, even in dilute solution, and the velocity has been measured. Good constants are obtained according to the velocity equation: $dx/dt = K(C_a - x)(C_{Br} - x)C_H$, where C_H , C_{Br} , and C_a are respectively the concentrations of the hydrions, bromidions, and acetylchloroaminobenzene.

Attention is called to the importance of investigations on the hydrolysis and esterification of amides, especially the latter, since no appreciable amount of water is formed in the reaction, and hence a very great disturbing factor is eliminated.

As regards the effect of salts on catalytic actions, the author does not agree with Euler's view (Abstr., 1900, ii, 269) that the salt causes an alteration in the dissociation of the water. Salt catalysis is considered to be a very complex phenomenon caused by a combination of effects, such as the following: (a) The catalysing salts may combine with the reacting substances, and form still more (or less) reactive double salts or double compounds. (b) A change in viscosity is known to have an effect on the velocities of reactions in aqueous-alcoholic solutions, and the salt effect may be dependent on the influence of the salt on the viscosity of the solution. (c) Combination may take place between the solvent and solute, thus affecting the concentrations of the reacting substances. (d) The thermodynamic potential, or driving force behind each reaction, depends not only on the reacting substances, but also on the surrounding field; the addition of salts affects the field and, therefore, the thermodynamic potential. T. S. P.

New Estimate of the Size of an Atom. H. STAFFORD HATFIELD (*Zeitsch. Elektrochem.*, 1909, 15, 389—390).—The difference of potential between a sphere of mercury of radius r and a flat surface of mercury in contact with the same solution is shown to be $E = (0.98 \times 10^{-6})/r$ volt.

Both the curved surface and the solution are negative compared with the flat surface, so that as the radius diminishes the difference of potential between the curved surface and the solution diminishes, and finally disappears when E is about 0.5 volt. The corresponding value of r is 1.9×10^{-6} cm. The author regards this as an upper limit of the size of an atom. T. E.

Space Relation of Forces in the Atom. FRANK A. HEALY (*Chem. News*, 1909, 99, 302).—From the consideration of eight fields of force (or charges), four of one polarity and four of opposite polarity, arranged symmetrically and equidistant around a sphere, it is apparent that both within and without the sphere the sum of the fields of force will be zero. If, now, one charge be doubled, the internal field value will no longer be zero; designate its value m , then, by successively doubling all the positive charges and then all the negative charges; the internal field will have the values $m, 2m, 3m, 4m, 3m, 2m, m, 0$. When the individual charges are trebled, the same series of values are obtained, both for the internal and external field, and this is repeated as often as a unit charge is successively added. This succession of values is considered to be identical with the normal succession of valency in the periodic table of the elements. J. V. E.

Practical Method for the Simultaneous Calculation of Atomic Weights: General Results. GUSTAV D. HINRICHS (*Compt. rend.*, 1909, 148, 1760—1763).—A table is given containing a résumé of the results obtained by the author in his calculations of atomic weights (Abstr., 1907, ii, 945). It contains (1) the ratio (R) of the molecular weights of the compounds used in the determination of atomic weights, and also the increase of this ratio for a variation of 0.1 in each of the atomic weights. (2) The difference between the ratio of the actual weights of compounds taken and the ratio R . This is called the analytical excess ($=e$), and gives an idea of the accuracy of the experiments. (3) The difference (ϵ) between the experimental and absolute values of the atomic weights. The difference ϵ is given by the equation $10\Sigma\epsilon\Delta = e + K$ (Abstr., 1907, ii, 945). This equation can only be solved by trial, and from the values of ϵ obtained it can be told whether the experimental determinations should be repeated more carefully, varying the quantities of material used, or whether it is probable that there is an error in the absolute atomic weights used (Abstr., 1909, ii, 400).

T. S. P.

True Values of the Atomic Weights. Mathematical Value of the Method of Calculation. LOUIS DUBREUIL (*Bull. Soc. chim.*, 1909, [iv], 5, 660—667).—In previous papers (Abstr., 1908, ii, 936, 1035; this vol., ii, 563) the author has developed Hinrichs' theorem (Abstr., 1893, ii, 317; 1907, ii, 945), that experimentally determined atomic weights (Dubreuil's apparent atomic weights) must always be variable for the same substance, and has given equations whereby true atomic weights may be calculated from the data obtained in any series of reactions. In the present paper a criticism is given of the usual plan, depending on the method of least squares, of calculating true values from experimental data, and it is pointed out that the author's method differs fundamentally from this.

Finally, it is shown that in Hinrichs' equation (Abstr., 1893, ii, 317) $R = a(1 - x + y + n)$, where R is the true value, a the apparent value, x and y quantities dependent on the impurities present, and n a function of the conditions of the experiment, x, y , and n do not tend

to become zero with the weight of the substance employed in the reaction, as Hinrichs supposed. T. A. H.

True Values of the Atomic Weights. What is the Mathematical Value of the Author's Method? LOUIS DUBREUIL (*Bull. Soc. chim.*, 1909, [iv], 5, 708—715).—A discussion of the author's method of calculating atomic weights (Abstr., 1908, ii, 936), in which it is pointed out that the equation of condition established by Hinrichs (Abstr., 1907, ii, 945) is indeterminate unless some quite arbitrary assumptions are made. Hinrichs' geometrical solution is a special case of the hypothesis adopted by the author, namely, that the sum of the squares of the deviations of the true atomic weights from whole numbers shall be a minimum. In calculating the International Atomic Weights, the assumption made is that the deviation in the case of oxygen is zero. Hitherto the method has been justified by results. E. H.

True Values of the Atomic Weights. The Determinations of Stas. LOUIS DUBREUIL (*Bull. Soc. chim.*, 1909, [iv], 5, 715—722).—A description is given of Stas' determinations of the value of the ratio $\text{LiCl}:\text{LiNO}_3$ (Stas, *Oeuvres complètes*, 1). Stas' results are recalculated by the author's method (Abstr., 1908, ii, 936, and preceding abstracts), and the following values obtained for the atomic weights: Lithium 6.9853, chlorine 35.4877, oxygen 16.0299, and nitrogen 14.0075. E. H.

Release of Valency Electrons by Collision. JOHANNES STARK (*Jahrb. Radioaktiv. Elektronik.*, 1909, 6, 168—180. Compare Abstr., 1908, ii, 574).—According to the author's valency theory, chemical dissociation and ionisation are both phenomena which are due to the release of valency electrons by collision of particles. These particles may be neutral atoms or molecules, positive or negative ions, or one of them may be an electron. In order that a valency electron may be released, the kinetic energy of the two colliding particles must be greater than the energy of combination of the valency electron with its corresponding atom. In a similar way the kinetic energy of the colliding particles must exceed a certain value in order that the vibrations of a bound electron may give rise to emission of light. The value of the coefficient which characterises the energy transformation depends on the nature of the colliding particles, and it is pointed out that this view offers an explanation of the phenomenon of catalysis. H. M. D.

Supposed Permeability of Glass for Iodine Vapour. BERNHARD TOLLENS (*Ber.*, 1909, 42, 2013. Compare Zengelis, this vol., ii, 134; Stock and Heynemann, this vol., ii, 563).—Iodine was preserved in sealed thin-walled test-tubes for two months. In no case was the slightest loss observed. The observations of Zengelis are denied. E. F. A.

Mercury Pump. MARCEL GUICHARD (*Bull. Soc. chim.*, 1909, [iv], 5, 571—574).—A very simple form of mercury pump is described,

which can be constructed from a series of pieces of glass tubing without resort to glass-blowing. The apparatus to be exhausted is connected with a tube *a*, 1 cm. in diameter, which reaches nearly to the bottom of a tube *b*, 2.5 cm. in diameter, which is closed by a rubber stopper and contains mercury. The narrow fall tube *c* terminates above the mercury in *a*, and passes through a hole in the rubber cork. Mercury is allowed to fall from a reservoir into *b* through a similar narrow, thick-walled tube. It is convenient to reduce the pressure down to about 2 cm. of mercury by means of a water pump set up in connexion with the mercury pump. H. M. D.

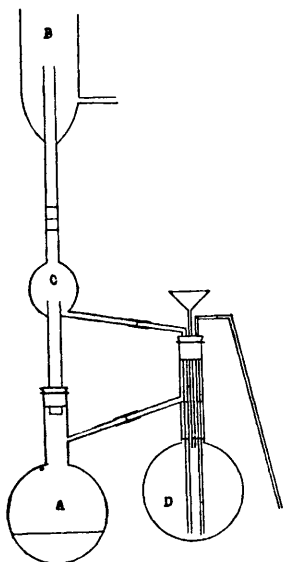
Constant Level Reservoir. W. P. FITZGERALD (*J. Amer. Chem. Soc.*, 1909, 31, 839—840).—An apparatus is described which is capable of supplying liquid to a funnel as rapidly as filtration takes place. It consists of a cylindrical glass vessel having a neck at the top and provided with a narrow tube at the lower end and a side aperture towards the upper end for the admission of liquids to be filtered. The neck is fitted with a perforated rubber stopper carrying a glass rod, which passes to the bottom of the cylinder and acts as a stopper to the narrow tube. When in use, the apparatus is so supported that the lower end of the narrow tube extends to about 3/16 inch below the edge of the filter paper. The glass rod is pushed down until it closes the narrow tube, and the liquid to be filtered is poured in through the side aperture. The glass rod is then gently raised until sufficient liquid has entered the funnel to close the lower opening of the narrow tube. The side aperture is now closed with a rubber stopper, and the glass rod is raised an inch or two. As the level of the liquid falls in the funnel, the lower opening of the narrow tube is exposed, with the result that air enters the cylinder and a further quantity of liquid flows into the funnel. After a filtration has been made, the precipitate may be washed by filling the apparatus with water.

The apparatus can be used to maintain a constant level in an evaporating dish or in a water-bath, and can also serve as a separatory funnel. E. G.

Apparatus for Intermittent or Continuous Extraction. HENRI VIGREUX (*Bull. Soc. chim.*, 1909, [iv], 5, 699—702).—The apparatus consists of four parts: (*A*) a glass cylinder open at both ends and having near the lower end four symmetrically placed circular holes blown in it; the upper end of this cylinder is flattened somewhat on one side, in order to reduce the size of the opening; (*B*) a piece of glass tubing about twice the length of *A*, and provided at the centre with a bored cork sliding on it; the upper end of this tube is slightly indented at one point to carry the siphon; (*C*) a U-siphon of narrow glass tubing having one arm slightly longer than *B* and the other end about half the length of *B*; (*D*) a pear-shaped glass holder, the upper end of which is corked and carries a condenser, and the lower end is drawn out so that it can be fitted by means of a cork to a flask containing solvent. In using the apparatus, *C* is placed in *B* and the latter in *A*, the junction being wrapped round with cloth and then fine wire gauze, to act as a filter. The apparatus is then placed in *D*, and the powder

to be extracted is filled in round it. Thus mounted the apparatus can be used intermittently, but if the siphon *C* is omitted it extracts continuously. The apparatus is figured in the original. T. A. H.

An Apparatus for the Extraction of Liquids with Ether. AUGUSTUS H. FISKE (*Amer. Chem. J.*, 1909, 41, 510—515).—The construction and working of the apparatus is obvious from the diagram. The liquid to be extracted is placed in *D* and the ether in *A*. To obviate the necessity of taking the apparatus to pieces when the liquid in *D* is to be renewed, a siphon is provided to draw off the spent liquid, and a funnel for refilling.



The apparatus was tested on a solution of succinic acid and found to be just as efficient, per c.c. of solution extracted, as the van Rijn apparatus (*Abstr.*, 1896, ii, 17), while it will extract four times as much solution in the same length of time.

T. S. P.

A Lecture Experiment to Demonstrate the Velocity of the Explosive Wave in Explosive Mixtures of Gases.

FRIEDRICH EMICH (*Ber.*, 1909, 42, 2462—2464).—The apparatus consists of an iron tube, 10 mm. diameter and 10 m. long, in the form of a coil, the two ends of which are bent at right-angles to the main coil and

are placed close together and along the same radius of the disc. Each end carries a stopcock, and one is provided with a sparking apparatus for igniting the gaseous mixture. A small amount of soot is introduced into the two open ends. A disc of stout, white paper is made to rotate with known velocity just above the ends of the tube. To determine the velocity of the explosive wave, the disc is rotated, the stopcocks are opened, and the mixture sparked. The measurement of the angle between the two marks made by the soot and a knowledge of the rate of rotation of the disc give the data required for the calculation of the velocity of the explosive wave.

J. J. S.

Filtering Apparatus for Microscopic Colouring Matters and Sterilised Solutions. M. DOMINIKIEWICZ (*Chem. Zeit.*, 1909, 33, 670—671).—The smaller of the two apparatus consists of a conical glass vessel which at the lower end is widened to a broad basis, whilst the neck is covered with a small glass bell filled with cotton wool. After the solution of the dye has been sterilised and deposited most of the suspended matters, it is drawn off, when wanted, through the lateral tube by opening the stopcock, when it passes through a little filtering tube plugged with cotton wool.

The larger apparatus consists of a separating funnel fitted laterally

with a similar filtering arrangement. The sterilised solution is contained in an ordinary reagent bottle closed with a doubly perforated rubber cork ; through one of the openings passes the stem of the funnel and through the other a glass tube, the end of which is enlarged and plugged with cotton wool. The top of the funnel is also furnished with a small bell containing cotton wool. When the colouring matter is required for use, the lower stopcock is temporarily opened, and the solution is drawn up into the funnel by applying suction. It is then run off by opening the stopcock on the lateral tube, when it passes through the filtering arrangement.

L. DE K.

Inorganic Chemistry.

Temperature of the Oxyhydrogen Flame. EDMOND BAUER (*Compt. rend.*, 1909, 148, 1756—1757).—Using the same methods as were described previously (Abstr., 1909, ii, 106, 453), the author has determined the temperature of the oxyhydrogen flame. A flame containing a slight excess of hydrogen emits and absorbs the residual rays of fluorspar to a considerable extent, the ratio of emission to absorption being 17.20; applying Planck's formula to the numbers so obtained, the temperature of the flame is found to be 2240°.

Application of the method based on the reversal of the sodium *D*-line gives temperatures varying from 2200° to 2300°, according to the proportion of oxygen.
T. S. P.

Formation of Ozone by means of Ultra-violet Light. FRANZ FISCHER (*Ber.*, 1909, 42, 2228—2230; *Physikal. Zeitsch.*, 1909, 10, 453—454. Compare Abstr., 1905, ii, 580; 1906, ii, 224).—The formation of ozone by means of ultra-violet light is confirmed (compare Bordier and Nogier, *Compt. rend.*, 1908, 47, 354).
J. J. S.

Affinities of the Nitrogen Atom. JOHN C. THOMLINSON (*Chem. News*, 1909, 99, 290).—The author considers that thermo-chemical data indicate that nitrous oxide, nitric oxide, and nitrogen dioxide contain pentavalent oxygen.
H. M. D.

Electrolytic Oxidation of Ammonia. ANDRÉ BROCHET and GEORGES BOITEAU (*Bull. Soc. chim.*, 1909, [iv], 5, 667—675. Compare Millot, Abstr., 1885, 979; 1888, 242).—When ammonia solution is electrolysed, using electrodes of Acheson graphite, a mixture of ammonium carbonate and nitrate is produced. The quantity of nitrate formed increases if ammonium carbonate or nitrate is first added to the solution. A similar reaction takes place if platinum or iron electrodes are used to electrolyse solutions of ammonium carbonate or nitrate in ammonia. Under all the conditions tried, the yield of

nitrate is low; it increases with the current density, but the rate of formation diminishes when the concentration of nitrate in the solution becomes considerable. This last phenomenon is probably due to the instability of the nitrite, which, as Traube and Biltz's experiments (Abstr., 1904, ii, 727) indicate, is first formed, although in the present experiments only traces of nitrite were found in the solutions.

Contrary to the experience of Kappeler (*Inaug. Diss. Bâle*), it is found that the gas evolved at the anode when ammonium carbonate or nitrate is electrolysed is a mixture of nitrogen and hydrogen and contains no oxygen.

In using iron electrodes, some ferric hydroxide is formed, and the cathode becomes coated with finely divided iron. The iron appears to be torn from the cathode, perhaps in the form of hydride, and is oxidised in contact with the anode. This action is inhibited by the addition of chromic acid, and the electrolysis then proceeds as with platinum electrodes.

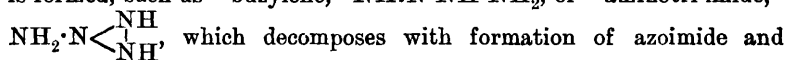
T. A. H.

Oxidation of Hydrazine. IV. ARTHUR W. BROWNE and F. F. SHETTERLY (*J. Amer. Chem. Soc.*, 1909, 31, 783—799).—A continuation of the work described in earlier papers (Abstr., 1907, ii, 863; 1908, ii, 373; this vol., ii, 233). The results are given of experiments on the oxidation of hydrazine by cupric sulphate and oxide, Fehling's solution, potassium chromate, mercuric oxide and chloride, arsenic and antimony pentoxides, ozone, chromic sulphate, selenious, selenic, and telluric acids, molybdenum trioxide, ferric oxide, and nickel and cobalt sesquioxides.

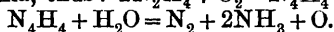
Cupric sulphate and cupric oxide in presence of alkali yield small quantities of ammonia under certain conditions, but in no case is azoimide produced. Fehling's solution gives a large amount of ammonia at temperatures between 15° and 95°, but only traces at 100°; azoimide is not formed. Fehling's solution can therefore be used for the estimation of hydrazine if it is employed in excess and maintained at the b. p. during the whole of the reaction. Potassium chromate, in presence of sulphuric acid, yields ammonia in an amount depending on the concentration of the acid and the temperature, and, in some cases, a small quantity of azoimide is produced. When a solution of hydrazine sulphate is heated with mercuric oxide in acid or alkaline solution, neither ammonia nor azoimide is formed, but if the yellow oxide is added gradually to a slightly alkaline solution of the sulphate at 0°, appreciable quantities of both ammonia and azoimide are produced. Mercuric chloride effects the oxidation without formation of either ammonia or azoimide. Arsenic oxide yields traces of both compounds. Ozone, under certain conditions, gives a small quantity of azoimide, but no ammonia. Chromic sulphate yields azoimide. Selenious acid does not give any azoimide, selenic acid yields an appreciable quantity, and telluric acid furnishes large quantities of both azoimide and ammonia. Molybdenum trioxide in acid solution yields appreciable quantities of both azoimide and ammonia. Ferric oxide gives large quantities of ammonia, but no azo-

imide, whilst nickel and cobalt sesquioxides yield ammonia together with traces of azoimide.

From a consideration of the action of all the oxidising agents studied in this and the earlier papers, the oxidation of hydrazine, with special reference to the formation of azoimide and ammonia, seems to proceed in three different ways. (1) With formation of fairly large quantities of azoimide and ammonia, as effected by hydrogen peroxide, potassium chlorate, and potassium persulphate in acid solution. (2) With formation of little or no azoimide, but large amounts of ammonia, as effected by potassium permanganate, manganese dioxide, and ferric oxide in presence of sulphuric acid. (3) With formation of little or no azoimide or ammonia, as effected by potassium iodate, mercuric oxide, and mercuric chloride. It is suggested that in the first case an intermediate condensation product is formed, such as "buzylene," $\text{NH}\cdot\text{N}\cdot\text{NH}\cdot\text{NH}_2$, or "aminotri-imide,"



ammonia, thus: $2\text{N}_2\text{H}_4 + \text{O}_2 = \text{N}_4\text{H}_4 + 2\text{H}_2\text{O}$ and $\text{N}_4\text{H}_4 = \text{N}_3\text{H} + \text{NH}_3$. In the second case, it is suggested that an intermediate product, such as "tetrazone," $\text{NH}_2\cdot\text{N}\cdot\text{N}\cdot\text{NH}_2$ is formed, which breaks up into nitrogen and ammonia, thus: $2\text{N}_2\text{H}_4 + \text{O}_2 = \text{N}_4\text{H}_4 + 2\text{H}_2\text{O}$ and



Oxidising agents of the third class seem to decompose hydrazine sulphate in acid solution at 100° without formation of intermediate condensation products.

The following is a list of the principal oxidising agents, arranged in the order of the maximum yield of azoimide obtained with each. Potassium persulphate, 40.3%; hydrogen peroxide, 38.5%; potassium chlorate, 22.4%; potassium perchlorate, 22.4%; vanadium pentoxide, 13.6%; potassium bromate in presence of silver sulphate, 11.7%; potassium iodate in presence of silver sulphate, 11.2%; potassium bromate, 6.68%; lead dioxide, 4.10%; potassium permanganate, 3.19%; manganese dioxide, 2.32%.

The preparation of azoimide can be satisfactorily accomplished by the action of hydrogen peroxide on hydrazine sulphate, but a better yield can be obtained by Thiele's method (Abstr., 1908, ii, 940). The detection of hydrazine is readily effected by converting it into azoimide by a convenient oxidising agent, and identifying the azoimide by means of the ferric chloride test (Dennis and Browne, Abstr., 1904, ii, 558). When very small amounts of hydrazine are to be detected, Thiele's method of oxidation, involving the use of ethyl nitrite, is recommended.

Attention is drawn to some analogies between the behaviour of hydrazine and of some of its organic derivatives when treated with various oxidising agents. E. G.

Formation of Oxygen Compounds of Nitrogen and of their Metallic Salts (Iron and Lead) in the Production of Ozone for the Sterilisation of Water. EDMOND BONJEAN (*Compt. rend.*, 1909, 148, 1765—1766).—In some plants which have been put down for the sterilisation of water by means of ozone, iron and lead

have been used in the ozonisers and tubes leading from them. The author has found large quantities of a mixture in varying proportions of ferric oxide and nitrate in such plants, and from the analysis of samples collected at different places between the ozonisers and the water to be sterilised, he concludes that the following reactions take place: Ferric oxide is first formed in the ozonisers; being in the form of a very fine powder it favours the formation and then the fixation of oxides of nitrogen in the tubes leading from the ozonisers. The greater the distance from the ozonisers the more pronounced is the oxidation of the oxides of nitrogen to nitric acid and the more the metal of the tubing (iron or lead) is attacked, with the formation of ferric nitrate or lead nitrate. These products may cause a stoppage in the tubes, and if they are carried into the water to be sterilised, serious consequences may result to the consumers of the water.

T. S. P.

Concentration of Hydrogen Ions in Dilute Solutions of Phosphoric Acid, Monosodium Phosphate, and Disodium Phosphate. WILHELM E. RINGER (*Chem. Weekblad*, 1909, 6, 446—452. Compare Ringer, this vol., ii, 309).—The results of a number of determinations of the concentration of hydrogen ions in dilute solutions of phosphoric acid, monosodium phosphate, and disodium phosphate are given.

A. J. W.

Ionisation Relations of Ortho- and Pyro-phosphoric Acids and their Sodium Salts. G. A. ABBOTT and WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1909, 31, 729—763).—This investigation was undertaken with the object of obtaining a knowledge of the ionisation relations of ortho- and pyro-phosphoric acids, and thus elucidating the behaviour of these acids in inorganic reactions. A summary is given of previous work on the subject.

Methods are described for the preparation and analysis of solutions of the pure acids and their sodium and ammonium salts. The conductivity of solutions of various concentrations of the acids and their sodium salts and also of ammonium disodium phosphate have been determined at 18° and the results are tabulated.

Measurements of the hydrolysis of the ammonium phosphates and pyrophosphates, $\text{Na}_3(\text{NH}_4)\text{PO}_4$, $\text{Na}(\text{NH}_4)\text{HPO}_4$, $\text{Na}_3(\text{NH}_4)\text{P}_2\text{O}_7$, $\text{Na}_2(\text{NH}_4)_2\text{P}_2\text{O}_7$, and $\text{Na}_2(\text{NH}_4)\text{HP}_2\text{O}_7$, have been made by means of distribution experiments, the method being based on the fact that when aqueous ammonia is shaken with chloroform, the ammonia distributes itself between the two solvents in a ratio which is constant at a given temperature. From the results thus obtained, the ionisation constants of the successive hydrogen atoms of ortho- and pyro-phosphoric acids were calculated on the assumption that all the salts were completely dissociated, and the values were afterwards corrected for the effect of non-ionised substances present in the solutions. The final values obtained are as follows. Ortho-phosphoric acid: $\text{H}_2\text{PO}_4^- + \text{H}^{+2}$, 1.1×10^{-2} ; $\text{HPO}_4^{--} + \text{H}^+$, 1.95×10^{-7} ; $\text{PO}_4^{---} + \text{H}^+$, 3.6×10^{-13} . Pyrophosphoric acid: $\text{H}_3\text{P}_2\text{O}_7^- + \text{H}^{+2}$, 1.4×10^{-1} ; $\text{H}_2\text{P}_2\text{O}_7^{--} + \text{H}^{+2}$,

1.1×10^{-2} ; $\text{HP}_2\text{O}_7^{---} + \text{H}^+$, 2.9×10^{-7} ; $\text{P}_2\text{O}_7^{-----} + \text{H}^+$, 3.6×10^{-9} .

From these results it is evident that ortho-phosphoric acid, with reference to the first equivalent of hydrogen, behaves as a fairly strong acid; with reference to the second hydrogen, it behaves as a weak acid, intermediate between carbonic acid and hydrogen sulphide, and with reference to the third, like a very weak acid, intermediate between the acid radicles HCO_3^- and HS^- of the two acids mentioned. These facts are in harmony with the heats of neutralisation and with the behaviour of the acid towards indicators.

Pyrophosphoric acid, with reference to the first hydrogen equivalent, is a strong acid, but not quite so strong as hydrochloric or nitric acid. The ion $\text{H}_3\text{P}_2\text{O}_7^-$ is somewhat weaker, its ionisation constant being almost identical with that of ortho-phosphoric acid at the same ion-concentration. The ion $\text{H}_2\text{P}_2\text{O}_7^{--}$ is a weak acid of almost the same strength as the phosphate ion, H_2PO_4^- , whilst the ion $\text{HP}_2\text{O}_7^{---}$ is still weaker, but not so weak as the phosphate ion, HPO_4^{--} . These facts are in agreement with the behaviour of the acid towards indicators.

The relation of these results to the molecular structure of the acids is discussed. By means of the ionisation constants, corrected values have been obtained for the conductivities of the salts, and these are presented in tabular form together with the limiting conductivity at zero concentration and the percentage of ionisation at different concentrations. It is shown that the equivalent conductivity of the ions is proportional to their valency, and that the ionisation values for the salts studied are in accord with the principles that, at the same concentration, the ionisation is approximately the same for all salts having the same valency product, and that the non-ionised fraction is greater the greater the value of the valency product. E. G.

Rate of Hydration of Pyrophosphoric Acid in Aqueous Solution. G. A. ABBOTT (*J. Amer. Chem. Soc.*, 1909, 31, 763—770).—In aqueous solution, pyrophosphoric acid is unstable, and gradually changes into ortho-phosphoric acid. This change is greatly accelerated by rise of temperature, and, at 100° , in a 0.05 formalar solution is practically complete in about two hours. This hydration is accompanied by a marked decrease in the conductivity of the solution, and the rate of change can therefore be determined by conductivity measurements.

A series of determinations has been made by measuring the changes of conductivity of a 0.05 formalar solution at 75° and 100° , and of a 0.0125 formalar solution at 75° . The measurements were made in the platinum-lined steel bomb devised by Noyes and Coolidge (*Abstr.*, 1904, ii, 226) for investigating the conductivity of aqueous solutions at high temperatures. In order to discover the law governing the rate of hydration of the acid, the velocity constant (specific reaction rate) was calculated (1) on the assumption that the hydration is proportional to the hydrogen-ion concentration as well as to that of the unchanged pyrophosphoric acid, and (2) on the assumption that the rate is independent of the hydrogen-ion concentration and

proportional only to the concentration of the pyrophosphoric acid. The results indicate that the hydration of the acid in dilute aqueous solution takes place at a rate which is approximately proportional to its own concentration, and which increases with that of the hydrogen ion in the solution, but not nearly so rapidly as proportionality would require.

The actual rate of the reaction is approximately as follows. A 0.0125 formolar solution at 75° is hydrated to the extent of 25% in 88 minutes, 50% in 220 minutes, and 75% in 470 minutes. A 0.05 formolar solution at 75° is hydrated to the extent of 25% in 52 minutes, 50% in 135 minutes, and 75% in 290 minutes, whilst, at 100°, a solution of the same strength is hydrated to the extent of 25% in 5 minutes, 50% in 12.5 minutes, and 75% in 27 minutes. From the results for the 0.05 formolar solution, it is evident that the rate is 10.6 times as great at 100° as at 75°. From the general principle, $\log(k_{t_2}/k_{t_1}) = \text{const.} \times (t_2 - t_1)$, it follows that at 25° and 0° the rate would be $1/(10.6)^2$ and $1/(10.6)^3$ as great respectively as at 75°, and that the time required to produce 25% hydration in a 0.05 formolar solution would therefore be about 100 hours at 25° and 1030 hours at 0°. It also follows that the rate of the reaction increases 2.57 times for each 10° rise of temperature.

E. G.

Ordinary Carbon. HENRI LE CHATELIER and S. WOLOGDINE (*Compt. rend.*, 1909, 148, 1715—1718).—Owing to the fact that different kinds of ordinary carbon possess different heats of combustion and different densities, it has been supposed that they are really different allotropic modifications. The authors, in continuation of their work on graphite (*Abstr.*, 1908, ii, 177), have examined various kinds of ordinary carbon to see if they contained the graphitic modification, the presence of which in varying amounts would account for results hitherto obtained.

Acetylene-black and retort-carbon were found to contain graphite, whilst lamp-black, sugar-carbon, wood-charcoal, and the filaments of incandescent lamps were found to be free from graphite.

The conclusion is drawn that there is only one kind of ordinary carbon, the density of which is approximately 1.8; a lower density is due to the presence of occluded gas. Varieties of carbon which contain graphite have a density decidedly higher than 1.8. T. S. P.

Inertness of Adsorbed CO_3^{--} Ions. PAUL ROHLAND (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 33—35).—When cement is digested with solutions of carbonates or hydrogen carbonates, these are taken up from the solution by the cement. On treating this with dilute hydrochloric acid, no carbon dioxide is evolved, and this is attributed to the adsorption of the carbonate ions. On the other hand, carbon dioxide is immediately liberated by the action of concentrated hydrochloric acid. If a solution of ammonium carbonate is used instead of the alkali metal carbonates, carbon dioxide is set free when the cement is digested with a dilute (2*N*) hydrochloric acid solution.

H. M. D.

Silicon Chlorides. ADOLPHE BESSON and L. FOURNIER (*Compt. rend.*, 1909, 149, 34—36. Compare this vol., ii, 399).—The silicon chlorides obtained by the action of an electric discharge on silicochloroform are of the saturated series, so that the action which occurs in an atmosphere of hydrogen or of hydrogen chloride is accompanied by a liberation of hydrogen and hydrogen chloride. The fraction of the product intermediate between Si_2Cl_6 and Si_3Cl_8 shows, however, an undoubted deficit of chlorine, and may contain small quantities of unsaturated chlorides. The mixture of chlorosilicomethane and dichlorosilicomethane obtained by acting on amorphous silicon with hydrogen chloride (this vol., ii, 398), when submitted to the electric discharge, seems to give the same mixture of saturated compounds instead of unsaturated substances. Seemingly excess of hydrogen chloride acts on unsaturated silicon chlorides with liberation of hydrogen. By the action of the electric discharge on hydrogen and silicon tetrachloride, a mixture of saturated silicon chlorides is produced, which are, however, present in proportions differing from those in the mixture described previously.

The substance boiling at about $150^\circ/15$ mm., described as dodecachlorosilicopentane is now found to be *decachlorosilicobutane*, $\text{Si}_4\text{Cl}_{10}$, with b. p. $149\text{--}151^\circ/15$ mm.

Dodecachlorosilicopentane, $\text{Si}_5\text{Cl}_{12}$, boils at about $190^\circ/15$ mm., and is an extremely viscous liquid. A glassy, yellow residue, stable at 200° , is a mixture containing perhaps some unsaturated chlorides.

R. J. C.

Curious Property of Neon. J. NORMAN COLLIE (*Proc. Roy. Soc.*, 1909, 82, A, 378—380).—When neon is shaken in a tube with mercury, a red glow is observed, which is as bright at a pressure of 120—200 mm. as when the gas is at atmospheric pressure. Most of the tubes lose their property of glowing after long-continued shaking, but regain it when a spark is passed. By unequal heating, or passing mild or violent discharges through them, tubes were obtained glowing in certain parts and not in others. There is no glowing in the presence of traces of moisture; carbon monoxide diminishes the glow, but traces of hydrogen have very little effect. The glow is even more intense in a silica tube than in a glass tube.

G. S.

Actinium and Ionium. BÉLA SZILÁRD (*Le Radium*, 1909, 6, 80).—Methods are described which demonstrate that the elements ionium and actinium occur simultaneously in many of the uranium group of minerals in the absence of thorium. Their reactions are described both in the absence and presence of other rare earths. F. M. G. M.

Electrolytic Preparation of Amalgams of the Alkali and Alkali-earth Metals. GEORGE MCP. SMITH and H. C. BENNETT (*J. Amer. Chem. Soc.*, 1909, 31, 799—806).—A method is described for preparing amalgams of the alkali and alkali-earth metals by the electrolysis of a salt solution with a mercury cathode. The process is simpler and less laborious than that of Kerp and Böttger (*Abstr.*, 1900, ii, 656) and yields better results.

Mercury is placed in a beaker and brought into contact with a platinum wire fused into the end of a glass tube; the latter contains a little mercury, into which the negative wire of the circuit dips. The mercury is covered with the solution to be electrolysed. The anode consists of a piece of heavy platinum foil so arranged that the surface immersed is parallel to that of the mercury.

Experiments on the preparation of amalgams of caesium, rubidium, potassium, sodium, lithium, barium, strontium, and calcium are described. In several instances the amalgams obtained were found to contain a larger proportion of the alkali-metal than the corresponding amalgams obtained by Kerp and Böttger (*loc. cit.*). Thus the solid lithium amalgam contained 0.875% of lithium, corresponding with LiHg_4 , whilst Kerp and Böttger's contained only 0.70%, corresponding with LiHg_5 .
E. G.

Hydrates of Potassium Carbonate. ROBERT DE FORCRAND (*Compt. rend.*, 1909, 148, 1731—1734).—Although six different hydrates of potassium carbonate have been described, the only one of which the existence is certain is the hydrate $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$. The author has consequently taken up the study of these compounds, and in the present communication gives data relative to the hydrate above mentioned ($1.5\text{H}_2\text{O}$).

This hydrate is produced by the evaporation of a saturated solution at all temperatures between 10° and 75° . The presence of a little free potassium hydroxide or of the hydrogen carbonate has no influence on the result. In some cases crystals, which were dry at their surfaces, gave water of crystallisation varying from 1.62 to $1.99\text{H}_2\text{O}$, but this was shown to be due to the presence of occluded mother liquor. Dehydration in a current of inert dry gas gives the anhydrous salt without the formation of intermediate hydrates. The heats of solution at 15° of K_2CO_3 , $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$, and of a saturated solution of potassium carbonate ($\text{K}_2\text{CO}_3 + 7.2\text{H}_2\text{O}$) were found to be 6.382, -0.654 , and -0.020 Cals respectively. The conclusion is drawn that anhydrous potassium carbonate is a powerful desiccating agent, but that this is not true of the hydrate with $1.5\text{H}_2\text{O}$.

In one experiment the hydrate with $2\text{H}_2\text{O}$ was obtained; on dehydration it gave the hemihydrate ($0.5\text{H}_2\text{O}$).
T. S. P.

The $4/3$ Sodium Carbonate. JOSEF HABERMANN and A. KURTENACKER (*Zeitsch. anorg. Chem.*, 1909, 63, 65—68).—When a solution of sodium hydrogen carbonate is evaporated at its boiling point in a current of air, an impure salt crystallises. When dissolved in hot water and 96% alcohol added until turbid, the normal carbonate first separates, and on repeating the treatment, pure crystals of the $4/3$ carbonate, $\text{Na}_2\text{CO}_3 \cdot 2\text{NaHCO}_3$, are obtained. The same product results when carbon dioxide is led into the boiling solution of sodium carbonate. Sodium sesquicarbonate, $\text{Na}_2\text{CO}_3 \cdot 2\text{NaHCO}_3$, is not obtained under any conditions, and it appears that the salt,



is the only stable one.

Under similar conditions, potassium carbonate only yields mixtures of the salts K_2CO_3 and $KHCO_3$. C. H. D.

The Binary Systems of Sodium Metasilicate with Lithium, Magnesium, Calcium, Strontium, and Barium Metasilicates, of Lithium Metasilicate with Potassium, Magnesium, Calcium, Strontium, and Barium Metasilicates, and the Ternary System $Na_2O-Al_2O_3-SiO_2$. ROBERT C. WALLACE (*Zeitsch. anorg. Chem.*, 1909, **63**, 1—48).—The tendency of silicates to solidify as a glass is an obstacle to their investigation by thermal analysis. Lithium metasilicate, however, crystallises well on cooling. Carbon tubes are used for fusing the mixtures, the thermocouple being protected by a porcelain tube coated with graphite.

Several of the systems examined form a continuous series of solid solutions, the freezing-point curve having a pronounced minimum. These are $Na_2SiO_3-SrSiO_3$, $Na_2SiO_3-BaSiO_3$, and $Na_2SiO_3-Li_2SiO_3$. The crystallisation interval appears to be very small in all cases, so that the solidus curve lies close beneath the liquidus. All the mixtures form homogeneous, monoclinic crystals.

Mixtures of Na_2SiO_3 with 20—80% $MgSiO_3$ solidify only as glasses. The two ends of the series consist of solid solutions. Potassium metasilicate cannot be crystallised; its mixtures with 60—100% Li_2SO_3 form solid solutions.

In a second group of mixtures, two series of solid solutions are formed, separated by a gap, so that the freezing-point curve has a well marked eutectic point. This group includes the mixtures $Li_2SiO_3-CaSiO_3$, $Li_2SiO_3-MgSiO_3$, $Li_2SiO_3-BaSiO_3$, and $Li_2SiO_3-SrSiO_3$. The eutectic arrests are well marked on the cooling curves. The microscopic appearance is in accord with the thermal observations. The molecular volume is only a linear function of the composition within the limits of the gap between the solid solutions; curved lines are obtained outside these limits.

In the ternary system $Na_2O-Al_2O_3-SiO_2$ the solid phases observed are corundum (Al_2O_3), sillimanite (Al_2SiO_5), nepheline ($NaAlSi_3O_8$), and sodium metasilicate. Sodium silicate forms solid solutions with silica up to at least 20% of the latter. The molten products are highly viscous, and it is impossible to say whether complete miscibility occurs in the solid state, as glasses are always formed (compare Kultaschew, *Abstr.*, 1903, ii, 545). Mixtures corresponding with $NaAlO_2$ melt at 1800° by the Wanner pyrometer, and form crystals isomorphous with corundum. The crystals are only very sparingly soluble in water. Mixtures of silica and alumina are infusible at 1900° if containing more than 70% Al_2O_3 . All the mixtures of this series correspond with sillimanite (compare Stein, *Abstr.*, 1907, ii, 763). The melting point of sodium metasilicate is lowered by addition of sodium aluminate, a mixture with 10% $NaAlO_2$ crystallising at 960° ; further additions give very infusible mixtures, forming glasses on cooling. Nepheline forms solid solutions with at least 50% $NaAlO_2$; nepheline and sodium silicate form very viscous masses. Both nepheline and sillimanite crystallise from mixtures of $NaAlO_2$, SiO_2 , and Al_2O_3 , contrary to Morozewicz's conclusion (*Abstr.*, 1899, ii, 762).

In the ternary diagram, a large area of mixtures, rich in silica, represents only glasses. The other fields have been mapped with reference to the solid phases which separate.

When thin plates of albite or nepheline glasses are heated with sodium tungstate at 950° , crystallisation sets in, but only to a minute depth, the interior of sections 0.05 mm. thick remaining glassy. The velocity of crystallisation of albite glass at 950° is 0.008 mm. per hour, and only 0.01 mm. per hour after heating with sodium tungstate. It is therefore only the surface crystallisation which is accelerated by the mineralising agent. C. H. D.

Forms of Matter. II. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 62—68. Compare this vol., ii, 306).—Observations are recorded which show that microcrystalline precipitates of metallic silver are obtained from silver hydrosols. In agreement with previous experiments on barium sulphate and aluminium hydroxide, the smallest particles of silver tend to increase in size and form definitely crystalline aggregates.

Silver hydrosol reacts with solutions of acids, bases, and salts, and the reaction is supposed to take place in two stages. In the first of these, hydrogen is set free, and this reacts with dissolved oxygen to form water in the second stage according to the equations: (1) $\text{Ag} + \text{HCl} = \text{AgCl} + \text{H}$ or $\text{Ag} + \text{NaCl} + \text{H}_2\text{O} = \text{AgCl} + \text{NaOH} + \text{H}$, and (2) $2\text{H} + \text{O} = \text{H}_2\text{O}$. The various special reactions studied by the author indicate clearly that silver in extremely finely divided condition is very much more active than the ordinary form of metallic silver.

H. M. D.

So-called Electrolytic Peroxide of Silver. GEORG BABOROVSKÝ and GOTTLIEB KUŽMA (*Zeitsch. physikal. Chem.*, 1909, 67, 48—63. Compare Abstr., 1908, ii, 378).—Silver peroxide was prepared by electrolysis of solutions of silver nitrate and of silver sulphate, and its composition was determined by direct and indirect analysis. A platinum dish was used as anode, a platinum spiral as cathode, and the anode and cathode compartments were separated by a porous cell. The amount of silver and of nitric acid in the peroxide, as well as the free nitric acid formed and the silver remaining in the anode liquid, were determined by analysis, and the active oxygen was determined in the precipitate directly as well as indirectly by inserting a voltameter in the circuit. Similar experiments were made with solutions of silver sulphate.

When the assumption is made that the small amount of nitrate in the precipitate is present as silver nitrate, the results indicate that the peroxide present has the formula Ag_3O_4 . The composition of the "peroxide" as given by Šulc (Abstr., 1897, ii, 98; 1900, ii, 595) is $\text{Ag}_7\text{NO}_{11}$, but when the above assumption is made as to the mode of combination of the nitrogen, the results in this case also are best represented by the formula Ag_3O_4 . G. S.

Calcium Monoborates. R. MANDELBAUM (*Zeitsch. anorg. Chem.*, 1909, 62, 370—382).—When calcium hydroxide is added, little by little, to an equivalent quantity of boric acid in solution, and the mixture is

warmed at 60—70°, the precipitate at first formed is amorphous, and has, approximately, the composition $\text{CaO}, \text{B}_2\text{O}_3, 4\text{H}_2\text{O}$. When the shaking at 60—70° is continued for several days, and the mixture is kept, the precipitate becomes crystalline, and has the composition of a pure monoborate hexahydrate, $\text{CaO}, \text{B}_2\text{O}_3, 6\text{H}_2\text{O}$. Two-thirds of the water is driven off at 105°, the remaining water being lost only at a red heat. This indicates the formula $\text{Ca} \begin{smallmatrix} \text{O} \cdot \text{B}(\text{OH})_2 \\ \text{O} \cdot \text{B}(\text{OH})_2 \end{smallmatrix}, 4\text{H}_2\text{O}$ for the hexahydrate. The amorphous compound has $D 1.84\text{—}1.92$, the crystalline, $D 1.822$.

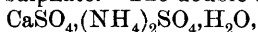
For the analysis, the boric acid was estimated by the author's method (this vol., ii, 701), and the calcium either by weighing as sulphate after expelling the boron with hydrofluoric acid, or by warming with an excess of *N*/5-hydrochloric acid and titrating with sodium hydroxide, using methyl-orange as an indicator. The water could only be estimated by covering the salt with ignited lead oxide and heating to dull redness in a combustion tube in a current of dry air, the water being collected and weighed.

Determinations of the solubility and hydrolysis of the two borates at different temperatures indicate that the conversion of the tetra- into the hexa-hydrate begins at 42°, and reaches a maximum at about 65°.

C. H. D.

Some Double Sulphates of Calcium. BARRE (*Compt. rend.*, 1909, 148, 1604—1606).—The author has measured the solubility at different temperatures of calcium sulphate in solutions of ammonium sulphate and potassium sulphate, and has demonstrated the existence of the double sulphates: $\text{CaSO}_4, (\text{NH}_4)_2\text{SO}_4, \text{H}_2\text{O}$; $2\text{CaSO}_4, (\text{NH}_4)_2\text{SO}_4$; $\text{CaSO}_4, \text{K}_2\text{SO}_4, \text{H}_2\text{O}$. In each case two series of measurements were made, the solid phases being respectively the double salt and the sulphate of ammonium or potassium, and the double salt and calcium sulphate; the temperature varied from 0° to 100°.

The solubility of calcium sulphate is considerably increased in the presence of ammonium sulphate. The double sulphate,



is stable between 0° and 100° in the presence of an excess of ammonium sulphate; it is not formed if the solution contains less than 35% of ammonium sulphate. The double salt, $2\text{CaSO}_4, (\text{NH}_4)_2\text{SO}_4$, is formed in the presence of an excess of calcium sulphate and at temperatures above 80°.

Calcium sulphate is less soluble in a solution of potassium sulphate than in water. The double sulphate, $\text{CaSO}_4, \text{K}_2\text{SO}_4, \text{H}_2\text{O}$, is stable between 0° and 99° in the presence of an excess of either of the component salts. In the given temperature interval the double sulphate, $2\text{CaSO}_4, \text{K}_2\text{SO}_4, 3\text{H}_2\text{O}$ (compare Ditte, *Abstr.*, 1877, i, 440), does not exist.

T. S. P.

Parallel Growths of Different Substances. STEFAN KREUTZ (*Min. Mag.*, 1909, 15, 232—237. Compare *Abstr.*, 1908, ii, 366).—Parallel growths were obtained of sodium nitrate on barytocalcite

(BaCaC_2O_6) and of lithium nitrate on the rhombohedral carbonates, rhodochrosite and chalybite. The molecular volumes and topic axes of these substances are compared. L. J. S.

Solid Solution: The Retention of Aluminium by Barium Sulphate Precipitates. HENRY JERMAIN MAUDE CREIGHTON (*Zeitsch. anorg. Chem.*, 1909, 63, 53—58).—Precipitates produced from ammonium sulphate and barium chloride in presence of aluminium chloride retain aluminium. The retained quantity, measured by the excess weight of the precipitate over that calculated, increases with the quantity of aluminium chloride present until a constant value is reached. With a constant quantity of aluminium chloride, it increases with the quantity of ammonium sulphate. The results indicate the formation of a solid solution, and not of a compound. C. H. D.

Magnesium Oxychlorides. HANS HOF (*Chem. Zeit.*, 1909, 33, 693—694. Compare Abstr., 1908, ii, 946).—The author prepares magnesium oxychloride by electrolysis, with the use of a diaphragm, a strong solution of magnesium chloride until magnesium hydroxide appears in the cathode liquid. The filtered solution, after some twenty-four hours, deposits a white mass, which is cautiously washed with absolute alcohol and then with ether. The analysis agrees fairly well with the formula $\text{MgCl}_2 \cdot 5\text{MgO} \cdot 14\text{H}_2\text{O}$.

Dried over sulphuric acid it loses $3\text{H}_2\text{O}$, and on heating at 180° $8\text{H}_2\text{O}$, thus yielding a product of the formula $\text{MgCl}_2 \cdot 5\text{MgO} \cdot 6\text{H}_2\text{O}$.

When, according to Bender, freshly ignited magnesium oxide is mixed with excess of magnesium chloride solution and the powdered, hardened mass extracted with absolute alcohol, avoiding a too long contact, the residual mass consists of $\text{MgCl}_2 \cdot 5\text{MgO} \cdot 13\text{H}_2\text{O}$, of which $8\text{H}_2\text{O}$ are expelled when dried at 180° . If magnesium chloride is mixed with excess of magnesium oxide and the powdered mass exposed to the action of carbon dioxide, the excess of magnesium is gradually carbonated, but the MgO of the oxychloride is also attacked to some extent, and in an experiment mentioned by the author the proportion between magnesium chloride and oxide was as 1 to 4.4. L. DE K.

Action of Soluble Substances on Insoluble Substances. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1909, 508—509. Compare Abstr., 1908, ii, 843).—Carbonate of zinc (1 mol.) is not decomposed by sodium chloride (2 mols.) dissolved in water after exposure to diffused daylight for some weeks; in the same circumstances, cadmium carbonate is not decomposed by sodium chloride, and manganese carbonate is not acted on by sodium nitrate. Cerussite is not decomposed by boiling with a large excess of sodium nitrate for some hours, but powdered lead chromate is slightly acted on in the same circumstances. Lead iodide is slightly soluble in boiling aqueous solutions of the nitrates of sodium and potassium.

G. S.

Reactions of Some Salts. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1909, 691—692).—A mixture of two molecules of

sodium chloride in aqueous solution and 1 molecule of zinc carbonate was exposed to the light for five months without any reaction taking place.

Under similar conditions, manganese carbonate and sodium nitrate also did not react; the experiment lasted from January 22nd to May 26th, 1909 (compare preceding abstract). T. S. P.

Conglomerates obtained by Compressing Mixtures of the Powders of Two Metals. GUSTAV TAMMANN [with G. MASING] (*Zeitsch. Elektrochem.*, 1909, 15, 447—450).—Mixtures of two metals in the form of filings are submitted to a pressure of 5000 atmospheres and the blocks examined microscopically, and by determining their behaviour on heating and their electrical conductivity. It is found that immediately after compression, the block consists of the unchanged metals lying side by side, combination or solution then goes on slowly; for example, a mixture of lead and thallium had the conductivity corresponding with a mixture immediately after compression. This increased by about 10% in one day, and in the course of a month it had increased by 60 to 75%. The increase is much faster if the mixture is heated to 160°. The formation of mixed crystals of bismuth and thallium as a blue fringe between the metals can be seen after five hours at 120°, and at 165° another yellow line of the compound, Bi_3Tl_3 , becomes visible. The change takes about a year at the ordinary temperature.

The combination or mutual solution of two metals is therefore not brought about by pressure alone, but results from subsequent diffusion in the solid state, which is, of course, very much accelerated by raising the temperature (compare following abstract). T. E.

The Formation of Alloys by Pressure and the Reactivity of Metals in the Solid State. G. MASING (*Zeitsch. anorg. Chem.*, 1909, 62, 265—309).—It was found by Spring (Abstr., 1881, 498; 1882, 273; 1882, 921; 1893, ii, 168; 1895, ii, 37) that filings of different metals, compressed together under 7500 atmospheres, yielded masses which behaved as alloys. So far as fusible metals are concerned, it was shown by Hallock (Abstr., 1889, 817) that a mixture of the component metals melts slowly to form the eutectic, even without previous compression (compare also Benedicks and Arpi, Abstr., 1907, ii, 666). Pressure has, moreover, very little influence on the velocity of chemical reactions, and is not likely to increase the velocity of diffusion in solid solutions; it is therefore improbable that the formation of true alloys should occur under the influence of pressure alone.

An apparatus is described for compressing mixtures of metals under 5000 atmospheres. Heating and cooling curves were taken of each mixture after compression.

Compressed mixtures of zinc and cadmium and of copper and silver in the eutectic proportions melt at a temperature above the eutectic temperature, on account of the coarseness of grain as compared with the eutectic formed in freezing. Mixtures of magnesium with lead, tin, zinc, bismuth, and antimony, all of which are capable of forming

compounds, but not solid solutions, undergo combination to some extent even in the solid state, as, on heating, partial fusion is found to take place at the lower eutectic point of each series. The reaction between antimony and magnesium begins below 300° , and becomes explosive at $450-550^{\circ}$.

Magnesium and cadmium, which form a continuous series of solid solutions, diffuse into one another in the solid state, so that equal weights of the two metals, after compressing and then heating twenty-five hours at 300° , do not begin to melt until 420° , that is, above the melting point of cadmium (320°).

In the case of bismuth and thallium (compare preceding abstract), which form a compound and also solid solutions, diffusion may be recognised even at the ordinary temperature. At 120° the diffusion is appreciable even in a few hours. Diffusion takes place in mixtures of lead and thallium at 200° . Diffusion of tin into copper takes place at 200° , whilst zinc and copper diffuse into each other readily at 400° . Aluminium and magnesium combine in the solid state.

The electrical conductivity may be used as a sensitive method of detecting diffusion. A compressed mass of lead and thallium is thus shown to be only a mechanical mixture, whilst heating causes a considerable fall in the conductivity, owing to the formation of a solid solution.

The effect of pressure is therefore only to bring the fragments of metal into close contact, and it has no influence in furthering either combination or diffusion. C. H. D.

¹ **The Phosphates of Lead.** H. ALDERS and ARTHUR STÄHLER (*Ber.*, 1909, 42, 2261—2270).—Tertiary lead phosphate, $\text{Pb}_3(\text{PO}_4)_2$, when prepared by precipitating a lead salt with excess of alkali phosphate, always contains alkali, which is not removed by boiling. The pure salt is only obtained from hot sodium phosphate and an excess of lead acetate, or by boiling the diplumbic salt with water. Secondary lead phosphate, PbHPO_4 , is obtained in a pure state by recrystallisation from dilute phosphoric acid. Primary lead phosphate, $\text{Pb}(\text{H}_2\text{PO}_4)_2$, is obtained by heating either of the other phosphates with 90% phosphoric acid, and crystallises from concentrated phosphoric acid in slender needles, which are stable in air after washing with ether. It is decomposed by water.

An investigation of the equilibrium between lead phosphates and phosphoric acid shows that the secondary salt has the greatest stable range, its formation from the tertiary salt beginning at a concentration of 0.047% H_3PO_4 , whilst the formation of the primary salt only begins at 70% H_3PO_4 . C. H. D.

Dimercurammonium Bromide. H. GAUDECHON (*Compt. rend.*, 1909, 148, 1763—1765).—If a hot solution of mercuric bromide is poured into excess of a cold solution of ammonium hydroxide, either a white precipitate having the composition $\text{NHg}_2\text{Br}, 3\text{NH}_4\text{Br}$, or else a yellow precipitate of the composition $\text{NHg}_2\text{Br}, \text{NH}_4\text{Br}$ is obtained; on washing either of these with water, the compound $\text{NHg}_3\text{Br}, \text{H}_2\text{O}$ is left.

On the other hand, if the ammonium hydroxide is added gradually to the warm solution of the mercuric bromide, a whitish-yellow precipi-

pitite is obtained, which becomes deep yellow on prolonged washing with water to remove soluble bromides. This substance has the composition $\text{Hg}_9\text{N}_4\text{Br}_6$ or $(\text{NHg}_2\text{Br})_4\text{HgBr}_2$. If it is repeatedly treated with warm concentrated ammonium hydroxide until no more ammonium bromide is formed, a canary-yellow product is left, which has the composition NHg_2Br . This compound will not combine with water to form the compound $\text{NHg}_2\text{Br}\cdot\text{HO}_2$, neither can it be obtained from the latter by heating. When quickly heated, it explodes at a red heat, but when heated slowly, it decomposes at about 400° with the formation of mercurous bromide and mercury. It corresponds with NHg_2I , the anhydrous chloride having not yet been prepared.

T. S. P.

New Method of Isolating Terbium. GEORGES URBAIN (*Compt. rend.*, 1909, 149, 37—39. Compare Abstr., 1905, ii, 711).—The rare earth metals may be arranged in a table according to the solubilities of their salts, but in some cases, as for instance the nitrates crystallising with $5\text{H}_2\text{O}$, the order is anomalous. Thus the nitrates of gadolinium and terbium, unlike the other salts of these metals, have solubilities which differ somewhat widely. Bismuth nitrate, $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$, is slightly less soluble in nitric acid than terbium nitrate, and more soluble than gadolinium nitrate. By adding a large excess of bismuth nitrate to the gadolinium and terbium nitrates to be separated, and by systematically crystallising for a sufficient time, complete separation of the gadolinium from the terbium is attained. The terbium obtained by this new method is identical in arc spectrum and paramagnetic coefficient with that prepared previously by laborious fractional precipitations with ammonia, thus proving the homogeneity of the element (compare Urbain and Jantsch, this vol., ii, 116).

The function of bismuth nitrate which acts as a separator, preventing the crystallisation of terbium nitrate, recalls the use of copper in the electrolytic separation of silver from lead (compare Gillett, this vol., ii, 521).

R. J. C.

The Electrical Reduction of Aluminium. FR. BOCK (*Zeitsch. angew. Chem.*, 1909, 22, 1309—1311).—When aluminium oxide in molten cryolite is electrolysed (Hall's patent), considerable difficulty is caused by what is known as the "anode effect," namely, a rapid decrease in the amount of current, probably brought about by a film of gas developing on the graphite anode.

With the object of minimising this effect and increasing the yield of aluminium per ampere hour, experiments with different sized crucibles and various anodes have been made, and the results are recorded. The main conclusions arrived at being that the nature of the anode and also its form play an important part, and, notwithstanding the disturbing influence of the "anode effect," a satisfactory yield of aluminium may be obtained by this method. The best results were obtained when using an anode constructed of four graphite plates, $1.9\text{ cm.} \times 12.5\text{ cm.} \times 12.5\text{ cm.}$, equally spaced to fit into a crucible cathode $17.8\text{ cm.} \times 17.8\text{ cm.} \times 17.8\text{ cm.}$; the yield of aluminium under these conditions corresponding with a current efficiency of 49% per ampere hour.

J. V. E.

Separation of Graphite From White Cast Iron Heated Under Pressure. GEORGES CHARPY (*Compt. rend.*, 1909, 148, 1767—1769).—When white cast iron is annealed at temperatures which need not exceed 600—700°, the carbon separates in the form of graphite. The author has investigated whether this action takes place when the iron is submitted to high pressures during the heating.

A special apparatus, made of steel was used, in which the alloys of iron and carbon under investigation could be heated electrically to temperatures varying between 600° and 1200°, and under pressures which in some cases were as high as 15,000 atmospheres. Pressure was put on the alloys while cold until no further diminution in volume took place, and then they were electrically heated; at a certain temperature a diminution in volume took place, and had to be compensated by increasing the pressure.

When a white iron containing 3% of carbon and 4% of nickel, or one containing 3% of carbon and 2% of silicon, was heated at 1100° under a pressure of 150 kilograms per sq. mm. (15,000 atmospheres) until the above-mentioned diminution in volume took place, graphite was found to be present after cooling. The longer the heating the greater the proportion of graphite.

Similar results were obtained when carbide of iron (Fe_3C) was used instead of white iron. T. S. P.

Genetic and Constitutive Relations in the Magnetic Properties of Ferrites and of Iron Oxides. SIEGFRIED HILPERT (*Ber.*, 1909, 42, 2248—2261).—The number of compounds having marked magnetic permeability is very small, consisting chiefly of compounds derived from ferric oxide. The author has examined a number of ferrites of the general formula $\text{MO}, \text{Fe}_2\text{O}_3$, observing the approximate temperature at which the permeability disappears.

Crystalline sodium and potassium ferrites, prepared in the wet way, are indifferent in a strong magnetic field. Prepared by fusion, they are slightly magnetic, losing this property at 150°. Calcium and barium ferrites, prepared in the wet way, are non-magnetic unless heated to 800° and cooled. Calcium ferrite, prepared by fusion, melts at 1200° and has a transformation point at 160°. Magnesium, zinc, and lead ferrites are also non-magnetic until fused. The transformation point of lead ferrite is near 200°. Cuprous ferrite, prepared by fusion in nitrogen at 1250°, is crystalline, and is only slightly magnetic. Precipitated cupric ferrite is magnetic. It becomes crystalline at 900°, and may be obtained in compact masses by compressing a mixture of cupric and ferric oxides and sintering at 1000°. The transformation point is at 280°. Precipitated cobaltic ferrite loses its magnetic properties at 280—290°.

A mixed lead and cupric ferrite is as strongly magnetic as pure cupric ferrite if rapidly cooled from 1000°, but loses this property if slowly cooled, or if melted at 1300°. The permeability is restored by heating to 900° and slowly cooling.

Ferric hydroxide, prepared by oxidising freshly precipitated ferrous hydroxide with ammonium persulphate, is non-magnetic, but if first oxidised by air to the Fe_3O_4 stage, the persulphate gives a highly

magnetic product, becoming changed into ordinary ferric oxide at or above 400° . A cobaltic ferrite prepared in the same way is also magnetic.

The ferric hydroxide obtained by the action of air on ferrous carbonate is non-magnetic if rapidly prepared, but if oxidised slowly, so that ferroso-ferric oxide is first formed, the final product is magnetic.

The magnetic ferrites all contain Fe_2O_3 as an acid-forming oxide, and it is probable that the magnetic ferric oxides described also retain the same constitution: $2(\text{FeO})^+ + 2(\text{Fe}_2\text{O}_3)^- + \text{O} = (\text{Fe}_2\text{O}_3)^+, 2(\text{Fe}_2\text{O}_3)^-$, this molecular arrangement, however, being unstable, and lost on heating. C. H. D.

Uranyl Chloride. WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1909, 148, 1769—1770).—A solution of barium chloride is added drop by drop to a freshly prepared and concentrated solution of uranyl sulphate until all the sulphuric acid is precipitated. Evaporation of the filtrate on the water-bath gives a yellow, deliquescent mass, consisting of uranyl chloride, UO_2Cl_2 ; hydrated crystals, $\text{UO}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$,

can also be obtained.

Reduction of the chloride by hydrogen, under the influence of heat, gives the black modification of uranous oxide. If the chloride is fused with a large excess of potassium hydroxide in an open tube, the red peruranate, K_2UO_5 , is produced; this gradually loses oxygen with the formation of the yellow uranate, K_2UO_4 .

The addition of excess of concentrated ammonium hydroxide to a solution of uranyl chloride containing a small quantity of barium chloride at once gives a deep yellow precipitate of barium uranate, BaUO_4 . T. S. P.

Peruranic Acid. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1909, 692).—A 12-volume solution of hydrogen peroxide was added in small portions at a time to a dilute solution of a mixture of uranous and uranic sulphates. A bright yellow precipitate was formed; after remaining in contact with the solution for forty-eight hours in the dark, it was washed until neutral, and then dried over sulphuric acid. Analysis showed it to be a peruranic acid of the formula $\text{UO}_4 \cdot 2\text{H}_2\text{O}$. T. S. P.

Orthopervanadates. PETR. G. MELIKOFF and E. JELHCHANINOFF (*Ber.*, 1909, 42, 2291—2294).—In former investigations of peracids (Melikoff and Pissarjewsky, *Abstr.*, 1899, ii, 491), ortho-salts of pervanadic and percolombic acids were not obtained, being unstable under the conditions of experiment. The vanadium salts may be obtained by using concentrated (30%) hydrogen peroxide.

Ammonium orthopervanadate, $(\text{NH}_4)_3\text{VO}_6 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, is prepared by dissolving ammonium vanadate in ammonia, cooling to 0° , adding hydrogen peroxide, and precipitating with alcohol. The product, after washing with ether and drying, is pale blue.

With a large excess of hydrogen peroxide, an indigo-blue salt containing more oxygen, probably $\text{VO}_2(\text{OH})(\text{O}\cdot\text{ONH}_4)_2$, is obtained.

Potassium orthopervanadate, $\text{K}_3\text{VO}_6 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, prepared as above, forms a blue oil, but after dissolving in a little potassium hydroxide and again precipitating with alcohol, forms a blue, flocculent precipitate. Excess of hydrogen peroxide gives an acid salt.

Only salts with two active oxygen atoms at most could thus be obtained, whilst the pertantalates readily form salts with four active atoms.
C. H. D.

Influence of Temperature on the Hydrolysis of Bismuth Halides. WALTER HERZ and ALFRED BULLA (*Zeitsch. anorg. Chem.*, 1909, 63, 59—62).—The authors claim priority against Dubrisay (this vol., ii, 406), whose figures for the hydrolysis of bismuth chloride agree in the main with theirs (this vol., ii, 320). Experiments have now been carried out at 50° . As at 25° , the only solid phases formed are BiOCl and BiOBr .

The hydrolysis of bismuth chloride is lessened by rise of temperature. The ratio $[\text{BiCl}_3]/[\text{HCl}]^2$ increases somewhat at high concentrations. The hydrolysis of bismuth bromide is almost independent of the temperature. The decomposition of bismuth iodide by water at 50° is so slow that measurements of the hydrolysis could not be made.
C. H. D.

Preparation of Colloidal Gold by means of Solutions of Humus. PAUL EHRENBURG and HANS PICK (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 30—31).—In 1830, Schübler found that the addition of gold chloride to a solution of humic acid gave rise to a purple-red solution. The authors find that this is due to colloidal gold, solutions and suspensions of different colours being obtained under different conditions. In sunlight the action is considerably accelerated, but this is due to the rise of temperature, and not to any special actinic effect.
H. M. D.

Rhodium. ALEXANDER GUTBIER and L. VON MÜLLER (*Ber.*, 1909, 42, 2205—2207. Compare this vol., ii, 523).—Rhodium may be separated readily from the halogens in such compounds as chloro-pentamminerhodium chloride by heating a hot dilute aqueous solution of the compound with a slight excess of 10% hydrazine hydrate solution. A rhodium mirror is produced, and this, on subsequent boiling, becomes detached as small, glistening flakes, which can be filtered easily. The halogen can be estimated in the filtrate in the usual manner.
J. J. S.

Mineralogical Chemistry.

Gas from Volcanic Fumerolles. ARMAND GAUTIER (*Compt. rend.*, 1909, 148, 1708—1715).—As a result of his researches on the gases extracted from various rocks and on the origin of these gases

(Abstr., 1901, ii, 171, 322, 399; 1903, ii, 222), the author has formulated a new theory of volcanic phenomena (Abstr., 1906, ii, 538, 548). He has now analysed gases collected from the fumaroles of Vesuvius at different times, with the following results.

I. Gas collected from a fumarole not far from the summit of the cone, three months after the eruption in April, 1906.

II. Gas collected from fumaroles in October, 1907, eighteen months after the eruption:

	HCl.	CO ₂ .	CO	H.	O.	N (argon etc.).	H ₂ O.
I.	0.78	11.03	nil.	1.24	3.72	15.49	67.74
II.	Nil.	0.80	0.15	0.54	4.59	21.23	72.69

The following gases were not present: carbon monoxide, hydrocarbons, oxides of nitrogen, sulphur dioxide, hydrogen sulphide, hydrogen fluoride, fluorides of silicon and boron. There was no deposit of sulphur. A trace of formic acid was noticed. Carbon oxysulphide was very carefully searched for, but never found.

Other samples of gas collected at the same date gave similar results.

The gases, II, issuing from the fumaroles rapidly attack steel or copper, although they do not contain hydracids. They have an odour recalling that of bromine or chlorine.

T. S. P.

The Optical Rotatory Power of Mineral Oils, Etc. FRANZ HENLE (*Ber.*, 1909, 42, 2453—2454).—Polemical in regard to the paper by Rakusin (this vol., ii, 586).

P. H.

Metallic Sodium as the Supposed Cause of the Natural Blue Colour of Rock-salt. GIORGIO SPEZIA (*Centr. Min.*, 1909, 398—404. Compare Abstr., 1908, ii, 396).—Since a blue colour may be produced artificially in rock-salt by heating it in sodium vapour, it has been suggested by H. Siedentopf (Abstr., 1906, ii, 443) that the blue colour is due to the presence of metallic sodium in a colloidal state, in the same way that the colour of red glass is due to the presence of colloidal gold. Several comparative experiments made by the author on naturally- and artificially-coloured blue rock-salt and on colourless rock-salt do not, however, support this view. When the blue salt is dissolved in water the colour disappears, and the solution, although slightly alkaline, is no more so than a solution of colourless rock-salt. The natural blue colour is destroyed at a temperature of 275°, whilst the artificially-produced colour is still retained at 400°.

L. J. S.

Formation of Delvauxite. EMIL DITTLER (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 35).—The author describes a light brown, sponge-like mineral found in the iron ore deposits of Grillenberg, near Payerbach, which represents one of the stages in the formation of the mineral gel delvauxite. Analysis gave 34.23% Fe₂O₃, 17.38% P₂O₅, and about 50% H₂O, as well as small quantities of sulphate and traces of arsenic; the mineral may be regarded as a precursor of delvauxite. It has the typical characters of a gel. After dehydrating

by exposure to 90% sulphuric acid, it takes up water, alcohol, and very dilute sulphuric acid with great avidity, and this absorption is accompanied by a considerable increase in volume. It decolorises ammoniacal phenolphthalein solution almost immediately, and absorbs readily basic dyes. On heating the mineral for a considerable period, it loses its colloidal properties. H. M. D.

Results of the Geological and Mineralogical Exploration of Eguéi. G. GARDE (*Compt. rend.*, 1909, 148, 1616—1619).—Eguéi is situated about 300 kilometres north-east of lake Tchad, in the desert. Four different minerals, namely, trona, thenardite, gypsum, and a phosphate of iron, have been found by the author in the clay. The phosphate of iron is either light or dark brown in colour; it is mono-refrangent, but contains some parts which are birefringent. Analysis gave the following results:

P ₂ O ₅ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	H ₂ O.	Residue.
33·30	44·20	1·50	2·28	20·47	0·75 = 99·50

corresponding with the formula



This does not correspond exactly with any known mineral. The new mineral has probably been formed from vivianite.

T. S. P.

Plumboniobite. OTTO HAUSER and L. FINCKH (*Ber.*, 1909, 42, 2270—2274).—A new mineral related to samarskite, but containing lead, occurs in mica mines at Morogoro in the Uluguru Mountains, German East Africa, together with pitchblende. *Plumboniobite* forms dark brown or black, imperfectly crystalline masses, brown in thin sections, D¹⁵ 4·801—4·813, H 5—5·5, fracture conchoidal. The analyses (II) and (III) refer to light-coloured material, (I) to darker.

	Cb ₂ O ₅ .	Ta ₂ O ₅ .	TiO ₂ .	UO ₂ .	SnO ₂ .	ThO ₂ .	ZrO ₂ .	Y ₂ O ₃ .	Al ₂ O ₃ .	PbO.	CuO.	FeO.	MnO.
I.	46·15	1·18	1·20	13·72	0·15	0·06	trace	14·26	0·28	7·62	trace	5·70	0·11
II.	47·00		1·42	13·74	0·14	0·08	—	14·51	0·23	7·08	0·25	6·33	0·32
III.	46·03	1·20	0·90	13·60	—	—	—	14·12	0·17	7·55	1·21	5·15	0·28
	CaO.		H ₂ O.		N ₂ , He.		CO ₂ .		Total.				
I.	3·05		6·38		0·22		0·19		100·27				
II.	3·11		6·51		6·51				100·72				
III.	2·84		6·23		6·23				99·89				

The yttrium earths contain ytterbium and gadolinium; the cerium earths are absent. Helium is only present in very small quantity. The mineral is a pyrocolumbate. C. H. D.

Alamosite, a New Lead Silicate from Mexico. CHARLES PALACHE and H. E. MERWIN (*Amer. J. Sci.*, 1909, [iv], 27, 399—401).—The mineral was found at Alamos, Sonora, Mexico, in association with quartz, cerussite, leadhillite, and wulfenite. It forms radiated fibrous aggregates with more or less pronounced spheroidal form, a snow-white colour, and adamantine lustre; isolated fibres are colourless and transparent. The crystals are monoclinic, with $a:b:c=$

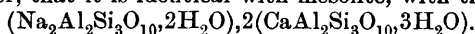
1.375 : 1 : 0.924; $\beta = 84^\circ 10'$; they are elongated in the direction of the axis of symmetry, and have a perfect cleavage parallel to the plane of symmetry. The mineral is decomposed by strong nitric acid with gelatinisation. Analyses gave results agreeing with the formula PbSiO_3 .

SiO_2 .	PbO .	CaO .	FeO .	Residue from PbO .	Insol. (quartz).	Total.	Sp. gr.
21.11	78.13	trace	0.09	0.53	0.08	99.94	6.488

The mineral is thus analogous to wollastonite (CaSiO_3), although, owing to the appreciable difference in the length of the a -axis and in the different cleavage, it is perhaps not isomorphous with this.

L. J. S.

The Identity of Poonahlite with Mesolite. HERBERT LISTER BOWMAN (*Min. Mag.*, 1909, 15, 216—223).—The acicular zeolite poonahlite (of H. J. Brooke, 1831), found associated with apophyllite and stilbite near Poonah, has usually been classed with scolecite. The following analysis, as well as the geometrical and optical characters, show, however, that it is identical with mesolite, with the formula :



SiO_2 .	Al_2O_3 .	CaO .	Na_2O .	K_2O .	H_2O .	Total.	Sp. gr.
46.71	26.45	9.35	5.33	0.11	12.56	100.51	2.264—2.272

The transparent, acicular crystals have a prism angle of $88^\circ 30' 49''$, and a perfect prismatic cleavage. Their optical characters indicate anorthic symmetry. The double refraction is very low (0.0004), and the optic axes, with very strong axial dispersion, are nearly perpendicular to the prism faces; the needles therefore show very characteristic blue and yellow colours when examined between crossed nicols.

L. J. S.

Identity of Guarinite and Hiortdahlite. FERRUCCIO ZAMBONINI [with analysis by GEORGE T. PRIOR] (*Min. Mag.*, 1909, 15, 247—259).—The rare Vesuvian mineral, guarinite, found as small, yellow crystals in the sanidine bombs of Monte Somma, was described by Guiscardi in 1857 as a calcium titano-silicate with orthorhombic symmetry. A later analysis by Rebuffat (*Abstr.*, 1896, ii, 309) gave it as a complex silicate of calcium, aluminium, and sodium. A new examination of the crystals proves them to be anorthic, with interfacial angles and optical characters identical with those of hiortdahlite. A micro-chemical test showed presence of zirconium, and this suggested that the ammonia precipitate, believed by Guiscardi and Rebuffat to be titanium or aluminium, was really zirconium. The following new analysis (made on 0.3341 and 0.0612 gram of material) completely proves the identity of guarinite with hiortdahlite, the only important difference being in the amount of fluorine (5.83% in hiortdahlite):

SiO_2 .	ZrO_2 .	Cb_2O_5 .	Ta_2O_5 .	FeO .	MnO .	CaO .	MgO .	K_2O .	Na_2O .	F.	Total less O for F.	Sp. gr.
30.53	19.70	1.68	0.21	1.91	1.56	35.80	0.57	0.43	6.13	1.28	99.26	3.25

The corresponding formula is $3\text{CaSiO}_3[\text{Ca}(\text{F}, \text{OH})]\text{NaZrO}_3$.

L. J. S.

Labradorite-norite with Porphyritic Labradorite Crystals. JOHAN H. L. VOGT (*Quart. Journ. Geol. Soc.*, 1909, **65**, 81—102).—A labradorite-norite from Napp Farm on Flakstadö, one of the Lofoten and Vesteraal Islands off the northern coast of Norway, consists of large porphyritic crystals of labradorite reaching 18 cm. in length, set in a ground-mass of plagioclase (61·88%), titanomagnetite (9%), hypersthene (13%), diallage (13%), biotite (3%), apatite (0·12%), and spinel (0·01%). The labradorite phenocrysts form nearly 23% of the mass of the rock, and have the composition given under I; the optical extinction angles indicate that the outer zones are slightly more acid than the central portions. Analysis II is of the still more acid plagioclase of the ground-mass; and III is of the whole of the ground-mass.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	P ₂ O ₅ .	Total.	Sp. gr.
I.	52·42	—	31·25*	—	—	—	11·98	3·44	0·97	—	100·06	2·708
II.	55·18	—	29·02†	—	—	—	10·02	4·88	1·00	—	100·10	2·685
III.	47·75	1·74	18·71	6·08	7·11	5·32	9·47	2·70	1·20	0·05	100·13	—

* Including a little Fe₂O₃ and TiO₂.

† Including a very little Fe₂O₃.

The order of crystallisation was: (1) plagioclase phenocrysts; (2) plagioclase and magnetite; (3) plagioclase, magnetite, and pyroxenes. Graphic representations are given to illustrate the crystallisation of a ternary system of plagioclase, magnetite, and pyroxene with binary and ternary eutectics.

L. J. S.

Sodalite-trachyte from Pico de Teyde, Teneriffe. HEINRICH PREISWERK (*Centr. Min.*, 1909, 393—396).—The rock consists of laths of anorthoclase in a ground-mass of sanidine, sodalite, and glass, with some diopside, magnetite, biotite, and apatite. Analysis I, by Naima Sahlbom. Analyses are also given of: II, phonolite containing nosean and aegirite; III and IV, basalt from Teneriffe. The basalts contain a low percentage of silica with high titanium dioxide and alkalis.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	(110°).	Total.
I*.	59·46	0·45	19·49	1·45	2·30	0·24	1·66	1·05	4·34	9·34	0·26	0·21	100·63
II.	54·24	0·51	20·84	2·26	2·09	0·15	2·99	1·21	3·84	9·22	1·89	1·24	100·48
III.	42·77	3·08	15·80	3·34	10·85	0·18	9·77	9·04	1·65	3·49	0·27	0·35	100·59
IV.	41·49	3·50	16·27	3·08	8·57	0·45	11·70	8·97	1·24	3·26	0·31	0·15	99·48

* Also Cl 0·38.

L. J. S.

Crystalline Schists of the Urals. LOUIS DUPARC (*Compt. rend.*, 1909, **148**, 1683—1685).—The crystalline schists of the northern Urals are found immediately beneath argillaceous schists of the Lower Devonian period, and above a mixture of true quartzites and conglomerates of unknown age. The crystalline schists are divisible into two distinct types, the one acidic, representing metamorphosed sediments from the quartzite, and the other, which is rarer, basic, produced by erosion and metamorphosis of the intrusive green stones which are frequently encountered. In accord with mineralogical and chemical character, the first type may be subdivided into (a) quartzite, (b) sericite quartzite, and (c) sericite gneiss with albite, whilst the

basic type is subdivided into (a) albito-epidote amphibolite, (b) albito-chlorite schist, and (c) albito-epidote glaucophanite. Complete analyses are given of a typical specimen of each of these six classes of schist.

R. J. C.

Physiological Chemistry.

Effect of Forced Breathing and Oxygen on the Distress Caused by Muscular Work. C. GORDON DOUGLAS and JOHN S. HALDANE (*Proc. physiol. Soc.*, 1909, i—iv; *J. Physiol.*, 39).—Forced breathing performed before violent muscular exercise lessens the subsequent distress, and lowers the respiratory quotient. This is because the carbon dioxide is washed out of the body, so that muscular work does not cause such an excess of that gas in the blood as would otherwise occur.

The previous breathing of oxygen, unless forced, has no appreciable effect, because normal breathing of oxygen has no effect on respiration, and there is no storage of oxygen so breathed in the body.

W. D. H.

Influence of Age and Size on the Gaseous Metabolism of Children. ARTUR SCHLOSSMANN and HANS MURCHHAUSER (*Biochem. Zeitsch.*, 1909, 18, 499—509).—A discussion on the relationship between gaseous metabolism and the body surface. The elimination of carbon dioxide and absorption of oxygen were at three different periods proportional to the area of the surface, independently of the age of the child.

W. D. H.

Method for Measuring the Loss of Water by the Organism Through the Lungs and Skin. Variation of this Loss with Altitude. H. GUILLEMARD and ROBERT MOOG (*Compt. rend.*, 1909, 148, 1624—1627).—The loss of water through the lungs and skin is measured indirectly by finding the total loss in weight of the body during a definite period, and by determining the composition of the gases expired during this interval. The ratio between total weight of water eliminated and total loss in weight is about 0.88 near the sea level, and somewhat less at high altitudes.

W. O. W.

The Absorption of Nitrous Oxide by the Blood. RICHARD SIEBECK (*Chem. Zentr.*, 1909, i, 18, 1491).—The absorption coefficient of water for nitrous oxide is smaller than that of blood. The increased absorption is not due to the plasma, the coefficient of which is 97.5% of that of water. On the other hand, a solution of red corpuscles has markedly greater coefficient than water, and the absorption in this solution obeys Henry's law, and is independent of the absorption of carbon dioxide and oxygen.

S. B. S.

The Electrochemical Measurement of Alkalinity in Blood and Serum. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1909, 18, 317—339).—The difference of potential produced by platinum hydrogen electrodes immersed in the blood or serum and in acid or alkaline solutions of known hydrogen or hydroxyl concentration was measured, and the alkalinity of the blood thereby determined. Special forms of electrodes, suitable for small quantities of fluid, are described, by means of which equilibrium in the system is attained in a few minutes. The hydrogen-ion concentration in blood-serum was found to vary between 0.036 and 0.20×10^{-7} , the value depending chiefly on the amount of carbon dioxide present. By passing this gas through serum, the concentration of hydrogen ions could be increased to 1.4×10^{-7} , whilst by the passage of air it could be diminished to 0.8×10^{-9} . The influence of temperature and of the addition of acids and alkalis on the hydrogen-ion concentration of blood and serum was also studied. S. B. S.

The Sugar of the Blood. VI. The Distribution of Sugar in the Blood in Hyperglycæmia. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1909, 18, 375—379).—In cases of hyperglycæmia, whether in diabetes or experimentally produced, the corpuscles as well as the plasma partake of the increase in sugar. S. B. S.

The Sugar of the Blood. VII. Permeability of Blood Corpuscles for Dextrose. PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1908, 18, 514—520).—In previous researches it has been shown that a considerable portion of the blood sugar is carried by the corpuscles. It is now shown that, *in vitro*, the corpuscles do not take up an excess of sugar from solutions in which they are placed. In the circulating blood, the corpuscles are permeable to dextrose; outside the body they are not. W. D. H.

Coagulation of Blood. LEO F. RETTGER (*Amer. J. Physiol.*, 1909, 24, 426—435).—A discussion of current theories of coagulation, together with experiments on solutions of fibrinogen in relation to solutions of thrombin. It is doubted whether thrombin is an enzyme; it is not destroyed by boiling, and minimal amounts will not produce complete coagulation; minimal amounts produce correspondingly small clots. The existence of a proferment is regarded as unproved, and the existence of kinases or coagulins as improbable. The coagulation of the blood is a quantitative reaction, and is probably a mutual precipitation of two colloids, fibrinogen and thrombin. Thrombin appears to be a protein, but not a nucleo-protein. It will readily be understood that on this view the action of anti-thrombin, calcium salts, and decalcifying agents is interpreted on new lines, but on this and many other points this very suggestive paper cannot be advantageously summarised in a short way. W. D. H.

The Coagulation of the Blood. II. JOHN MELLANBY (*J. Physiol.*, 1909, 38, 441—503. Compare this vol., ii, 158).—The venoms of the Australian and Indian vipers contain substances which generate fibrin

ferment from prothrombin, and coagulate any fibrinogen solution to which they are added. They may be assumed to consist of kinase and calcium salts. But as potassium oxalate increases their coagulating power, they probably consist of pure kinase, the necessary calcium being provided in adsorbed form by the fibrinogen. They cause intravascular clotting when rapidly injected, but if slowly injected, non-coagulable blood is obtained. The blood and tissues are able to deal with a slow formation of fibrin, and so general clotting does not ensue. Such blood owes its stability to absence of fibrinogen; as fibrinogen is regenerated, the blood re-acquires the power to clot. Cobra venom owes its anti-coagulating power to an anti-kinase, not to anti-thrombin. The failure of peptone blood to clot is attributed, not to anti-thrombin, but to excess of alkali secreted by the liver. Hirudin (leech extract) contains both anti-thrombin and anti-kinase.

W. D. H.

Blood Coagulation and Calcium Ions. BERTRAM J. COLLINGWOOD (*Proc. physiol. Soc.*, 1909, lxxix; *J. Physiol.*, 38).—The addition to freshly drawn blood of an equal volume of 2% solution of disodium hydrogen phosphate delays, but does not prevent, clotting. The salt, therefore, does not precipitate that portion of the calcium in the blood which is essential to coagulation. If, however, an alkaline solution of calcium chloride is prepared approximating to the calcium content and alkalinity of the blood, and an equal bulk of 2% disodium hydrogen phosphate added to it, all the calcium is precipitated. If the calcium in the blood was in simple solution, a similar precipitation should be expected there, but that, as just stated, is not the case. The conclusions drawn are that the blood carries calcium in some other way than in a state of simple solution, and that calcium ions are not essential to clotting.

W. D. H.

The Influence of Cholesterol on Hæmolysis by Soaps. WILHELM MEYERSTEIN (*Arch. exp. Path. Pharm.*, 1909, 60, 385—389).—Cholesterol inhibits the rate of hæmolytic action of sodium oleate in simple mixtures; total inhibition is readily produced when the cholesterol and oleate solution are first heated together. The protecting action of cholesterol appears to be due to the fact that it is in solution; it does not act then directly on the blood-corpuscles, but links on to the soap and inhibits the hæmolytic action of the latter. Similar results were obtained with other substances, such as kephalin, cerebroside, and even other soaps, as with cholesterol.

S. B. S.

Cobra Poison and Hæmolysis. II. IVAR BANG (*Biochem. Zeitsch.*, 1909, 18, 441—498. Compare Abstr., 1908, ii, 721).—Cobra venom dissolves red corpuscles in a solution of sucrose without the addition of an activator. This is hindered by salts, and this inhibition is an action of the cation, directed not against the corpuscles, but against the poison. The inactivation by sodium chloride is reversible when the corpuscles are replaced in their own serum. All

salts of strong acids and of acetic acid produce inactivation, whilst the salts of weak acids (carbonates, chromates, phosphates) do not. The reactivation by serum is attributed mainly to sodium carbonate. The poison itself is probably an acid, and the basic components of the corpuscles are believed to be the points to which the poison attaches itself; they act as the receptor. The blood is inactivated by remaining in sucrose solution, and the part played by the lipoid cell membrane in the passage of intracellular and extracellular saline materials is discussed.

W. D. H.

The Biochemistry of Phasin. OTTO WIENHAUS (*Biochem. Zeitsch.*, 1908, 18, 228—260).—The seeds of various *Papilionaceae* yield extracts which agglutinate blood-corpuscles without exerting any other definite toxic action. The extracts from various plants have been examined, and especially those from white beans (*P. vulgaris*). The saline extract was precipitated with alcohol, and the precipitate contained the active substance. This was redissolved in water and reprecipitated with alcohol, and the precipitate was dried. The majority of experiments were carried out with an extract of this powder (phasin). It is but slightly toxic, although large doses on intravenous injection will kill small animals; cats and pigeons can tolerate doses of 1000 or 620 mg. No agglutination of blood takes place *in vivo*. The agglutin acts in very dilute solutions on blood-corpuscles of various species; also on the stroma and on formalised blood, and on suspensions of cells from different organs. The agglutin is not destroyed by prolonged heating; it retains its effect after heating for four days at 110—113°. It also resists digestion with proteolytic enzymes. The agglutin can be regenerated from its combination with stroma by means of dilute acids.

S. B. S.

The Catalase from Blood. C. GESSARD (*Compt. rend.*, 1909, 148, 1467—1468. Compare Cotton, Abstr., 1901, ii, 295).—A repetition of experiments already described. The author confirms the observations of Ville and Moitessier (Abstr., 1903, ii, 120) and of Senter (Abstr., 1903, ii, 661) relating to the existence of hæmase. Fibrin can be completely freed from this enzyme by centrifugalisation.

W. O. W.

Action of Digestive Enzymes on Each Other. WILLIAM BAIN (*Proc. Roy. Soc. Med.*, 1909, 2, *Therap. Pharmac. Section*, 165—172).—After two hours' digestion in pepsin-hydrochloric acid at 36°, the tryptic action of medicinal doses of various pancreatic digestive preparations is entirely destroyed; during one and a-half hours' digestion, the tryptic action is not completely destroyed. This suggests that doses of such preparations should be given after food at a time when the contents of the stomach are rapidly entering the intestine. The amylolytic action of pancreatic preparations is similarly destroyed in an hour, but the lipolytic enzyme retains about half its normal activity under the same treatment. Trypsin destroys the activity of pepsin and papain.

W. D. H.

The Influence of Drugs on Gastric Secretion. Part IV. Inorganic and Organic Arsenic Compounds. JOHANN FEIGL and ADOLF ROLLETT (*Biochem. Zeitsch.*, 1909, 19, 156—180).—The technique was the same as that previously described for the investigation of iodine compounds (Abstr., 1908, ii, 311). Inorganic arsenious and arsenic salts and organic arsenic compounds, such as cacodylic acid and atoxyl, given by the mouth in very dilute solution, cause the secretion of one to three times the quantity of gastric juice produced by the same amount of pure water. G. B.

Relations of Secretin and Entero-kinase to Pancreatic Enzymes. JOHN MELLANBY and V. J. WOOLLEY (*Proc. physiol. Soc.*, 1909, xi—xii; *J. Physiol.*, 39).—Conversion of the rennet zymogen in pancreatic juice into rennet is rapidly accomplished by entero-kinase, and less rapidly by the addition of water. The conclusion is therefore drawn that the action of entero-kinase is hydrolytic. Antiseptic autolysis of the pancreas yields an extract containing all its enzymes; this is considered to be an indication that secretin does not combine with the zymogens to form active enzymes. W. D. H.

Metabolism during Typewriting. THORNE M. CARPENTER and FRANCIS G. BENEDICT (*J. Biol. Chem.*, 1909, 6, 271—288).—The results obtained with two men typing 1500 to 1600 words per hour show an increase of metabolism so that, per hour, 10—14 grams of carbon dioxide are produced, and 10—13 grams of oxygen are consumed, in excess of that which occurs during rest. Expressed in calories, the increase is about 25. Slow walking along a level road increases the metabolism by about 160 calories (Zuntz). W. D. H.

The Influence of Protein and Carbohydrate on Metabolism. A. GIGON (*Chem. Zentr.*, 1909, i, 1493; from *Skand. Arch. Physiol.*, 21, 351—367).—The experiments were carried out in a Sondén-Tigerstedt respiration apparatus. The protein selected was casein, the carbohydrate, dextrose. In the inanition period the excretion of carbon dioxide per hour was 23·8 grams. After the administration of sugar this rose to 29·9, and of casein to 28. If both foods were given, the figure rose to 34, the increase being the sum of those produced by the two foods separately. The excretion of nitrogen and phosphoric acid was not affected by the administration of sugar. W. D. H.

Purine Metabolism in Selachians. I. VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1909, 18, 506—513).—The special point investigated was the uricolytic power of the liver of *Scyllium catulus*; it is very considerable, and is more rapid than in any other organ previously investigated. W. D. H.

Metabolism in Cystinuria. T. SHIRLEY HELE (*J. Physiol.*, 1909, 39, 52—72).—In the three cases examined, the cystine output was 0·3 to 0·5 gram per diem. Very slight alterations were produced by diet, but it was not possible to vary the diet so greatly as in Alsberg and Folin's case. Cystine given by the mouth to one patient

was excreted almost entirely as sulphate. Cadaverine was only found once. Arginine given by the mouth to one patient was not excreted as putrescine. Diamino-acids were not found in the urine (one case); leucine and tyrosine were also absent, and glycine was not present in excess in the urine.

W. D. H.

Oxidation in the Egg. II. OTTO WARBURG (*Zeitsch. physiol. Chem.*, 1909, 60, 443—452. Compare Abstr., 1908, ii, 963).—Further observations are recorded on the respiratory changes in the echinoderm egg, fertilised and unfertilised, and the increase in oxidation which occurs in hypertonic solutions. These results are discussed in relation to J. Loeb's hypothesis that the increase of oxidation which occurs in hypertonic sea-water is a factor in the production of artificial parthenogenesis.

W. D. H.

Does Caviare Contain Purine Bases? KURT LINNERT (*Biochem. Zeitsch.*, 1909, 18, 209—210).—No purine bases were found when attempts to isolate them were made by the method of Burian and Walker Hall.

S. B. S.

The New Formation of Amino-acids in the Animal Organism. EMIL ABDERHALDEN and CASIMIR FUNK (*Zeitsch. physiol. Chem.*, 1909, 60, 418—425).—It is well known that glycine originates in the body, for the administration of benzoic acid leads to a greater excretion of hippuric acid than can be derived from the glycine pre-formed in the tissues; further, dogs fed on casein, which is free from this amino-acid, show no differences from dogs fed on proteins which contain it. On the other hand, the removal of tryptophan from the food, or the administration of proteins in which it is absent, has a serious effect. Henriques has shown that gliadin keeps rats in equilibrium, and so draws the conclusion that lysine originates in the body. The rat, however, is not a suitable experimental animal for this purpose; but it is shown that dogs thrive well on gliadin. The gliadin, however, contained 0.35% of lysine. If Henriques' gliadin also contained lysine, his conclusion needs revision.

W. D. H.

Mode of Oxidation in the Animal Organism of Phenyl Derivatives of Fatty Acids. IV. Fate of Phenylpropionic Acid and its Derivatives. V. Fate of Phenylvaleric Acid and its Derivatives. VI. Fats of Phenylalanine, Phenyl- β -alanine, Phenylserine, Phenylglyceric Acids, and Phenyl-acetaldehyde. HENRY D. DAKIN (*J. Biol. Chem.*, 1909, 6, 203—220, 221—234, 235—244).—IV. The results confirm those previously advanced as to the combustion of phenylpropionic acid in the body; part of the benzoylactic acid formed is probably converted into benzoic acid without going through the stage of acetophenone. Under some conditions, cinnamoylglycine was isolated from the urine of animals that had received injections of sodium phenylpropionate. If phenyl- β -hydroxypropionic acid is given to dogs, benzoylactic acid appears in the urine. Glycine derivatives of phenylpropionic acid, phenyl-

β -hydroxypropionic acid, and cinnamic acids are far less readily attacked in the organism of dogs and cats than salts of the free acids.

V. Five acids of the type $\text{Ph} \cdot \text{CCCC} \cdot \text{COOH}$, namely, phenylvaleric, β -hydroxyphenylvaleric, phenyl- Δ^{α} -pentenoic, phenyl- Δ^{β} -pentenoic, and cinnamylideneacetic acids, undergo oxidation in the body in such a way that four carbon atoms are removed from the side-chain in two pairs. In every case benzoic acid is the end product, the intermediate products being acetophenone, β -hydroxyvaleric acid, and probably cinnamoylglycine. This may be termed successive β -oxidation, and it appears to be a general biochemical reaction. Embden's results on the perfusion of the liver with salts of fatty acids are in harmony with this view. γ -Hydroxyphenylvaleric and cinnamylidenemalonic acids are scarcely attacked when administered to cats.

VI. The substances named are injected intravenously or subcutaneously in dogs and cats, and the urine examined. With phenylalanine, a large amount was recovered in the urine as such; α -carbamido- β -phenylpropionic acid was also present. In the case of phenyl- β -alanine, a small amount was recovered unchanged; β -hydroxyphenylpropionic acid, acetophenone, and hippuric acid were also obtained in the urine, but no cinnamoylglycine. After the administration of phenylserine, the only substance detected in the urine was hippuric acid. In dogs, two isomeric phenylglyceric acids led to the appearance of the unchanged acids in the urine, with a small quantity of hippuric acid. In cats no hippuric acid was found. After the subcutaneous injection of phenylacetaldehyde, a small amount of phenacetic acid was found in the urine.

W. D. H.

Theory of Catalase Action. OSCAR LOEW (*Pflüger's Archiv*, 1909, 128, 560—565).—There is no doubt that hydrogen peroxide is always formed when organic substances, labile hydrogen atoms, and molecular oxygen participate in oxidation; and it is believed that this acid occurs in living cells, and that catalase plays the part of energetically destroying the hydrogen peroxide.

W. D. H.

Extracts of Selachian Organs. I. Extract of Acanthias Muscle. A. SUWA (*Pflüger's Archiv*, 1909, 128, 421—426).—Among the substances in extracts of the muscle of the fish *Acanthias vulgaris* are betaine, a substance but rarely found in animals, and trimethylamine oxide, $\text{ON}(\text{CH}_3)_3$, which has never been found previously either in animal or vegetable tissues. Creatine is present in small quantities, but creatinine is absent.

W. D. H.

Distribution of Phosphoproteins in Tissues. II. R. H. ADERS PLIMMER and R. KAYA (*J. Physiol.*, 1909, 39, 45—51).—Phosphoprotein is present in dog's pancreas; its amount in the gland lessens on secretion, and it can be detected in the juice secreted. It is present in sheep's salivary glands and in frogs' eggs; as development progresses, it diminishes in amount just as in hens' eggs. It is absent from cod's testis.

W. D. H.

The Occurrence of Lipases in Tissues. A. PAGENSTECHER (*Biochem. Zeitsch.*, 1909, 18, 285—301).—The investigations were carried out by determining the increase of acidity which resulted when olive oil, egg-yolk, and monobutyrin were treated with extracts of various organs for twenty-four hours in an incubator. The extracts were made by shaking for twenty-four hours the finely minced organs with saline solution and toluene, and expressing the juice. Muscular tissue and brain were found to have the smallest lipolytic action. Lungs and kidneys are more active, whereas the liver and spleen have the greatest activity. S. B. S.

The Internal Secretion of Chromaffine Tissue. R. H. KAHN (*Pflüger's Archiv*, 1909, 128, 519—554).—It is found, contrary to the statements of Schur and Wiesel, that neither in narcosis nor muscular work is there an increase or decrease of adrenaline in the blood, corresponding with a change in the adrenaline content, or the coloration of the chromaffine tissue. Waterman and Smit's statement that in puncture diabetes the blood contains a mydriatic substance was not confirmed. Mayer's statement that after extirpation of both suprarenal bodies, puncture diabetes cannot be induced was confirmed; the animals remained in a healthy state for some time after the double extirpation. The view that adrenaline is a hormone which stimulates muscular activity and causes the mobilisation of glycogen is therefore untenable. W. D. H.

Possibility of Maintaining Life of Animals after Complete Excision of the Thyroid Gland by the Use of Calcium or Magnesium Salts for their Nourishment. ALBERT FROUIN (*Compt. rend.*, 1909, 148, 1622—1624).—The cachexia strumipriva incident on extirpation of the thyroid gland has been successfully combated by administering calcium or magnesium salts (chloride or lactate). Strontium chloride is without influence on the symptoms. Animals treated in this way increased in weight, and survived the operation several months; when the administration of the calcium salt was stopped, they continued to live without showing tetany or cachexia. These results appear to be due to elimination of carbamic acid by the calcium salt, since it is found that the urinary excretion of carbamates is increased, and that the ingestion of sodium carbamate produces tetany in thyroidectomised animals, whilst no objectionable symptoms follow if calcium chloride is administered simultaneously.

Salts of calcium have a similar action in tetanus, consequent on a pancreatic fistula or Eck's fistula (compare MacCallum, *J. Expt. Med.*, 1909, 11, 18). W. O. W.

Peritoneal Exudation in a Carp. FRANZ ZARIBNICKY (*Zeitsch. physiol. Chem.*, 1909, 60, 408—410).—As in cold-blooded animals the total amount of blood is only $1/63$ of the body-weight, information regarding its composition is scanty. In the present experiment, however, the blood of the carp was not investigated, but a peritoneal exudation, of which 500 c.c. were obtained. After removal of the fibrin it had D 1.015; it was alkaline to litmus, and contained 1.68% of coagulable protein, 0.077% of fat, 0.2% of total nitrogen, and 0.6% of ash. Urea, uric acid, allantoin, purine bases, and sugar

were absent. By fractional salting out, the protein present was separated into globulin and albumin. W. D. H.

Distribution of Nitrogen in the Precipitation by Acids and by Rennet of Cow's, Buffalo's, Goat's, Human, and Ass's Milk. WILLI FRIEDHEIM (*Biochem. Zeitsch.*, 1909, 19, 132—155).—It was known before that in the curdling of cow's milk by rennet more nitrogenous substances remain in solution in the whey than when the curdling is brought about by acids. It is now shown that the same difference exists in the case of the other kinds of milk mentioned. The difference amounts to about 10% of the total nitrogen, except in the case of ass's milk, where it is about 5.5% of the total. G. B.

The Acidity of Urine. WILHELM E. RINGER (*Zeitsch. physiol. Chem.*, 1909, 60, 341—463).—A 0.208% solution of phosphoric acid was taken, and the concentration of hydrogen ions determined with hydrogen electrodes. Sodium hydroxide was then added so that the percentage of phosphoric acid remained constant. From a number of measurements, a curve was constructed which showed the "acidity" of the sodium dihydrogen phosphate and the disodium hydrogen phosphate in various concentrations. Urines were then taken and the hydrogen ions estimated in the same way, and in some cases titration with phenolphthalein was performed, and a comparison with the curve first referred to enabled the proportion of the two phosphates to be determined; it was found that the greatest amount of the phosphoric acid is present as H_2PO_4 ions. The long-continued passage of hydrogen through the urine somewhat lessened its acidity; this is perhaps due to carbon dioxide; nevertheless, air free from carbon dioxide causes a slight rise of acidity. After the deposition of urates, the acidity (taken the next day) falls a little. W. D. H.

The Output of Organic Phosphorus in Urine. G. C. MATHISON (*Bio-Chem. J.*, 1909, 4, 233—239).—The amount of organic phosphoric acid varies considerably, but is usually more than 0.1 gram per diem, or about 6% of the total. Glycero-phosphoric acid is not broken down in digestion experiments *in vitro*. When added to the diet, it increases the total output of phosphates, but not of organic phosphorus. Vigorous exercise does not influence the latter. W. D. H.

Effects of Chocolate and Coffee on Uric Acid and the Purines. PIERRE FAUVEL (*Compt. rend.*, 1909, 148, 1541—1544. Compare Abstr., 1906, ii, 564).—In the case of persons on a vegetarian diet, chocolate and coffee increase the excretion of purine bases, but diminish the uric acid excretion. This diminution does not appear to be due to retention by the organism, since sodium salicylate produces under these conditions only a slight increase, and this is followed on the next day by a corresponding diminution of the excretion. During the prolonged use of chocolate and coffee on a diet otherwise free from purine bases, the excretion of uric acid rapidly becomes constant and remains at the minimum of endogenous origin. W. O. W.

Excretion of Quinine in Urine. M. NISHI (*Arch. exp. Path. Pharm.*, 1909, 60, 312—323).—See this vol., ii, 710.

Peptolytic Enzymes in Cancer. EMIL ABDERHALDEN and PETER RONA (*Zeitsch. physiol. Chem.*, 1909, 60, 415—417).—When blood-free carcinoma tissue is subjected to pressure, the juice obtained is capable of splitting glycyl-*L*-tyrosine. This is true for all cancers of the adeno-carcinoma type, and also for normal tissues. When the growth consists mainly of connective tissue stroma (Scirrhus), this does not occur. This accords with the observations of Hess and Saxl. Twelve tumours in all were investigated, an admittedly small number.

W. D. H.

Blood Changes in Cyanosis due to Congenital Heart Disease. H. S. FRENCH, MARCUS S. PEMBREY, and JOHN H. RYFFEL (*Proc. physiol. Soc.*, 1909, ix—x; *J. Physiol.*, 39).—In this condition there is chronic deficiency of oxygen, and this is compensated for by an increase in the number of red-corpuscles. A few estimations of lactic acid in the urine are appended in comparison with estimations in health and other diseases, but the figures given are obviously too scanty for correct deductions to be drawn.

W. D. H.

Diabetic Lævulosuria and the Detection of Lævulose in Urine. L. BORCHARDT (*Zeitsch. physiol. Chem.*, 1909, 60, 411—414. Compare Abstr., 1908, ii, 578).—Polemical. It is held that dextrose is the only sugar in diabetic urine, and that no grounds exist for the statements that lævulose ever occurs in the urine.

W. D. H.

The Physiological Action of Colloidal Metals. CARLO FOÀ and ALBERTO AGGAZZOTTI (*Biochem. Zeitsch.*, 1909, 19, 1—82).—The intravenous injection of colloidal silver (collargol) is fatal to dogs in a dose of 2.5 mg. per kilo. of body-weight. The body temperature may be raised 2—2.5°. Large doses produce phosphaturia and nephritis. The effects of electrically prepared silver are similar, but dogs show marked tolerance to sub-fatal doses, so that ultimately more than double the dose may be given which ordinarily would be fatal.

For colloidal arsenious sulphide the fatal dose in dogs is 9 mg. per kilo.; it does not raise the body temperature, and there is no tolerance.

Of the other colloids examined, platinum and ferric hydroxide are relatively inert; mercury resembles silver in that it raises the body temperature.

The protective effect of an injection of some colloids, for example, collargol, following an injection of a bacterial toxin is probably due to the enhanced power of the organism to oxidise toxins, and not to any direct action on the toxins themselves.

G. B.

Action of Methyl and Ethyl Alcohol on Muscle. FRITZ VERZAR (*Pflüger's Archiv*, 1909, 128, 398—420).—In frog's muscle both methyl and ethyl alcohols first increase and then decrease the excitability. Methyl alcohol has about one half the toxicity of ethyl alcohol.

W. D. H.

Physiological Action of Pressor Amines. HENRY H. DALE and WALTER E. DIXON (*J. Physiol.*, 1909, 39, 25—44).—In an

investigation dealing with most of the functions of the body, it was found that *isoamylamine* and *p*-hydroxyphenylethylamine have an action like that of adrenaline, both reproducing the inhibitory and specially the motor effects of sympathetic nerves. *isoAmylamine* is the weaker of the two, and both are less powerful than adrenaline. Both are absorbed from the subcutaneous tissues and from the alimentary canal, and produce their effects when so administered.

W. D. H.

The Active Principles of Ergot. GEORGE BARGER and HENRY H. DALE (*Proc. physiol. Soc.*, 1909, lxxvii-lxxix; *J. Physiol.*, 38).—The rise of blood-pressure produced by aqueous extracts of ergot cannot be wholly attributed to ergotoxine, and after this substance is removed, their pressor action remains considerable. Further investigation showed that the extracts contain the two substances recently separated from putrid animal tissues; of these, *p*-hydroxyphenylethylamine (Barger, *Trans.*, 1909, 95, 1123) is far more abundant than *isoamylamine*. The action of this substance on the uterus, like that on the vascular system, simulates the action of sympathetic nerves. Whether these bases are produced by the enzymes of the fungus itself, or in any degree by bacteria during the process of extraction, is unsettled, but in either case the notorious variability of the official liquid is readily intelligible.

W. D. H.

A Reversed Action during Anæsthesia. The Action of Certain Convulsants. CHARLES R. MARSHALL (*Proc. physiol. Soc.*, 1909, lxxxii; lxxxiii-lxxxiv; *J. Physiol.*, 38).—An effective dose of tutin or coriamyrtin increases the frequency of respiration in normal animals, but diminishes it in those anæsthetised with chloroform. The reversion is not so marked if ether is used as the anæsthetic. It is probably due to the depressant influence of anæsthetics on the medullary centres, and attention is drawn to previously described instances of similar reversed or modified actions.

Both tutin and coriamyrtin act on the brain in the same manner as absinthin and picrotoxin; coriamyrtin is the more toxic of the two; their predominant effect is epileptiform convulsions. The action is mainly on the cerebrum and to a less degree on the pontine nuclei. The spinal cord and bulb are not affected.

W. D. H.

Action of Substances which Temporarily Abolish the Respiration. CHARLES R. MARSHALL (*Proc. physiol. Soc.*, 1909, lxxxiv-lxxxv; *J. Physiol.*, 38).—One of certain tropeines investigated, namely, protocatechyltropine, was found temporarily to paralyse the respiration when intravenously (but not subcutaneously) administered in animals. Tappeiner has described a similar action in various methochlorides and other quaternary compounds. Protocatechyltropine is a tertiary base. Evidence is adduced that the action is a central, not a peripheral, one, neither is it due to the circulatory disturbances which are produced.

W. D. H.

Myosis and Reduction of Blood Pressure Caused by Normal Human Urine. J. E. ABELOUS and E. BARDIER (*Compt. rend.*, 1909, 148, 1471-1472).—The material precipitated from urine by

alcohol is submitted to dialysis, and the colloidal fraction, which shows the reactions of a proteose, precipitated by ammonium sulphate. The precipitate is dissolved in water, dialysed, and the colourless solution treated with alcohol. The grey powder thus obtained is soluble in water, and when injected into a vein produces intense myosis, accompanied by considerable lowering of the blood pressure. The name "urohypotensin" is suggested for this substance.

W. O. W.

Carbon Monoxide Poisoning by Explosion Gases. LOUIS LEWIN and OTTO POPPENBERG (*Arch. exp. Path. Pharm.*, 1909, 60, 434—460).—Analyses were made of the gases obtained by explosion of a number of different explosives. The physiological action of these gases on animals was investigated, the conditions of the experiments being so chosen as to imitate as nearly as possible the conditions in practice. It was shown that carbon monoxide alone was in most cases sufficient to account for the symptoms. Explosives containing the nitro-group, such as dynamite, etc., yield on explosion nitric oxide. The amounts obtained by explosion were estimated, and it was shown that this gas could also account for toxic symptoms.

S. B. S.

The Poisonous Action of the Cyanogen Compounds Employed as Artificial Manures. WALTER STRITT (*Zeitsch. Hyg. Infekt. Krank.*, 1909, 62, 169—198).—Comparative experiments have been made on frogs, rabbits, and dogs with cyanamide, dicyanodiamide, and calcium cyanamide. The results showed that all these substances are poisonous, cyanamide having the highest toxicity, and calcium cyanamide the least. Probably about 10 grams of calcium cyanamide would constitute a lethal dose of this substance for an adult, but this amount could hardly be administered by accident or design without the knowledge of the individual.

F. M. G. M.

Chemistry of Vegetable Physiology and Agriculture.

The Nuclein Ferments of Yeast. M. N. STRAUGHN and WALTER JONES (*J. Biol. Chem.*, 1909, 6, 245—255).—Yeast contains guanase, but adenase and xantho-oxydase are absent. W. D. H.

The Fermentation of Amino-acids. JEAN EFFRONT (*Mon. Sci.*, 1909, [iv], 23, i, 145).—In the fermentation of glycine, asparagine, and glutamic acid by brewers yeast, all the nitrogen is transformed into ammonia. The fermentation of betaine gives rise to trimethylamine. These bases remain combined with volatile organic acids. The amount of these acids produced during fermentation is always in

excess of the calculated amount, inasmuch as a certain quantity is derived from the protoplasm of the yeast. The composition of these acids varies with the nature of the amino-acid undergoing fermentation; acetic acid is the principal product from glycine and betaine, asparagine furnishes chiefly propionic acid, whilst butyric acid in considerable amount arises from the fermentation of glutamic acid. In all these instances, however, the three acids are produced to a certain extent, and the paper contains tables showing these proportions.

F. M. G. M.

Biochemical Change of Asparagine and Aspartic Acid into Propionic and Succinic Acids. CARL NEUBERG and CESARE CAPPEZZUOLI (*Biochem. Zeitsch.*, 1909, 18, 424—430).—By the action of a putrefactive mixture on aspartic acid, formic, propionic, and succinic acids were formed. Corresponding amounts of ammonia and unchanged aspartic acid were recovered. Asparagine yielded the same products, but larger amounts of propionic and succinic acids were obtained.

S. B. S.

The Behaviour of Racemic Glutamic Acid in Putrefaction. CARL NEUBERG (*Biochem. Zeitsch.*, 1908, 18, 431—434).—The racemic glutamic acids behave on putrefaction in the same way as the natural dextrorotatory acid, yielding formic, butyric, and succinic acids. The formation of an optically active form could not be ascertained.

S. B. S.

The Behaviour of *d*-l-Aminovaleric Acid (*d*-l-Valine) in Putrefaction. CARL NEUBERG and LÁZLÓ KARCZAG (*Biochem. Zeitsch.*, 1908, 18, 435—439).—*d*-l-Aminovaleric acid on putrefaction undergoes deamination, yielding a valeric acid, presumably isovaleric acid. A small part of the amino-acid is converted into butylamine. The residual aminovaleric acid was levorotatory in hydrochloric acid, indicating an asymmetric attack by the bacteria.

S. B. S.

Decomposition of Uric Acid by Bacteria. F. LIEBERT (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 54—64).—It has previously been shown that carbamide and carbon dioxide are products of the bacterial decomposition of uric acid. Gérard (Abstr., 1896, ii, 668) assumed that alloxan was an intermediate product, and Ulpiani (Abstr., 1904, ii, 138; Ulpiani and Cingolani, 1905, ii, 190) that tartronic acid was produced. Neither of these substances was isolated, and these assumptions are probably erroneous. When the aerobic bacteria *Bacillus pyocyaneus*, *B. fluorescens liquefaciens*, *B. fluorescens non liquefaciens*, and *Bacterium calco-acetum* are employed, it is shown that uric acid is oxidised to allantoin and carbon dioxide, the allantoin then being further oxidised to carbamide and oxalic acid. It is further shown that during these changes there is a successive production of two distinct floras of bacteria, the above-named characteristic of the neutral or feebly acid medium, and the others which are developed in the alkaline liquid, namely, *B. odoratum* and *B. musculi*.

B. pyocyaneus and *B. Stutzeri*, in the presence of uric acid and potassium nitrate, cause denitrification of the latter.

Under anaerobic conditions at 35°, and in the presence of magnesium phosphate to combine with ammonia, the organism *B. acidi urici*, a spore-forming, mobile microbe, decomposes uric acid, with the formation of 3 mols. of carbon dioxide, ammonia, and acetic acid. W. R.

The Bacterial Degradation of the Primary Scission Products of Proteins. WALTER BRASCH (*Biochem. Zeitsch.*, 1909, 18, 380—390).—The degradation of glutamic acid to butyric acid by various bacteria isolated from putrefaction mixtures was investigated. It was found that the aerobic bacteria play but a small part in this chemical action, which appears to be brought about chiefly by *Bacillus putrificus* (Bienstock). Butyric acid resists further degradation by this organism.

S. B. S.

Assimilation of Nitrogen of the Air by Soil Micro-organisms. FR. STRAÑÁK (*Zeits. Zuckerind. Böhm.*, 1909, 33, 599—614).—Whilst *Azotobacter* is very widely distributed, being found in arable, meadow, and forest soils of various kinds, and even in seawater, it is found to be absent in many virgin soils, especially peat land, in Bohemia, and also in soils situated at considerable elevations. It occurs, however, in virgin soils, bearing a luxuriant vegetation of blue and green algæ.

Experiments in which pure cultivations of *Azotobacter* were supplied with various carbohydrates showed that the following amounts of nitrogen (in mg. per litre) were assimilated: arabinose, 180.2; lævulose, 155.4; dextrose, 152.3; xylose, 143.0; galactose, 141.5; sucrose, 125.1; maltose, 86.0; lactose, 81.6, and rhamnose, 49.8. Pure cultivations of *Azotobacter* with mannitol assimilated 74.9—124.6 mg. N per litre, whilst impure cultivations assimilated 155—206 mg.

In presence of nitrates, *Azotobacter* cannot assimilate free nitrogen. When solutions containing much nitrate are inoculated with *Azotobacter* and *Radiobacter*, the latter denitrifies the nitrate, and the free nitrogen thus produced is then assimilated by the *Azotobacter*.

Inoculation experiments with *Azotobacter* applied directly to the plots gave increased yields of mangolds, oats, and potatoes. Still better results were obtained when, instead of direct inoculation, the cultures were first added to small quantities of soil (5 kilos.) containing dextrose (250 grams), and kept for three months at 24° before being employed as inoculating material.

N. H. J. M.

Assimilation of Nitrogen as Ammonia, Nitrates, and Amides by Micro-organisms. STEVEN BIEREMA (*Centr. Bakt. Par.*, 1909, ii, 23, 672—726).—Sodium nitrate is readily assimilated by soil organisms in presence of sucrose, glycerol, and calcium lactate, but less readily with lævulose, starch, maltose, and calcium succinate as sources of carbon. Ammonium nitrate is less readily assimilated, whilst magnesium ammonium phosphate proved to be one of the best sources of nitrogen, notwithstanding its very slight solubility. Formamide and acetamide are not very readily assimilated; the latter

serves, however, as source of both nitrogen and carbon. Guanidine carbonate alone has very little effect; better results were, however, obtained in presence of calcium lactate, and sucrose + glycerol. Uric acid is completely converted into ammonium carbonate, but less readily than urea. Leucine and tyrosine, especially the former, are readily assimilated. Ammonium formate is only slightly assimilated; ammonium acetate gives better results, especially in presence of dextrose, whilst ammonium butyrate is still more readily utilised.

A number of quantitative experiments with various ammonium salts and organic nitrogenous compounds are described.

N. H. J. M.

Mechanism of Denitrification among Indirect Denitrifying Bacteria. LÉON GRIMBERT and BAGROS (*J. Pharm. Chim.*, 1909, [vi], 30, 5—10).—Further evidence is brought forward in favour of the view already expressed (Abstr., 1900, ii, 97) that the liberation of a mixture of nitrogen and carbon dioxide by *Bacillus Coli* and *B. d' Eberth*, from media containing meat extract, peptone, and nitrates, is due to reduction of the nitrate to nitrite and interaction of the latter with amino-compounds in presence of acids generated by the fermentive action of the bacillus. In proof of this it is shown that nitrated peptone containing either of these bacilli gives off no gas until both a carbohydrate capable of being fermented to acid, and an amino-compound have been added.

T. A. H.

Hydrolysis of the Phosphorescent Infusoria of the North Sea (*Noctiluca miliaris*). OSKAR EMMERLING (*Biochem. Zeitsch.*, 1909, 18, 372—374).—The following amounts of hydrolysis products were obtained from 100 grams: Lysine, 0.212 gram; arginine, 1.65 grams; histidine, 3.47 grams; tyrosine, 0.52 gram; glycine, 5.90 grams; alanine, 2.4 grams; leucine, 0.42 gram; proline, 4.60 grams; aspartic acid, 0.17 gram.

S. B. S.

Influence of Certain Nutrient Media on the Development of Embryos of *Pinus Pinea*. JULES LEFÈVRE (*Compt. rend.*, 1909, 148, 1533—1536. Compare this vol., ii, 33).—The author confirms Lubimenko's conclusion (Abstr., 1906, ii, 624) that sucrose is essential to the development of the isolated embryo. He finds also that whilst peptones and asparagine act as nutrients in the presence of sucrose, yet when added alone they are without effect, and in large doses they inhibit the growth of the embryo. Other amides hinder development when added to the extent of 0.5%.

W. O. W.

Elaboration of Nitrogenous Matter in the Leaves of Living Plants. GUSTAVE ANDRÉ (*Compt. rend.*, 1909, 148, 1685—1687).—The author has determined the amount of total nitrogen, amidic nitrogen, and nitrates present in chestnut leaves at different periods of growth, and from the results has arrived at the conclusion that the rate of production of nitrogenous material is constant, but that during the period of fertilisation the rate at which amidic nitrogen is transferred from the leaves to other organs is considerably increased.

W. O. W.

Fermentative Cleavage of Ammonia in Higher Plants.

ALEXANDER KIESEL (*Zeitsch. physiol. Chem.*, 1909, 60, 453—459).—Etiolated seedling of *Vicia Faba* (twenty-three to twenty-four days) were passed through a mincing machine and the sap expressed. The total nitrogen, and the nitrogen as proteins, as bases and peptone, as ammonia, and as amides were determined in the original sap and in sap which has been treated with chloroform and toluene and kept for twenty-five days at 37°. The results showed that a considerable amount of ammonia, representing 11·21% of the total nitrogen, was produced. The losses of protein nitrogen and amide nitrogen were only 2·30 and 3·42% respectively, so that much of the ammonia must have been derived from other undetermined forms of nitrogen (chiefly amino-acids).

The negative results obtained by Butkewitsch may have been due to the destruction of the ferment in the process of drying, or to the employment of younger seedlings, in which the primary processes may conceal more or less the secondary ones.

N. H. J. M.

Autolytic Decomposition of Arginine in Plants.

ALEXANDER KIESEL (*Zeitsch. physiol. Chem.*, 1909, 60, 460—461).—The expressed sap of seedlings (two weeks' old) of *Lupinus luteus* was treated with chloroform and toluene and kept for about four weeks at 37°. It was found that the arginine, of which the original sap contained a considerable amount, completely disappeared. The sap gave with copper carbonate a green solution, from which a yellow, crystalline precipitate (indicating the presence of guanidine) was obtained by successive treatment with hydrogen sulphate and sodium picrate. The amount of nuclein bases was increased by autolysis.

N. H. J. M.

Behaviour of Asparagine in the Autolysis of Plants.

ALEXANDER KIESEL (*Zeitsch. physiol. Chem.*, 1909, 60, 476—481).—An experiment with seedlings of *Lupinus albus* showed that asparagine disappears during autolysis. An attempt was made to obtain the ferment which decomposes asparagine by precipitation with alcohol, but without result.

N. H. J. M.

The Moving Out of Calcium and Magnesium Ions from the Plant Cell. BRONISLAW NIKLEWSKI (*Ber. Deut. bot. Ges.*, 1909, 27, 224—227).—It was found by Hansteen that wheat grown in water cultures and supplied with calcium salts only made normal root growth, but not when the cultures contained either potassium, sodium, or magnesium salts alone; in all these cases, toxic symptoms showed themselves. Addition of a calcium salt, even in small quantities, completely restored the plant; thus no poisoning appeared with a ratio $K_2O/CaO=840$. The optimum root development took place when $K_2O/CaO=0\cdot84$.

The author offers an explanation of these facts, based on the following observations. Equal-sized pieces of beet were placed in each of the following solutions: (1) distilled water; (2) *N*/20-potassium chloride; (3) *N*/20-sodium chloride; (4) *N*/20-ammonium chloride. The amounts of lime and magnesia diffusing out from the cell in

the four cases were (1) 5.3 and 4.1; (2) 33.4 and 23.8; (3) 32.1 and 20.8; (4) 29.2 and 21.3 mg. per 500 c.c. of the solution, and were thus considerably increased when salts were present in the circumambient solution. The author therefore supposes that in Hansteen's experiment there has been a moving out of calcium and magnesium ions from the cell into the culture solution, the injurious effect of which is only counteracted when the calcium ions in the solution reach a certain concentration.

E. J. R.

Various Relations between Calcium and Magnesium in Nutritive Solutions. J. W. KONOWALOFF (*J. exper. Landw.*, 1909, 10, 317—320).—Sand-culture experiments with wheat, without calcium and with varying relations of CaO:MgO from 0.2:1 to 26.6:1, showed that the total yield increased with the amount of lime until the ratio CaO/MgO = 6.7/1, after which there was a fall. The yield of grain was highest when the ratio was 13.3/1. Similar results were obtained with white lupins and *Setaria italica*.

Water-culture experiments with oats showed that the total produce, including roots, was highest when the ratio CaO/MgO was 6.7/1 and 13.3/1 (both equal); with a greater amount of calcium the yield fell considerably. In a second experiment the highest yield was with the ratio CaO/MgO = 6.7/1.

N. H. J. M.

Carbon Dioxide Assimilation and Nutrition of Plants with Formaldehyde. THOMAS BOKORNY (*Pflüger's Archiv*, 1909, 128, 565—586. Compare Abstr., 1892, 1259; this vol., ii, 70).—Experiments with cress grown under a bell-jar, over a 30% solution of sodium hydroxide containing small amounts of formaldehyde, showed that formaldehyde vapour is absorbed by the upper portions of the plants and assimilated.

N. H. J. M.

The Nature of the Cutin contained in "Crude Fibre." W. SUTTHOFF (*Zeitsch. Nahr. Genussm.*, 1909, 17, 662—663).—The cutin separated from the "crude fibre" of various grasses, brans, and straws by the method described by König, Fürstenberg, and Murdfield (Abstr., 1906, ii, 793) is a wax-like substance, which contains a considerable quantity (from 15 to 34%) of silica. The dry, ash-free substance contains from 64.72 to 69.97% of carbon, and from 9.65 to 12.40% of hydrogen. When the substance is saponified, an alcohol, m. p. 55—56°, is liberated, the molecule of which contains 17 atoms of carbon, whilst the acid portion of the substance consists apparently of a mixture of fatty acids, m. p. about 30°.

W. P. S.

Sucro-clastic Enzymes in *Beta vulgaris*. R. A. ROBERTSON, JAMES COLQUHOUN IRVINE, and MILDRED E. DOBSON (*Bio-Chem. J.*, 1909, 4, 258—273).—The polarimetric method was employed in the investigation. Diastase occurs in all parts, in the leaf associated with invertase and maltase, in the stem with emulsin in addition, whilst in the root it is accompanied by maltase, inulase, and emulsin, invertase being absent. It is suggested that in the mixture of enzymes they may mutually affect each other's actions. Other complicating factors

are the influence of light and darkness (as in leaf and root), differences of osmotic pressure in various cells, differences in reaction of cell contents, and the presence of hydrolytic products. The apparently unlimited quantity of disaccharides capable of being formed in the living plant is in marked contrast to the small results obtained *in vitro*. The reactions concerned in carbohydrate metabolism in the plant are probably reversible, but the actual experimental results recorded on reversible zymolysis do not appear very conclusive. W. D. H.

Investigations of the Beans of *Phaseolus vulgaris* at Different Stages of Development. URS PFENNIGER (*Ber. Deut. bot. Ges.*, 1909, 27, 227—234).—The translocation of various nitrogen compounds from the pod to the seed is definitely established by the author, whose experiments show that the decrease of nitrogenous substance in the pod goes *pari passu* with the increase in the seed. The pods were found to contain protein, asparagine, allantoin, tyrosine, alloxuric bases, arginine, choline, and trigonelline, probably also lysine and leucine. In the early stages of development, 1.41% of nitrogen was present in the pod as protein, and 1.65% as non-protein, making a total of 3.06%; in the final stages the total nitrogen was 0.88% (due to the great increase in the non-nitrogenous compounds), of which 0.87% was protein. The seeds contained protein, tyrosine, alloxuric bases, arginine, choline, and trigonelline; the total nitrogen was at first 5.00%, 3.59% being protein and 1.41% non-protein; in the final stage the total nitrogen was 4.23%, 4.01% being protein.

Reduced to weights in grams, the results are as follows :

	100 pods contain			100 beans contain		
	Total N.	Protein N.	Non-protein N.	Total N.	Protein N.	Non-protein N.
1st Stage ...	1.56	0.72	0.85	0.0284	0.0204	0.0080
2nd Stage...	1.89	1.23	0.66	0.3325	0.2858	0.0467
3rd Stage ...	0.58	0.57	0.01	1.903	1.804	0.0989

It is noteworthy that the seed when ripe contains more non-protein nitrogen than in its earlier stages. E. J. R.

The Fruit of *Pyrus arbutifolia*. BURLEIGH B. REED (*Chem. News*, 1909, 99, 302).—The ripe berries were gathered in the vicinity of Sylvan Beach, New York, and they were dried and submitted to prolonged extraction with boiling alcohol and with boiling water. The extract was acid in reaction, and contained sugar, chiefly lævulose, to the extent of 68.27% of the berries. After drying and grinding the extracted fruit, it was successively digested with portions of ether for a long while; a small quantity (1.34% of the original fruit) of a yellow oil was obtained; D₁₅⁵ 0.80. The berries contained 4.4% of ash, which gave on analysis the following percentage composition :

SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	Mn.	Cr.	SO ₃ .	P ₂ O ₅ .
trace	2.54	6.71	16.2	5.67	38.94	24.11	0.027	0.001	2.90	2.87

Besides this the fruit was found to contain tartaric acid, citric acid, and 0.84% of nitrogen. J. V. E.

Relation between the Utilisation of Reserve Carbohydrates and the Flowering of *Ranunculus velutinus*. C. FERRARI (*Bied. Zentr.*, 1909, 38, 426; from *Staz. sper. agrar. ital.*, 1908, 41, 127).—Removal of the buds merely prolonged the vegetative period, without the marked development of the vegetative system observed by Mattiolo in the case of *Vicia Faba*. The plants retained their green colour, and the irregular spots on the upper sides of the leaves, which generally disappear during the flowering period, remained. The amount of insoluble starch was doubled.
N. H. J. M.

Determination of Temperature of Pasteurisation of Milk in Connexion with its Industrial Application. Influence of Heat on Conservation of Physiological Properties of Milk. PIERRE MAZÉ, P. GUÉRAULT, and DINESCU (*Compt. rend.*, 1909, 148, 1469—1471).—Unless carried out under suitable conditions, pasteurisation of the milk diminishes the yield of cheese, owing to changes brought about in the casein, whereby a considerable proportion escapes coagulation. The maximum yield is obtained when pasteurisation is carried out at 67—68°.
W. O. W.

Manuring Sugar Beet with Sodium Chloride. HEINRICH METTE (*Zeits. Zuckerind. Böhm.*, 1909, 33, 620—621).—The results of plot experiments with sugar beet showed that an application of sodium chloride (100 kilos. per $\frac{1}{4}$ hectare) increased the yield of roots and the percentage of sugar, and the conclusion is drawn that, whilst sodium chloride is without appreciable effect in the case of good soils with a normal rainfall, it is very efficacious on light soils in a hot climate with a deficient rainfall.
N. H. J. M.

Action of Manganese Sulphate on Various Crops. M. DE MOLINARI and O. LIGOT (*Bied. Zentr.*, 1909, 38, 427; from *Ann. Gembloux*, 1908, 609).—Manganese, copper, zinc, and ferrous sulphates failed to increase the yields of oats and barley. The soil contained, however, a good deal of manganese.
N. H. J. M.

Action of Sodium Nitrate, Ammonium Salts, Calcium Cyanamide, and Norwegian Calcium Nitrate. WILHELM SCHNEIDEWIND, DIEDRICH MEYER, H. FRESE, F. MÜNTER, and J. GRAFF (*Bied. Zentr.*, 1909, 38, 366—379; from *Arb. deut. landw. Ges.*, 1908, No. 146).—The results of pot experiments in which rye and barley were given with various nitrogenous manures showed that increase of grain was as follows (sodium nitrate=100): ammonium sulphate, 84; calcium cyanamide, 80—82; fish meal, 73; meat meal, 71; blood meal, 56; horn meal, 55, and leather meal, 15.

Field experiments are described in which the relative values of sodium and calcium nitrates, ammonium salts, and calcium cyanamide, applied to cereals, potatoes and sugar beet, are compared.

N. H. J. M

Influence of Soil Moisture on the Action of Calcium Cyanamide. SANTE DE GRAZIA (*Bied. Zentr.*, 1909, 38, 421; from *Staz. sper. agrar. ital.*, 1908, 41, 115).—The utilisation of calcium

cyanamide is greatest when the soil is moist for some time after it has been applied. In the case of dicyanodiamide, moisture has hardly any effect.

N. H. J. M.

Manurial Experiments with Calcium Cyanamide on Winter Cereals and Sugar Beet. ADOLF RITTER VON LIEBENBERG (*Bied. Zentr.*, 1909, 38, 379—385; from *Zeitsch. landw. Versuchs. Oesterr.*, 1908, 11, 153—180).—In an experiment with summer wheat it was found that only 25—38% of the nitrogen of calcium cyanamide was taken up, and not more than 50% in the case of sodium nitrate and ammonium sulphate. The manures showed no after effect when winter rye was grown on the same plots; the amount of nitrogen was even less than on the unmanured plot.

N. H. J. M.

Effect of Increasing Amounts of Phosphatic Manures on the Amounts of Organic Phosphorus and Nitrogen Compounds, and on the Relation between Phosphorus and Nitrogen in Maize Grain. A. PARROZZANI (*Chem. Zentr.*, 1909, i, 1036; from *Staz. sper. agrar. ital.*, 41, 729—738).—Applications of increasing amounts of phosphorus in the form of mineral phosphates increased the percentages of total phosphorus and of phosphorus as lecithin in the grain of maize, whilst the phosphorus as nuclein remained the same. No effect was produced on the amount of total nitrogen; there was, however, a slight gain in protein nitrogen, due to a considerably increased production of zein under the influence of phosphatic manure, whilst the amounts of other proteins were diminished.

The results indicate that phosphatic manures have a marked effect on the activity of chlorophyll assimilation, and that in absence of corresponding amounts of nitrogen the phosphorus tends to accumulate in the grain.

N. H. J. M.

Analytical Chemistry.

Analysis of Coal-Gas and Similar Gaseous Mixtures; Estimation of Nitrogen in Coal-Gas. GEORG VON KNORRE (*Chem. Zeit.*, 1909, 33, 717—719).—The first part of the paper consists in a criticism of the methods usually employed in analysing coal-gas.

Jäger's process (partial combustion with copper oxide) may be improved by first expelling the air from the small combustion tube by means of nitrogen, which may be readily made for the purpose by introducing air into the phosphorus pipette. The combustion tube is best made of fused silica. If nitrogen only is to be estimated, 100 c.c. of the coal-gas are at once passed slowly over the red-hot copper oxide.

L. DE K.

Reduction of Perchlorates by Titanium Sesquisulphate. ARTHUR STÄHLER (*Chem. Zeit.*, 1909, 33, 759).—A criticism of Rothmund's process (this vol., ii, 434). The author has used titanium sesquisulphate for the reduction of perchlorates previously (*Ber.*, 1903, 36, 166, 1549), but the results (titration of the excess of the sesquisulphate with iron solution) were not very satisfactory. Good results, however, may be obtained by estimating the chloride formed in the reaction as proposed by Rothmund. For small quantities of chlorine, Richard's nephelometer (*Abstr.*, 1904, ii, 287) is recommended.

L. DE K.

Estimation of Iodine in Protein Combinations. LOUIS W. RIGGS (*J. Amer. Chem. Soc.*, 1909, 31, 710—717).—In the estimation of the iodine in protein combinations by Baumann's method (*Abstr.*, 1896, ii, 487), a portion of the halogen is oxidised to iodate during the fusion. After the estimation of the iodine, present as iodide, by the usual method, it is necessary, particularly in the case of proteins of small iodine content, to reduce the iodate by Devarda's alloy and sodium hydroxide, and to estimate the iodine in the iodide thus formed. Mixtures of protein substances and potassium iodide, analysed by the foregoing process, do not give results comparable with those obtained by the analysis of a protein substance containing combined iodine.

Excess of nitrous acid reduces iodates in such a way that the iodine cannot be estimated colorimetrically in carbon tetrachloride. C. S.

Estimation of Sulphur in Coals and Cokes. M. HOLLIGER (*Zeitsch. angew. Chem.*, 1909, 22, 1361—1362).—A reply to Dennstedt (compare this vol., ii, 343, 435). The author thinks Dennstedt's process a good one, but advises the use of a small Peligot tube filled with hypobromite solution as a trap. The contents are afterwards tested for sulphuric acid.

L. DE K.

Estimation of Total Nitrogen by E. A. Mitscherlich's Method. VINCENT SCHENKE (*Chem. Zeit.*, 1909, 33, 712—713).—A reply to Mitscherlich and Herz and Mitscherlich and Merres (this vol., ii, 614). The author prefers his own process (*Chem. Zeit.*, 1896, 20, 1032, 1033). The following process is recommended in the presence of any appreciable amount of nitrites: 0.5—2 grams of the substance, and so much potassium chlorate that there is one part of this to three parts of nitrous acid, are placed in a round-bottomed flask, 50 c.c. of water are added, and then drop by drop 3 c.c. of dilute sulphuric acid (1:2). After a quarter of an hour, 2—4 grams of reduced iron are added, and then 15 c.c. of the dilute acid (Ulsch's process), and when the reduction of the nitrate to ammonia is accomplished, the organic substances are destroyed by evaporating with 30 c.c. of sulphuric acid and a few drops of mercury (Kjeldahl method). A blank experiment should be made, once for all, to test the purity of the reagents used.

L. DE K.

Detection of Nitrates in the Presence of Bromides. VILLEDIEU (*J. Pharm. Chim.*, 1909, 30, 66—67).—When testing for nitrates in

the presence of a large excess of bromides, it is advisable to remove the latter; this can, of course, be effected with silver sulphate, but in practice this is rather inconvenient on account of its slight solubility. The following test is recommended. The liquid, neutralised if necessary, is mixed with a slight excess of basic lead acetate, which precipitates nearly all the bromine, and the filtrate is then heated to boiling and the excess of lead precipitated by adding a little powdered sodium sulphate.

To the filtrate the usual test for nitrates with ferrous sulphate and sulphuric acid is then applied. L. DE K.

Estimation of Phosphorus in Urine. G. C. MATHISON (*Bio-Chem. J.*, 1909, 4, 233—239).—The estimation of total phosphorus in urine is best carried out by Plimmer and Bayliss's modification of Neumann's method; and inorganic phosphates by precipitation with magnesium citrate mixture, incineration, and calculation from the weight of the ash ($Mg_2P_2O_7$). Magnesia mixture gives incorrect results, owing to partial precipitation of calcium and of organic phosphorus. Organic phosphoric acid is determined by subtracting the inorganic from the total phosphoric acid, or by applying Neumann's method after the removal of inorganic phosphates. The uranium acetate method is inaccurate. Organic phosphorus must be estimated while the urine is fresh, as it decomposes in stale urine, especially if ammonia is present. It is readily dialysable. W. D. H.

Disappearance of Arsenic in the Form of Gaseous or Volatile Compounds during Putrefaction. MARIO TONEGUTTI (*Boll. Chim. Farm.*, 1909, 48, 259—264, 370—374).—The author's experiments show that the putrefaction of protein substances containing arsenic is not accompanied by the evolution of arsenical gases, although very small proportions of organic arsenical products having basic or ptomaine characters are formed, which are volatile at a temperature above 30° , probably between 50° and 60° . The disappearance of arsenic from corpses in the form of gaseous compounds is hence improbable. T. H. P.

Gravimetric Estimation of Boric Acid. KURT ARNDT (*Chem. Zeit.*, 1909, 33, 725—726).—The process is intended for the estimation of small quantities of boric acid in fused alumina; 15 grams of potassium hydroxide are fused in a nickel crucible until the mass runs quietly, and, when cold, 3 grams of the impalpable powder are sprinkled over the surface. The mass is now again heated to redness for three hours, the crucible being covered. When cold, the contents are dissolved in water, slight excess of sulphuric acid is added, and the solution is introduced into a Gooch goose-neck apparatus. The authors have slightly modified this apparatus so that it holds fully 150 c.c. The boric acid is then expelled by repeated distillation with methyl alcohol, the distillate is evaporated, as directed by Gooch and Jones (*Abstr.*, 1899, ii, 331), with a known weight of sodium tungstate, and the residue ignited and weighed.

When a solution of alumina and boric acid is mixed with ammonia,

a portion of the acid is retained obstinately by the precipitated hydroxide.
L. DE K.

Estimation of Boric Acid. R. MANDELBAUM (*Zeitsch. anorg. Chem.*, 1909, 62, 364—369).—The distillation of boric acid with methyl alcohol (Spindler, Abstr., 1905, ii, 480) may be used as an accurate method of estimation when modified. The borate, or substance containing borates, is warmed with 40% phosphoric acid, any carbon dioxide formed expelled by a current of purified air, the flask connected with a condenser, and a receiver containing a known excess of standard sodium hydroxide attached. Absolute methyl alcohol (150—170 c.c. for 0.2 gram B_2O_3) is run into the flask, which is then heated, a current of air saturated with methyl alcohol being bubbled through it. Finally, the sodium hydroxide flask is warmed to expel methyl alcohol, which distils through a second condenser into a receiver. The sodium hydroxide is then cooled, mixed with half its volume of glycerol, and titrated with sulphuric acid, phenolphthalein being used as indicator. The analysis occupies two to three hours.

C. H. D.

Elementary Analysis According to Carrasco-Plancher. ORESTE CARRASCO (*Chem. Zeit.*, 1909, 33, 733—734, 755—756).—An improvement of the apparatus described previously (Abstr., 1896, ii, 201). The copper oxide has been replaced by "platinum biscuit," and different combustion tubes are used according to the nature of the substance (solid, liquid, readily volatile, etc). Nitrogen-, sulphur-, and halogen-containing substances may also be analysed by means of the apparatus.

L. DE K.

Simultaneous Estimation of the Residue and Combined Carbon Dioxide in Waters. K. CHARITSCHKOFF (*Chem. Zeit.*, 1909, 33, 670).—A slight modification of the Rohrbeck-Geissler apparatus for the estimation of carbon dioxide in carbonates from the loss sustained on adding hydrochloric acid.

The lower, basin-shaped, part of the apparatus may be removed and weighed, and serves for estimating the residue of the water in the ordinary way. The upper part of the apparatus is then put on, and the carbon dioxide is estimated as usual.

L. DE K.

Estimation of the Alkalinity of Bleaching Powder Solutions. KENNEDY P. ORTON and W. J. JONES (*Analyst*, 1909, 34, 317—318).—A known volume of the solution is added to an excess of $N/10$ -hydrochloric acid contained in a Drechsel bubbler, and a rapid current of pure air is drawn through for forty-five minutes, the solution being meanwhile carefully shielded from light. After ascertaining that the liquid is free from chlorine by testing a drop with a drop of 0.1% solution of methyl-orange, which should not be bleached, the excess of acid is titrated with $N/10$ -sodium carbonate.

Allowance is then made for acid neutralised by the hypochlorite of the sample.

L. DE K.

A New Rapid Volumetric Method for the Estimation of Columbium in Presence of Tantalum, and its Application to the Analysis of Columbium Minerals. FLOYD D. METZGER and C. E. TAYLOR (*Zeitsch. anorg. Chem.*, 1909, 62, 383—394).—Columbium and tantalum could only be separated hitherto approximately by fractional crystallisation of the potassium double fluorides. It is now found that when succinic acid is added to a solution of columbium and tantalum in concentrated sulphuric acid, the solution may be greatly diluted and heated without precipitation taking place. The columbium may then be reduced with zinc and titrated with permanganate, which does not act on succinic acid.

The zinc used for reduction should be amalgamated, 0.5 gram of mercury dissolved in 25 c.c. of nitric acid and diluted to 250 c.c. being used for 600 grams of zinc. In making an analysis, 0.2—0.5 gram of the mixed oxides is fused in a platinum crucible with 5 grams of potassium hydrogen sulphate, mixed with 10 grams of concentrated sulphuric acid, heated until dissolved, and cooled. The solution is transferred to a beaker, and the crucible rinsed with 30 c.c. of sulphuric acid. Two grams of succinic acid are added, the whole stirred, and 20 c.c. of a saturated aqueous solution of succinic acid added, with stirring. The solution is made up to 200 c.c. with water, and warmed to 75°. The Jones reduction apparatus, packed with amalgamated zinc, is rinsed with 200 c.c. of 5% sulphuric acid at 75°, and then filled with 20% acid at the same temperature. The columbium solution is run through the apparatus, which is then washed out with 50 c.c. of 20% acid and 200 c.c. of 5% acid. The brown reduced solution is titrated with permanganate in an atmosphere of carbon dioxide. One c.c. $N/10\text{-KMnO}_4 = 0.007052$ gram Cb_2O_5 . The reaction corresponds with a reduction to $\text{Cb}_2\text{O}_{3.107}$. In the analysis of minerals, the volumetric method gives lower values for columbium and correspondingly higher values for tantalum than the method of fractional crystallisation. It is more exact than the latter. C. H. D.

Estimation of Lead in Tinned Utensils, etc. FRANZ KNÖPFLE (*Zeitsch. Nahr. Genussm.*, 1909, 17, 670).—The usual method of separating lead from tin in alloys by treating the latter with nitric acid and dissolving the lead nitrate from the metastannic acid cannot be employed if the alloy contains much iron, as the ferric nitrate dissolves a portion of the metastannic acid, which is re-precipitated with the lead when the latter is estimated as sulphate. The following method is therefore proposed: From 0.5—1.0 gram of the alloy is treated in a porcelain basin with nitric acid, D 1.50 to 1.52, exactly 1 c.c. of the acid being used for each 0.1 gram of metal. The basin is then covered with a clock-glass, and water is added drop by drop until red vapours no longer appear. The excess of acid is next evaporated on the water-bath, so as to leave a moist residue, to which is added a sufficient quantity of hot sodium phosphate solution and about 50 c.c. of hot water. The crystalline precipitate of stannic phosphate is collected on a filter, and the lead is then estimated in the filtrate in the usual way as sulphate. W. P. S.

Colorimetric Estimation of Lead in the Presence of Iron; Preparation of Lead-free Reagents by means of Ferric Hydroxide. JOHN M. WILKIE (*J. Soc. Chem. Ind.*, 1909, 28, 636—638).—Lead is precipitated completely from its solutions by ammonia provided there is a sufficiency of ferric iron present; this fact enables lead-free ammonium chloride, etc., to be prepared.

When estimating lead colorimetrically in presence of iron with sodium sulphide by Teed's method (Abstr., 1893, ii, 242), the author finds it necessary to reduce any iron to the ferrous state, and this is effected most conveniently by boiling the acid solution with a little sodium thiosulphate until colourless. Some potassium cyanide is then added, followed by excess of ammonia. Addition of tartaric acid is superfluous.

L. DE K.

Precipitation of Copper Oxalate in Analysis. FRANK A. GOOCH and H. L. WARD (*Amer. J. Sci.*, 1909, [iv], 27, 448—458).—A study of the best conditions to effect a complete precipitation of copper as oxalate, and containing a large number of experiments, the results of which are tabulated.

The best and most convenient procedure for the precipitation of either small or large amounts of copper consists in adding 2 or 4 grams of oxalic acid to 50 or 100 c.c. of the 5% acetic acid solution of the copper salt containing 5 or 10% of nitric acid. The precipitate is afterwards titrated with permanganate in presence of sulphuric acid.

L. DE K.

The Volumetric Estimation of Mercuric Salts. H. MORAWITZ (*Zeitsch. anorg. Chem.*, 1909, 62, 310—312. Compare this vol., ii, 185).—A reply to the criticisms of Andrews (this vol., ii, 440).

C. H. D.

Electro-chemical Behaviour of Manganese. C. NICOLIESCU OTIN (*Zeitsch. Elektrochem.*, 1909, 15, 385—386).—In estimations of manganese by Engels's method (electrolysis of a solution containing chrome alum and sodium acetate with an anodic current density of 0.006 to 0.01 ampere per sq. cm.), the author used a cathodic current density of about 0.05 ampere per sq. cm., and obtained some 7% of the manganese in the metallic form. He finds that this is prevented by using a low current density at the cathode, or by adding ammonium sulphate (about 2 grams per 100 c.c.) to the solution.

T. E.

Electrolytic Estimation of Manganese. C. NICOLIESCU OTIN (*Zeitsch. Elektrochem.*, 1909, 15, 386—389).—The deposit formed at the anode when a solution of a manganese salt and of ammonium sulphate (1 to 2 grams) is electrolysed, is shown to have the composition MnO_2 (after drying at 200—220°). Except in very small quantities, however, it does not adhere well to the matt platinum basin used as anode. This difficulty is overcome by adding from 3 to 8 c.c. of alcohol. Quantities up to 1.1 gram of MnO_2 may be estimated in this way, using an anodic current density of about 0.04 ampere per sq. cm. at 60°, or 8 or 10 times less at the ordinary temperature.

T. E.

Estimation of Iron by Permanganate in Presence of Hydrochloric Acid. G. CECIL JONES and JOHN H. JEFFERY (*Analyst*, 1909, 34, 306—316).—The old method recommended by Fresenius gives untrustworthy results. The method proposed by Reinhardt (*Abstr.*, 1890, 296) may, however, be employed advantageously as follows. The iron oxide is dissolved in 25 c.c. of hydrochloric acid, D 1.1, and reduced with as little stannous chloride solution as possible. Ten c.c. of saturated mercuric chloride are then added, and after ten minutes it is poured into 10 c.c. of Reinhardt's solution and diluted with water to 400 c.c. The liquid is then titrated with standardised permanganate; it is absolutely necessary that this should be added very slowly, drop by drop. The Reinhardt solution is prepared as follows: 200 grams of crystallised manganous sulphate are dissolved in 1000 c.c. of water, and a cooled mixture of 400 c.c. of sulphuric acid and 600 c.c. of water are added, also 1000 c.c. of phosphoric acid, D 1.13. L. DE K.

Reduced Iron. VIRGIL COBLENTZ and OTTO B. MAY (*Zeitsch. angew. Chem.*, 1909, 22, 1224—1227).—A criticism of the processes in use for the assay of reduced iron, the value of which depends on the percentage of actual metallic iron. The iodine titration process, and the methods based on the use of copper sulphate, are described, and the results communicated in a table.

The following process used in steel analysis seems promising; it is based on the estimation of the oxidised iron and siliceous impurities. One hundred and seventy c.c. of a nearly saturated solution of potassium cupric chloride and 5 grams of citric acid are placed in a flask, and 3 grams of the sample are added. After shaking for some time at a temperature not exceeding 15.5°, the undissolved iron oxides, etc., are collected, washed with cold water, and then with a weak solution of citric acid until free from copper. The mass is then dried, ignited, and weighed as ferric oxide. L. DE K.

Analysis of Special Steels. J. PEPIN LEHALLEUR (*Mon. Sci.*, 1909, 23, i, 263).—In the analysis of steels containing molybdenum, vanadium, wolfram, nickel, and chromium, the separation of the first of these metals from the others by means of ether should be carried out in hydrochloric acid solution (D 1.12). The ether is distilled off, and the residue evaporated with sulphuric acid. The warm aqueous extract is treated with hydrogen sulphide, and the precipitated sulphide ignited in a stream of hydrogen sulphide, but not in hydrogen, as this reduces the product to a sulphide lower than that corresponding with MoS_3 .

Vanadium is precipitated in ammoniacal solution as manganese vanadate, and redissolved in concentrated hydrochloric acid. Chromium is reduced from the chromate by ferrous ammonium sulphate, and the excess of this salt titrated with permanganate. Tungsten is estimated by attacking the alloy with concentrated hydrochloric acid, evaporating to dryness twice with nitric acid, and then with hydrochloric acid and potassium chlorate. The residue is dissolved in boiling dilute hydrochloric acid, and the liquid (A) decanted on to an ashless filter; the insoluble residue is treated with boiling dilute ammonium hydroxide,

when tungstic acid is dissolved together with a little silica. The liquid is poured on to the preceding filter, washed with dilute ammonium hydroxide, and the liquid collected in another vessel. The ammoniacal filtrate is concentrated, transferred to a tared platinum crucible, and evaporated to dryness with nitric acid until the residue is yellow. The crucible and contents are weighed, treated with hydrofluoric and sulphuric acids, and re-weighed, the loss giving the silica which has been volatilised. The filter paper is ignited and weighed, treated with hydrofluoric acid, and the remainder of the silica thus estimated. The residue is fused with sodium hydrogen sulphate, extracted with water, and added to the liquid (A), in which chromium is estimated by one of the usual methods. The nickel (after precipitation as sulphide) is estimated by electrolysis in ammoniacal solution with a maximum current of 4 amperes.

F. M. G. M.

Microchemical Reaction of Cobalt; Nickel and Cobalt Dimethylaminobenzeneazobenzenesulphonates. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1909, 14, 207—208).—The nickel compound when crystallised from hot water, in which it is only sparingly soluble, forms lustrous, yellow, hexagonal tablets. Magnesium also yields a similar precipitate, but this becomes crystalline in the cold, and the crystals are smaller than those of nickel.

The cobalt compound crystallises both from hot and cold solutions in long, slender prisms, forming long needles of a violet or black colour, often grouped in stars; when obtained from a rapid evaporation, small needles are formed, grouped in palisade-like form. The colour and size distinguish the cobalt crystals sufficiently from similar crystals of other metals.

L. DE K.

Estimation of Nickel and Cobalt according to Rosenheim-Huldschinsky. MAX PRITZE (*Chem. Zeit.*, 1909, 33, 694).—This process is based on the fact that cobalt-ammonium thiocyanate is soluble in a mixture of amyl alcohol and ether, whilst the nickel compound is not. When the solution, however, contains 50 or 100 times more nickel than cobalt, a small portion of nickel is also extracted. In order to free the cobalt completely from nickel, the author prefers treatment with dimethylglyoxime to a second shaking with the amyl alcohol-ether mixture.

L. DE K.

The Estimation of Vanadium in Steel. ÉMILE JABOULAY (*Rev. gen. Chim. pure appl.*, 1909, 12, 142).—This method is based on the fact that when a solution containing hypovanadic acetate and a large excess of ferrous acetate is boiled in contact with air, oxidation takes place and a precipitate is slowly formed which contains the vanadium, iron, and any chromium which may be present.

Modifications of the method, which are to be used when chromium, tungsten, molybdenum, or other metals are present, are also described in detail.

F. M. G. M.

Estimation of Bismuth in "Bismuthum Tribromophenylicum." O. SCHLENK (*Pharm. Zeit.*, 1909, 54, 538).—One to

two grams of the sample are heated to boiling with 20 c.c. of 10% sodium hydroxide solution until the bismuth hydroxide has separated. The liquid is diluted with water, and after decanting it through a filter, the precipitate is again treated repeatedly with the hot alkali, until this no longer gets turbid on adding hydrochloric acid (absence of tribromophenol). The precipitate is now collected on the filter, thoroughly washed with hot water, and then burnt with the filter in a porcelain crucible. It is then moistened with nitric acid, dried, and once more ignited.

L. DE K.

Comparison of the Iodide and Lime Methods for the Estimation of Glycerol in Wine. J. SCHINDLER and H. SVOBODA (*Zeitsch. Nahr. Genussm.*, 1909, 17, 735—741).—The iodide method described by Zeisel and Fanto (Abstr., 1902, ii, 585; 1904, ii, 95) for the estimation of glycerol in wine was found by the authors to be trustworthy and rapid; the apparatus devised by Stritar (Abstr., 1904, ii, 95) is of considerable use in carrying out the process. The lime method, in the case of dry wines or wines which do not contain more than 5 grams of sugar per 100 c.c., yields concordant results; the latter are, however, somewhat lower than those obtained by the iodide method. Possibly the loss of glycerol during evaporation is balanced by the presence of impurities. Preference must be given to the iodide method in the case of sweet wines, as the lime method gives results which are too low.

W. P. S.

Estimation of Glycogen and Starch; Detection of Horse Flesh in Sausages. MAURICE PIETTRE (*Ann. Chim. anal.*, 1909, 14, 206—207).—Twenty-five grams of the contents of the sausage are boiled in a reflux arrangement with 80 or 90 c.c. of alcoholic potassium hydroxide (aqueous potassium hydroxide, D 1.3, 20 c.c.; absolute alcohol, 80 c.c.), which removes the fatty and protein matters. The residue is collected on a filter, and washed first with hot 80 vol.% alcohol, and then with cold alcohol slightly acidified with hydrochloric acid until nearly the whole of the alkali is removed.

The mass is then heated with slightly alkaline water, which dissolves both starch and glycogen. On adding an equal volume of alcohol, the starch is precipitated, and may be collected and washed with cold 50 vol.% alcohol; the filtrate is then concentrated to a small volume, and the glycogen precipitated by adding excess of absolute alcohol. It may be recognised by its flocculent appearance and brown colour, and by the reaction with iodine in acetic acid solution. If desired, it may be collected, washed with alcohol, dried, and weighed.

L. DE K.

The Estimation of Mineral Acids in Vinegar. FERNAND REPITON (*Mon. Sci.*, 1909, [iv], 23, i, 172).—A criticism of the work published by Richardson and Bower (*J. Soc. Chem. Ind.*, 1906, 25, 836) on the same subject. The author considers his methods simpler and his results quite as accurate as those obtained by the above workers.

F. M. G. M.

Estimation of Fatty Acids in Soaps. M. DOMINIKIEWICZ (*Chem. Zeit.*, 1909, 33, 728).—Ten c.c. of soap solution (= about 0.5 gram of soap) are decomposed by heating with 10 c.c. of hydrochloric acid on the boiling water-bath for five minutes, and then centrifugalised for five minutes in a specially constructed apparatus (resembling a butyrometer). The fatty layer is then read off on a scale (temp. 99°); each division = 0.01 gram of acids. As, however, the sp. gr.'s of the acids are less than that of water, a correction must be applied when calculating the percentage by weight. In practice, the sp. gr.'s of fatty acids used in soap-making may be taken as about 0.835 (temp. 99°). L. DE K.

Estimation of Lactic Acid in Urine. JOHN H. RYFFEL (*Proc. physiol. Soc.*, 1909, v—vii; *J. Physiol.*, 39).—The urine is first steam-distilled with rather over 50% of sulphuric acid; the lactic acid then yields acetaldehyde quantitatively. The acid distillate is then just made alkaline and redistilled; to the distillate, Schiff's reagent (rosaniline hydrochloride bleached with sulphur dioxide) is added, and the depth of colour compared by a colorimeter with that obtained with the reagent and standard formaldehyde solution. W. D. H.

Reactions of Oxalates. TARAK NATH DAS (*Chem. News*, 1909, 99, 302).—For the analysis of salts containing oxalates, the following method is advocated as being more expeditious than the usual operation of ignition. The precipitate obtained in the course of analysis by adding ammonium chloride and ammonia is dissolved in nitric acid, and the decomposition of all oxalates and their conversion into nitrates is effected by adding excess of potassium chlorate and boiling for a few minutes.

Oxalates may be detected when in presence of carbonates, sulphites, etc., by treating the mixture with dilute nitric acid until the evolved gas no longer renders lime water cloudy (separation from carbonates), adding excess of potassium chlorate, and again boiling; if the lime water is now turned cloudy, the presence of oxalate may be inferred.

J. V. E.

Estimation of the Volatile Organic Acids of Tobacco and the Behaviour of the Oxalic Acid. RICHARD KISSLING (*Chem. Zeit.*, 1909, 33, 719—720).—A criticism of Tóth's method (*Abstr.*, 1908, ii, 238, 330; this vol., ii, 446). Tóth's statement that malic, citric, and oxalic acids yield an acid distillate on boiling with addition of sulphuric acid is erroneous. Oxalic acid is not decomposed on repeated evaporation with water, but the dry residue on being heated at 100° gradually volatilises by sublimation. When malic and citric acids are also present, the oxalic acid is but very imperfectly expelled. Acetic acid, if present, may be readily got rid of by heating on the water-bath until the odour is completely gone. L. DE K.

Detection of Benzoic Acid in Foods. Mlle. ANNA JONESCU (*J. Pharm. Chim.*, 1909, [vi], 30, 16—17).—In a private communication to the author, Leys has claimed priority for the discovery of the

hydrogen peroxide test for benzoic acid, described recently by the author (this vol., ii, 627). Leys' memoir (Abstr., 1901, ii, 488) only gives precise directions for the detection of "saccharin" by this method, and the author's object was to indicate that benzoic acid could be readily isolated from foods containing it and be detected by this test.

T. A. H.

Detection of Benzoic Acid in Meats and Fats. KARL FISCHER and O. GRUENERT (*Zeitsch. Nahr. Genussm.*, 1909, 17, 721—734).—In the method proposed, the benzoic acid, after it has been extracted from the substance under examination, is converted in part into salicylic acid by fusion with sodium hydroxide, and the presence of the latter ascertained by the well known coloration produced with ferric chloride. Fifty grams of the finely divided meat, or molten fat, are well mixed with 100 c.c. of 50% alcohol, acidified with sulphuric or hydrochloric acid (in the case of fats, the use of 20% alcohol is recommended); the alcoholic solution is then separated, rendered alkaline, and evaporated until the alcohol has been removed. The residual liquid is diluted to a volume of 50 c.c., 5 grams of sodium chloride are added, the mixture is acidified with sulphuric acid, heated to boiling, cooled, and extracted with ether. The ethereal extract is evaporated, the residue is fused in a silver crucible with a little sodium hydroxide, and the fused mass is dissolved in water. The solution obtained is acidified with sulphuric acid, extracted with ether, and the residue obtained on evaporating the ether is tested with a drop of 0.5% ferric chloride solution. The method will detect the following quantities of benzoic acid: in fresh meat, 0.01%; in smoked meats, 0.02%; in lard, butter, etc., 0.005%. The test described by Brevans (Abstr., 1902, ii, 112) is stated to be useless for the detection of benzoic acid in meats and fats. Tests which are based on the conversion of benzoic acid into benzaldehyde are capable of detecting the presence of 0.04% of the acid in fresh meats, but not in smoked meats; they are unsatisfactory in the case of fats.

W. P. S.

The Schardinger Reaction for Milk. KURT SCHERN (*Biochem. Zeitsch.*, 1909, 18, 261—284).—Schardinger has shown that milk at 45° decolourises a reagent containing methylene-blue and formaldehyde. This reaction is apparently due to the presence of an enzyme, as it is not produced if the milk is boiled previously. The author shows however, that the Schardinger reaction is not produced by all milks. Milk from cows in the earlier stages of lactation is inactive. The activity, however, increases with the stage of lactation, and is generally given with milk from cows in the later stages. For these reasons, the Schardinger reaction must be applied with care to milk examined for hygienic purposes.

S. B. S.

The Quantitative Estimation of Diphenylamine. DREGER (*Zeitsch. ges. Schiess, Sprengstoffwesen*, 1909, 4, 123).—When diphenylamine is brominated in alcoholic solution, *tetrabromodiphenylamine*, red needles, m. p. 102°, is precipitated on the addition of water. It is insoluble in water, sparingly soluble in alcohol, but soluble in the

ordinary organic media. The quantitative estimation is carried out as follows. An alcoholic solution of commercial diphenylamine is slowly treated with an excess of bromine in alcohol until no further precipitate is produced. About twice the volume of water is added with stirring, and the mixture heated until the alcohol and excess of bromine are removed and the precipitate becomes granulated; this is collected in a tared Gooch crucible, washed with warm water, and dried at 98—100°.

F. M. G. M.

Estimation of Urea in Urines. PHÆBUS A. LEVENE and GUSTAVE M. MEYER (*J. Amer. Chem. Soc.*, 1909, 31, 717—722).—An objection to Benedict and Gephart's method (this vol., ii, 103) is the partial hydrolysis of the uric acid and creatinine by the hydrochloric acid at 150°. The authors overcome the difficulty by removing the basic substances by means of phosphotungstic acid. In the modified method, 12.5 c.c. of urine are placed in a 50 c.c. flask, and a 10% solution of phosphotungstic acid in 10% sulphuric acid is added slightly in excess of the amount required to precipitate the basic substances. After twenty-four hours, the volume is made up to 50 c.c. with 10% sulphuric acid. The solution is filtered, and 20 c.c. of the filtrate are heated in an autoclave as in Benedict and Gephart's method.

C. S.

Isolation of Conium Alkaloids from Animal Tissues. WALTER J. DILLING (*Bio-Chem.*, 1909, J., 4, 286—292).—The most satisfactory method for the isolation of coniine from animal tissues to which it has been added is that of distillation. Coniine appears to be decomposed both by the action of living cells and during putrefaction. Conhydrine and ψ -conhydrine can be isolated by extraction with alcohol and precipitation by phosphotungstic acid, but the results are inconstant.

W. D. H.

Factors which Influence the Estimation of Creatinine. F. C. COOK (*J. Amer. Chem. Soc.*, 1909, 31, 673—693).—Folin's colorimetric method for the estimation of creatinine (*Abstr.*, 1904, ii, 375) gives satisfactory results for the total creatinine in beef extracts and similar products, but is not trustworthy for the estimation of the original creatinine in meat products. After a brief historical discussion of the colour reaction which takes place when a creatinine solution is treated with picric acid and an alkali, the author tabulates the results of experiments on solutions of meat extract, creatine, and creatinine to ascertain what is the influence on the colour of the amount of picric acid and of alkali, and also the influence of dilution, of keeping, of coagulable proteins, and of proteoses and peptones. The results show that in all cases in Folin's method it is desirable to take 25 or 30 c.c. of 1.2% picric acid solution, and 10 c.c. of 10% sodium hydroxide. The values for creatine and creatinine, alone, in meat, or in meat extract, are lowered by dilution; the error appears to be fairly constant, and averages 0.00019 gram of creatinine per 10 c.c. of dilution. Before taking readings, the solution should remain five minutes after adding the reagents. The presence of coagulable

protein, or of proteoses and peptones, lowers the values for solutions containing creatine, creatinine, or meat extract. The autoclave method of Benedict and Myers (*Abstr.*, 1907, ii, 492), modified so as to be applicable to meat products, gives the most satisfactory results in estimating creatine. C. S.

New Reactions of Hydrastine, Hydrastinine, and Narcotine. A. LABAT (*Bull. Soc. chim.*, 1909, [iv], 5, 742—743).—When 0.1 c.c. of solutions of hydrastine (0.33%), hydrastinine (1%), or narcotine (1%) in 10% sulphuric acid is added to 2 c.c. of sulphuric acid, and the mixture heated on a water-bath with 0.1 c.c. of solutions of certain phenols, very beautiful colorations are produced. With a 5% alcoholic solution of gallic acid, the colour is an intense emerald-green, which gradually becomes blue. The absorption spectrum of the liquid exhibits bands in the red and between the red and yellow, the latter of which disappears more quickly on dilution. The solution when diluted with glacial acetic acid becomes violet. With a 5% guaiacol or catechol solution, a currant-red colour is first developed, which becomes violet. Finally, in the case of a 2% solution of morphine hydrochloride, the mixture gradually becomes violet.

The reaction with gallic acid is the most sensitive, being recognisable with 1 part of hydrastinine, hydrastine, or narcotine in 50,000, 40,000, or 20,000 parts of water respectively.

The reactions confirm the close analogies supposed to exist between the constitution of the three alkaloids. E. H.

New Reactions of Opianic Acid and their Applications to the Detection of Hydrastine and Narcotine. A. LABAT (*Bull. Soc. chim.*, 1909, [iv], 5, 743—745. Compare preceding abstract).—When a sulphuric acid solution of hydrastine or narcotine is oxidised with potassium permanganate, appreciable quantities of opianic acid are produced. By adding 0.1 c.c. of a 1% alcoholic solution of the latter acid to 2 c.c. of pure sulphuric acid, and treating the mixture with 0.1 c.c. of a solution of certain phenols, colorations are obtained. With a 5% solution of gallic acid a blue coloration is produced, and changes to the colour of dead leaves on heating on a water-bath. A 5% alcoholic guaiacol solution gives a currant-red colour, which changes to an intense blue on the water-bath, whilst the absorption spectrum of the solution then has bands in the red, between the red and the yellow, in the green, and between the green and the blue; these disappear on dilution in the reverse order to that in which they are given. Similar colorations are obtained with catechol. Similarly, with 20% alcoholic solutions of α - and β -naphthol, currant-red and wine-red colours are produced respectively. A 5% alcoholic solution of codeine gives a violet coloration which gradually changes to blue on a water-bath. An intense violet tint, becoming paler on the water-bath, is obtained with an alcoholic solution (2.5%) of β -methoxynaphthalene. E. H.

Estimation of Quinine and its Excretion in the Urine. M. NISHI (*Arch. exp. Path. Pharm.*, 1909, 60, 312—323).—Acid quinine

citrate ($C_{20}H_{24}O_2N_2, C_6H_8O_7$) can be prepared by saturating quinine with citric acid in ethereal solution, and the preparation of this compound renders the estimation of quinine an easy matter. In the urine, the quinine is first extracted with ether after the urine is made strongly alkaline. About 34.5% of the quinine given is recoverable in the urine, and the greater part of this (25.5%) is excreted during the first twenty-four hours. If the quinine is given by the mouth in combination with arsenic or iron, the absorption and excretion of quinine are not affected.

W. D. H.

Micro-chemical Detection of Alkaloids, particularly in the Leaves of *Pilocarpus pennatifolius*. O. TUNMAN (*Chem. Zentr.*, 1909, i, 1510—1511; from *Schweiz. Woch. Chem. Pharm.*, 1909, 47, 177—183).—The reagents are applied directly to the cells. Zinc chloride-iodine forms dark black droplets, which exhibit rapid motion, but dissolve after fifteen minutes. The disadvantage of this test is that the strong cellular walls of the epidermis is also attacked. If the preparations are soaked for a few seconds in a drop of dilute nitric acid (1 : 5) and then placed on another object glass with a little absolute alcohol, a crystalline deposit of pilocarpine nitrate will be noticed. When moistened on a slide with potassium mercuric iodide, and then with a few drops of hydrochloric acid, a grey, amorphous precipitate is formed. Solution of iodine in potassium iodide (1 part of each to 200 parts of water) causes in the pilocarpine-containing cells numerous dark brown or reddish-brown, lustrous, oily droplets, which unite to larger drops and then soon disappear. With slightly acidified iodine solutions, finely granulated masses are obtained. The same occurs with potassium bismuth iodide, but the precipitates are then of a bright red colour.

The author describes how the pilocarpine alkaloids are distributed. In the inner tissues some cells give decided reactions for alkaloids, whilst neighbouring tissues do not contain a trace.

L. DE K.

A New Method for Detection of Indole in Culture Media. G. MORELLI (*Zentr. Bakt. Par.*, 1909, i, 50, 413—415).—Indole gives a red coloration with oxalic acid. The test for indole is carried out by hanging a piece of filter paper, which has been dipped in saturated oxalic acid and then dried and sterilised, just above the culture medium.

S. B. S.

Detection of Coal-tar Colours in Wine by means of the Reaction between Iodine and Tannin. CARLO CONTI (*Boll. Chim. Farm.*, 1909, 48, 295—298).—A solution of tannin absorbs iodine, giving a liquid which does not react with starch paste, and, if not saturated with iodine, does not evolve iodine when distilled almost to dryness. When iodine is added to a red wine, all the natural colouring matter of the latter is precipitated, the reaction proceeding rapidly and completely in the warm. This reaction is applied to the detection of coal-tar dyes in wines, the procedure being as follows.

One hundred c.c. of the wine are freed completely from alcohol by evaporation, the cold residue being made up to the original volume

with water. To the liquid, heated at 40—50° on a water-bath and shaken, a 2% solution of iodine in potassium iodide solution is added until, on testing with starch paper, the coloration does not remain constant. The solution is heated in a water-bath so long as the precipitate does not become flocculent or assume an orange-red colour; it is then left for three to four hours and filtered. To 10 c.c. of the filtrate is added, drop by drop, a slight excess of sodium thiosulphate solution. Natural wine then appears pale yellow, whilst wine coloured artificially with an acid dye is rendered more or less red; the latter colour becomes more evident if the acid of the wine precipitates free sulphur from the excess of thiosulphate. In this way 1 part of colouring matter per 100,000 of wine is rendered evident. Should the coloration be doubtful, a thread of fat-free wool is boiled for twenty minutes in a portion of the residual liquid acidified with a few drops of hydrochloric acid. The wool is removed, well washed, and gently heated in dilute sodium thiosulphate solution. With a natural wine, the wool then has a yellow colour, whilst with a wine artificially coloured, it has a distinct red colour. This modification detects 1 part of colouring matter per 400,000 of wine.

T. H. P.

Detection of Urobilin in Urine. P. GUIGUES (*Chem. Zentr.*, 1909, 1, 1273; from *Bull. Sci. Pharm.*, 1909, 16, 88—89).—The author proposes to precipitate the urobilin by saturating the urine with ammonium sulphate after acidification with hydrochloric acid. The precipitate is washed with a saturated solution of ammonium sulphate, dried in a vacuum over sulphuric acid or calcium oxide, and then extracted with hot ethyl acetate. The solution which contains the urobilin is examined spectroscopically. The chief absorption bands lie between green and blue from $\lambda = 502\text{--}482$ or $501\text{--}483$. If zinc acetate is added, the bands move towards $\lambda = 517\text{--}497$.

L. DE K.

Estimation of the Oxidation Numbers of Urine with Potassium Permanganate. HILLE (*Chem. Zentr.*, 1909, 1, 1201; from *Apoth. Zeit.*, 1909, 24, 146—147).—The oxidation number of a urine is the number of mg. of oxygen absorbed by 1 c.c. of the sample. The operation, which is the same as in the Kubel process for the estimation of organic substances in water, is carried out as follows: 10 c.c. of diluted urine (10 grams: 100 c.c.) are mixed with 50 c.c. of water and 25 c.c. of dilute sulphuric acid (1:2), and heated to boiling. *N/10*-Permanganate is then added until the liquid is dark red, and the heating is continued for ten minutes. To the solution, which must still be decidedly red, 10 c.c. of *N/10*-oxalic acid are added, and then, again, permanganate until the liquid is permanently coloured after ten minutes boiling.

The oxidation numbers of normal urines seem to lie between 4 and 11. Diabetic and other abnormal urines absorb from 13—14 mg. of oxygen.

L. DE K. 6

General and Physical Chemistry.

Ultra-violet Band Spectrum of Phosphorus. ANTOINE DE GRAMONT and CHARLES DE WATTEVILLE (*Compt. rend.*, 1909, 149, 263—266).—Attention is called to the agreement in the constitution of the ultra-violet spark and flame spectra obtained independently by the two authors in operating with a solution of phosphoric acid. The results are tabulated in parallel tables. H. M. D.

Absorption, Fluorescence, Magnetic Rotation, and Anomalous Dispersion of Mercury Vapour. ROBERT W. WOOD (*Physikal. Zeitsch.*, 1909, 10, 466—471*).—The emissive and absorptive properties of mercury vapour have been examined, more especially in reference to the properties of the absorption band at λ 2536. The changes which take place in the absorption spectrum as the density of the vapour increases have been ascertained by means of photographic records.

The fluorescence spectrum of mercury vapour varies with the nature of the sparking electrodes, and the observations indicate that the line λ 2536 is due to the action of rays of very small wave-length. These rays are present in the spark spectrum of cadmium, but not in that of zinc. With rise of temperature the intensity of the fluorescence spectrum gradually diminishes, and ultimately the spectrum disappears.

The band at λ 2536 exhibits strongly developed anomalous dispersion. In accord with the asymmetry of the band, it is found that the magnetic rotation of the plane of polarisation is very largely altered in the neighbourhood of the band on the ultra-violet side, whereas on the other side of the band the rotation is not perceptibly increased. H. M. D.

Anomalous Rotation Dispersion. HERMANN GROSSMANN (*Ber.*, 1909, 42, 2646—2648. Compare Tschugaeff, this vol., ii, 631).—The effect of the solvent on the rotation dispersion of ethyl tartrate has been examined, and the following numbers obtained for $[\alpha]$.

	Red.	Yellow.	Green.	Pale blue.	Blue.
Pure ester	+6.96	+7.29	+7.50	+6.60	+5.67
In chlorobenzene	+8.23	+8.67	+9.50	+8.33	+7.50
In benzyl alcohol	+17.8	+20.2	+24.2	+26.6	+27.4
In pyridine	+33.4	+38.7	+49.0	+55.8	+60.5
In tetrachloroethylene ...	+2.71	+1.93	+0.58	-1.42	-4.43
In tetrachloroethane	-6.29	-8.93	+13.14	-17.37	-22.33

J. J. S

Action of Gravity on the Induced Activity of Radium. LOUIS WERTENSTEIN (*Compt. rend.*, 1909, 149, 268—271. Compare Curie, *Abstr.*, 1907, ii, 728).—From an examination of the rate of decay of the induced activity of radium deposited under the influence of gravity, it is shown that radium-A is entirely absent. This has evidently been transformed in the time

* and *Phil. Mag.*, 1909, [vi], 18, 240—249.

required for the deposition of the active particles. In further experiments described by the author, parallel plates were placed horizontally at different distances from one another, and exposed to radium emanation in a closed vessel. The decay curves obtained by examination of the induced activity deposited on the inner faces of the upper and lower disks differ in general very considerably. The difference depends on the distance between the parallel plates, and for a given distance it depends on the hygrometric condition of the air.

H. M. D.

Chemical Action of Penetrating Radium Rays on Water.

MIROSLAW KERNBAUM (*Compt. rend.*, 1909, 149, 116—117. Compare this vol., ii, 364).—The action of the β - and γ -rays of 0.1 gram of radium chloride on 30 c.c. of distilled water during forty-one days produced 165 cub. mm. of hydrogen without a trace of oxygen. By titration of the water with very dilute potassium permanganate, it was established with a possible error of 10% that the equivalent of oxygen remained in the water as hydrogen peroxide. The decomposition of water according to the equation $2\text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{H}_2$ requires 0.66 Cal. per 165 cub. mm. of hydrogen liberated, whence it follows that only 1/17,500 of the total energy developed by the radium was utilised in decomposing the water. In an experiment with a glass container having thinner walls, this fraction was increased to 1/11,600.

A powerful beam of Röntgen rays acting under exactly parallel conditions for one hundred hours failed to produce either hydrogen or hydrogen peroxide. The conclusion is drawn that the decomposition of water by radium is mainly, if not entirely, the work of β -rays. The simultaneous production of hydrogen and hydrogen peroxide is an abnormal phenomenon, although peroxide alone is formed, for example, by the contact of water with certain heavy metals. R. J. C.

Evolution of Radium Emanation. H. HERCHFINKEL (*Compt.*

rend., 1909, 149, 275—278).—The proportion of radium emanation which is evolved from solid radium salts, or barium salts containing radium, is very small compared with the proportion of actinium emanation which is separated from the rare earth salts which usually accompany actinium. With the object of obtaining information in regard to this difference in behaviour, the author has measured the quantity of emanation evolved by various precipitated substances containing radium. These include hydroxides, fluorides, chromates, oxalates, and sulphates, which were dried for twenty-four hours at 110° before being sealed up in tubes for the determination of the emanation which they give up. Whereas barium salts generally retain the emanation to a marked extent, it is possible to obtain a much larger proportion of the total emanation formed from the radium present, when this is associated with the hydroxides of iron or uranium, with ferric chromate or didymium fluoride.

H. M. D.

Ratio between Uranium and Radium in Radioactive Minerals. Mlle. ELLEN GLEDITSCH (*Compt. rend.*, 1909, 149, 267—268).—The method used by the author for the estimation of

radium in radioactive minerals (this vol., ii, 533) has been examined for possible sources of error, and found to give trustworthy results. The values obtained for the ratio of radium to uranium in French autunite, Joachimsthal pitchblende, and Ceylon thorianite are respectively 2.85, 3.58, and 4.19×10^{-7} . These results indicate that the ratio is variable within certain limits, and various hypotheses relating to the variability are discussed. In view of these observations, the number obtained for the average life of uranium on the assumption of a constant ratio cannot be accepted as correct. H. M. D.

Isolation and Relative Activity of Uranium-X. BÉLA SZILARD (*Compt. rend.*, 1909, 149, 113—115. Compare Schmidt, this vol., ii, 206).—The presence of traces of iron is advantageous in precipitating certain radioactive products, including uranium-X, by means of barium sulphate. Pure barium sulphate hardly precipitates any uranium-X in absence of uranium and iron (compare Moore and Schlundt, *Abstr.*, 1906, ii, 721), whereas ferric hydroxide carries down uranium-X very easily. Uranium acetate solution with addition of ferric acetate, ammonium acetate, and a little acetic acid is boiled for a few minutes and filtered hot. The precipitate of ferric hydroxide is washed, redissolved in acetic acid, and partly precipitated by the same process. Or, the first precipitate is dissolved in hydrochloric acid and the iron extracted with alcohol-free ether, leaving the uranium-X in the aqueous solution. On repeating the separation of uranium-X from the same lot of uranium daily for twelve days, the activity of the last four precipitates was constant, and equal to only 4% of the total uranium-X activity. It is therefore assumed that the residual uranium was practically free from uranium-X. Ionisation measurements show that the uranium-X in equilibrium with uranium is responsible for 0.237 of the total radioactivity. If it is assumed that uranium is decomposed 2,000,000 times as slowly as radium, only $2 \cdot 10^{-11}$ grams of uranium-X would be present in 1 gram of uranium in equilibrium. Pure uranium-X must then be ten milliard times as active as uranium in equilibrium. R. J. C.

Radioactivity of Compounds of Erbium, Potassium, and Rubidium. W. W. STRONG (*Amer. Chem. J.*, 1909, 42, 147—150).—A number of minerals and salts of the rarer elements have been examined for radioactivity by placing them in dishes covered with a screen containing several openings, above which a photographic plate is exposed to the salt below for about six months. The salts were collected about fifteen years ago, and include those of potassium, zirconium, caesium, lead, bismuth, yttrium, tungsten, sodium, molybdenum, niobium, rubidium, erbium, tantalum, lanthanum, vanadium, neodymium, praseodymium, and ruthenium. The majority of the potassium salts and all of the erbium and rubidium compounds produce photographic impressions. C. S.

Relations between the Inactive Gases and the Radioactive Elements. F. H. LORING (*Chem. News*, 1909, 100, 37—39).—It is shown that the inert gases and certain radioactive elements can be

arranged in series of four, so that the second differences between the atomic-weight numbers are in inverse geometrical progression.

H. M. D.

A Method of Registering the Length of the Path of α -Rays, and a Peculiarity of the Path. BÉLA SZILARD (*Compt. rend.*, 1909, 149, 271—273).—A zinc sulphide screen, prepared by covering a glass slip with a thin layer of the substance, is placed at a certain angle above a layer of the radioactive material. A photographic plate is placed in direct contact with the glass of the screen, and left exposed for a period which depends on the activity of the material under examination. With this arrangement, the only rays which can act on the plate are the luminous rays generated by the impact of the α -rays on the phosphorescent screen. That part of the screen which is within the range of the α -rays produces an effect on the immediately adjacent parts of the photographic plate, and from an examination of the plate and measurement of the angle of inclination of the screen, the range of the α -particles can be determined.

In the author's experiments, measurements were made with various specimens of polonium, differing very considerably in activity, and the times of exposure varied from three days to four months. The values of the range obtained in the different experiments agree very well, but are all about 2 mm. less than the range obtained by the ionisation method.

H. M. D.

Behaviour of Kunzite under the Influence of Becquerel Radiation. STEFAN MEYER (*Physikal. Zeitsch.*, 1909, 10, 483—484).—When subjected to the action of the β - and γ -rays of radium, the violet-red colour of kunzite changes to green. This colour change does not affect the fluorescence which kunzite exhibits under the influence of β -rays. This is also exhibited by a sample of the mineral which has been decolorised by heating. The fluorescent light is polarised in a direction parallel to the long axes of the kunzite fibres.

When kunzite, transformed by the action of β -rays, is placed in the path of a beam from an arc light, the green colour gradually disappears, and, after passing through an intermediate colourless stage, the original violet-red colour is obtained. The transformation is due to the action of the violet and ultra-violet rays. On warming, the fluorescence of the transformed green kunzite commences at a much lower temperature than that of the unchanged mineral.

H. M. D.

Influence of the Polarisation of the Exciting Light on the Emission of Electrons at the Surfaces of the Alkali Metals, JULIUS ELSTER and HANS GEITEL (*Physikal. Zeitsch.*, 1909, 10, 457—465).—Experiments are described which indicate that the photo-electric effect produced by polarised light at the surface of the alkali metals is dependent on the relative positions of the planes of incidence and polarisation. More electrons are liberated by light which is polarised at right-angles to the plane of incidence than by light which is parallel polarised. The maximum velocities of the electrons are approximately the same in the two cases. On the other

hand, the proportion of the total electrons, which have a velocity smaller than the maximum, is in all cases greater for light which is polarised at right-angles to the plane of incidence of the active light.

H. M. D.

Decomposition of Water by Ultra-violet Rays. MIROSLAW KERNBAUM (*Compt. rend.*, 1909, 149, 273—275. Compare this vol., ii, 364).—Fifteen c.c. of freshly boiled distilled water, contained in a quartz vessel, were subjected to the action of the rays from a mercury lamp for a period of 200 hours. By means of an attached manometer, gas was found to be evolved after some time. This appeared to be generated at a constant rate for a considerable period, but afterwards the rate of evolution diminished, and during the last thirty-five hours there was no further increase in the pressure. Examination of the gas showed it to be hydrogen, and hydrogen peroxide was detected in the water. Ultra-violet rays, like the β -rays of radium, decompose water, therefore, according to the equation: $2\text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{H}_2$.

H. M. D.

Conductivity and Viscosity in Mixed Solvents Containing Glycerol. M. R. SCHMIDT and HARRY C. JONES (*Amer. Chem. J.*, 1909, 42, 37—95).—The electrical conductivity of lithium bromide, cobalt chloride, and potassium iodide has been measured in glycerol at 25°, 35°, and 45°, and in mixtures of glycerol with water, methyl alcohol, and ethyl alcohol respectively in dilutions of 10 to 1600 litres; the results are given in tabular form and are also represented by curves. The conductivities in pure glycerol are comparatively low, and do not attain definite maxima in the dilutions used; in all cases the conductivities in the mixed solvents are less than the sum of the conductivities in the individual solvents. The molecular conductivity of cobalt chloride in ethyl alcohol is abnormally low, and it is shown by ebullioscopic measurements that in this solvent the salt is considerably polymerised. The temperature-coefficients of the conductivity of the salts in pure glycerol are abnormally high, being about 10% per degree between 25° and 35°, and more than 8% per degree between 35° and 45°, corresponding with the great diminution in viscosity of these solutions with rise of temperature. In the case of solutions of cobalt chloride in ethyl alcohol, the temperature-coefficient of the conductivity is negative.

The viscosities of the pure solvents, of the mixed solvents, and of $N/10$ -solutions of the three salts in mixtures of the solvents in varying proportions have also been determined at 25° and 35°. The temperature-coefficient of the fluidity of glycerol between 25° and 35° is 11.53% per degree, which is nearly equal to the temperature-coefficients of conductivity of the salts. The fluidities of the solutions are usually less than those of the corresponding solvents, but the fluidity of $N/10$ -solutions of potassium iodide in water, and in 25% and 50% glycerol and water, is greater than that of the solvents themselves. There is a close parallelism between the forms of the conductivity and fluidity curves; in no case is the law of averages obeyed. As a dissociating solvent, glycerol resembles water more than it does the alcohols.

The paper contains a summary of the previous results of Jones and his co-workers on this subject. G. S.

[Potential Measurements.] JEAN BILLITZER (*Zeitsch physikal. Chem.*, 1909, 67, 201—202).—Palmaer's criticisms (Abstr., 1907, ii, 424) of the author's experimental results are not justified, as the more important experiments have now been repeated by Freundlich and Mäkelä (this vol., ii, 368), and the author's results confirmed. G. S.

Chemical Action and Ionisation. G. REBOUL (*Compt. rend.*, 1909, 149, 110—113. Compare Broglie and Brizard, this vol., ii, 535).—According to the electronic theory of matter, chemical changes which disturb the internal equilibrium of the molecules might cause a liberation of ions from the atoms. An apparatus is described by which chemical operations were carried out on one plate of a charged condenser maintained in a suitably evacuated vessel, and the leak due to ionisation was measured by the electrometer.

Interactions unaccompanied by effervescence, such as the neutralisation of bases by acids, produce no ionisation, even when much heat is disengaged. Interactions accompanied by effervescence, such as the action of acids on metals, give rise to both positive and negative ionisation, the former usually predominating. Actions in which the gas between the condenser plates participates, such as the action of carbon dioxide on fused potash or the oxidation of metallic sodium, give rise to ionisation so long as the attack is superficial, but quickly disappearing when the action penetrates below the surface. Charges of both sign are produced with a preponderance of negative. Gaseous interactions may give rise to great conductivity, such as in the interaction of ammonia and hydrogen chloride, or a small conductivity, as when ammonia and fumes of nitric acid interact.

The conclusion is drawn that in every medium where molecular disturbance occurs, electric conductivity is found. Proof is lacking, however, that the effects described are due to electrons apart from material particles.

Note by A. GAUTIER (*ibid.*, 113).—In the Solfatare at Naples the steaming exhalations which arise everywhere on a hot day are visibly intensified by the kindling of a flame at one point. This phenomenon is attributable to the condensing effect of ions produced by the flame. R. J. C.

Theory of Volatilisation by Atomic Rays. JOHANNES STARK (*Zeitsch. Elektrochem.*, 1909, 15, 509—512). FRANZ FISCHER (*ibid.*, 512—514).—With reference to Kohlschütter's latest publication on the cathodic volatilisation of metals (this vol., ii, 639), Stark gives an approximately quantitative development of his theory of the phenomena (Abstr., 1908, ii, 1007). The kinetic energy imparted to an atom of mass, m_1 , carrying a positive charge, e , in passing through a cathode fall of potential, K volts, is $\frac{1}{2}m_1v_1^2 = eK/300$. When an atom moving with this velocity collides with a metallic atom on the surface of the cathode moving at a comparatively low velocity, and assuming elastic

impact, the velocity of the metallic atom (of mass m_2) after impact is $v_2 = 2 \sqrt{m_1/m_2} \times \sqrt{2eK/300}$. The volatilisation should thus increase, other things being equal, with the molecular weight of the gas. The volume of the atoms of the gas is also of importance, because a small atom has a greater chance of penetrating below the surface layer of the cathode before collision, and only collisions at the surface are likely to result in the escape of an atom of metal from the cathode. This may be why the volatilisation in hydrogen soon becomes independent of the cathode fall. The existence of a limiting value of the cathode fall below which volatilisation does not occur is regarded as of great interest, because if the atoms of metals are held together by electrical forces, a certain definite increase of the energy of an atom would be needed to overcome these forces and allow of the escape of an atom.

Both Stark and Fischer criticise Kohlschütter's views in the sense that the ratios of the quantities of different metals volatilised under similar circumstances approximate so very roughly to multiple proportions that they cannot be regarded as proving the formation of chemical compounds between the metals and the gases. T. E.

Influence of Pressure on the Electrolytic Conductivity of Solutions. FRIEDRICH KÖRBER (*Zeitsch. physikal. Chem.*, 1909, 67, 212—248. Compare Tammann, *Abstr.*, 1899, ii, 137).—The apparatus and method of measuring the influence of pressure on the electrical conductivity of solutions have already been described by Tammann. Observations were made on a number of solutions up to pressures of 3000 kilos. per sq. cm.

With increase of pressure the electrical conductivity increases, but the magnitude of the effect diminishes with increase of temperature. The isotherms of the change of resistance with change of pressure for dilute solutions of potassium chloride show minima at all temperatures up to 100°. The effect of pressure on the ionic friction and on the viscosity of the solvent corresponds for aqueous solutions of sodium chloride, but this behaviour is not general, and does not hold for solutions of potassium chloride. It is shown by a comparison of the results for dilute solutions of a number of potassium and sodium salts that the influence of pressure on the ionic friction for strong electrolytes is the sum of the effects on the individual ions.

Ions with small atomic weight usually show a larger diminution of frictional resistance with pressure than those with high atomic weight, but potassium and sodium ions form an exception to this rule. With increase of temperature, the isothermals representing the influence of pressure on the ionic friction for different electrolytes tend to approach each other, but it is shown from the results of experiments with hydrochloric acid that hydrogen ions form an exception to this rule.

Up to the highest pressures employed, the direction of the influence of pressure on the conductivity of strong electrolytes is independent of the concentration up to moderate concentrations; the magnitude of the effect becomes smaller as the concentration increases. For solutions of greater dilution than 1 mol. in 100 litres, the influence of pressure on the conductivity of the solvent water becomes of importance, and

an expression is given which represents this effect in dilute solutions with considerable accuracy.

The curves obtained by plotting the influence of pressure on the conductivity for solutions of zinc sulphate as ordinates against the concentrations as abscissæ show distinct maxima at a concentration of about 0.4 normal solution at 20° for all pressures.

The effect of pressure on the degree of dissociation of acetic acid at 20°, obtained by an indirect method, agrees with that calculated by Planck's formula, but with increase of temperature the influence of pressure on the dissociation increases, whereas according to Planck it should diminish. G. S.

Technique of Electric Transport and Dialysis Experiments with Organic Colloids. FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 485—489).—A description of apparatus employed in these measurements. T. H. P.

Electric Charge of Textile Substances Immersed in Water or in Electrolytic Solutions. J. LARGUIER DES BANCELS (*Compt. rend.*, 1909, 149, 316—319).—Cotton, wool, and silk, etc., have in distilled water a negative charge, and this increases in alkaline solutions. The charge diminishes in presence of acids, and may even become positive. The negative charge (in distilled water or an alkaline liquid) diminishes under the influence of positive ions (Ba, Cu, Zn), and increases in presence of positive ions (sulphate, ferrocyanide). The employment of tannin or potassium dichromate does not involve any appreciable modification in the charge which the textiles take in water. In dyeing, the charge may, in some cases, be modified. The charge of wool dyed with methylene-blue diminishes considerably, owing, perhaps, in part, to the free ions contained in solutions of the dye. N. H. J. M.

The Sun as a Source of Heat for Chemical Experiments. ALFRED STOCK and HANS HEYNEMANN (*Ber.*, 1909, 42, 2863—2866).—By focussing the sun's rays on some crystalline silicon contained in an evacuated glass vessel, the crystals were fused in a few seconds, showing that a temperature of 1450° had been attained; copper and cast iron were fused almost instantaneously. A thermo-electric couple heated in the same way registered a temperature of 1030°, whereas on allowing the air to enter the vessel the temperature did not exceed 675°. It is hoped to extend this investigation, using improved lenses or concave mirrors. P. H.

An Approximate Determination of the Boiling Point of Metals. HAROLD C. GREENWOOD (*Proc. Roy. Soc.*, 1909, 82, A, 396—408).—The metals were heated in a carbon tube resistance furnace, the temperature being measured by an optical pyrometer directed on the lower part of the crucible through a side-tube. The boiling point was measured by observing the temperature at which visible ebullition took place, the surface of the metal being watched through an absorbing glass. A current of hydrogen through the furnace facilitated ebullition

by diffusing into the crucible and removing the heavy vapour. Carbon tubes were used as crucibles, except in the case of metals which combine with carbon, which were heated in graphite crucibles brasqued with pure magnesia. The results obtained, which may require some correction when the temperature scale has been more accurately fixed, indicate the following boiling points: aluminium, 1800° ; antimony, 1440° ; bismuth, 1420° ; chromium, 2200° ; copper, 2310° ; iron, 2450° ; lead, 1525° ; magnesium, 1120° ; manganese, 1900° ; silver, 1955° ; tin, 2270° .
C. H. D.

Determination of Molecular Weights by the Ebullioscopic Method. RICHARD MEYER and KURT DESAMARI (*Ber.*, 1909, 42, 2809—2814).—In the determination of molecular weights of sparingly soluble substances in benzene or other solvents by the ebullioscopic method, it is imperative that a correction be applied for changes of atmospheric pressure. From Young's measurements the b. p. of benzene changes 0.0427° per 1 mm. between 70 and 90° , so that a change of only 0.5 mm. in the atmospheric pressure during the determination may affect the value of the molecular weight to the extent of 50—80%. The best plan is to note any change of atmospheric pressure on an aneroid barometer, reading directly to 0.1 mm., and apply a correction to the b. p. of benzene calculated from the above data. Numerous experiments are quoted, in which very different molecular weights of one and the same substance are obtained; by applying the correction, the values become concordant and approximate to the theoretical value.
C. S.

Vacuum Distillation Apparatus with an Electrically Heated Discharge Contrivance for Solid Substances with High or Low Melting Points. JULIUS BREDT and A. VAN DER MAAREN-JANSEN (*Annalen*, 1909, 367, 354—358).—The apparatus described is an improvement on that devised by Haehn (*Abstr.*, 1906, ii, 841), in that there is no "dead-space" between the heating arrangement and the distillation flask. The exit-tube of the distillation flask is heated by means of an electric current which is caused to flow through a nickel wire about 1.75 metres long and 0.2 mm. diameter, wound spirally on a glass rod, the whole being enclosed in a sealed glass tube which passes down the centre of the exit-tube. It is possible by this device to heat the exit-tube throughout its whole length to 300° , and substances such as colophony, phenanthraquinone, and sulphur may be distilled under reduced pressure without danger of the exit-tube becoming choked during the process. A figure of the apparatus is given in the original, which should be consulted for details as to the means of measuring and regulating the temperature of the exit-tube, etc.
W. H. G.

Law of Constant Dissociation Pressures. HENRY LE CHATELIER (*Compt. rend.*, 1909, 149, 250—254).—The author points out that the trustworthy experimental data which can be cited as evidence of the constancy of the dissociation pressure in the dissociation of solids giving rise to a single gaseous product of dissociation are very

limited in number. On the other hand, many observations would appear to indicate that this pressure is a fraction of the extent of the dissociation. These apparent discrepancies from the requirements of the phase rule are supposed to be due to the action of surface forces in the finely divided solid product of dissociation.

To prevent the interference of surface energy in measurements of dissociation pressure, the addition of a small quantity of a solvent, in which both the solid substances are measurably soluble, is recommended. In these circumstances the equilibrium pressure is quickly set up, and the variability conditioned by the fineness of subdivision of the solids is eliminated. H. M. D.

Method of Analysis by Miscibility Curves; Application to Edible Oils. ÉMILE LOUISE (*Compt. rend.*, 1909, 149, 284—286).—The temperatures have been determined at which acetone when mixed with certain oils gives rise to a homogeneous liquid. When these are plotted as ordinates, and the relative proportions of oil and acetone as abscissæ, curves are obtained which enable different oils to be easily distinguished from one another. The differences between the curves are made the basis of a method of examining oils. According to this, increasing quantities of the oil are added to 20 c.c. of acetone, and the temperature at which miscibility is attained is determined after each addition. The oil and the acetone must be carefully dried before use, and the latter should be standardised by determining the miscibility for petroleum distilling at 210—225°. From curves contained in the paper, it is evident that the miscibility determinations show very large differences for olive oil, on the one hand, and cotton seed and sesame oil on the other. H. M. D.

Rôle of the Solvent in Chemical Kinetics. HANS VON HALBAN (*Zeitsch. physikal. Chem.*, 1909, 67, 129—182).—The rate of decomposition of triethylsulphine bromide into diethyl sulphide and ethyl bromide has been investigated in a number of organic solvents at different temperatures. As regards their effect on the rate of the reaction, solvents can be divided into two classes: (1) those containing hydroxyl groups, such as the alcohols and acetic acid, in which the velocity is small: (2) other solvents, such as acetone and chloroform, in which the velocity is much greater. The variation of velocity within the groups is comparatively small. The reaction in acetone is greatly retarded by the addition of water, but the latter has much less effect on the reaction in acetic acid. The temperature-coefficient of the reaction is high, the quotient for 10° being sometimes as much as 6 at low temperatures, but it varies greatly with the solvent. In the great majority of cases, the variation of the velocity with temperature is satisfactorily represented by the well known Arrhenius formula.

The rate of formation and rate of decomposition of *p*-bromophenyl-dimethylallylammonium bromide in a number of organic solvents have also been investigated. In this case, also, the effect of temperature on the rate of decomposition is very great, but the rate of formation of the salt is much less affected by rise of temperature. It is shown by ebullioscopic measurements that, contrary to the statement of Wedekind and Teletoff (*Abstr.*, 1904, i, 37), higher ammonium salts,

such as phenylbenzylmethylallylammonium iodide, split up only into two components in boiling chloroform.

The bearing of the above results is discussed at length. There is no general relationship between the rate of reaction and the properties of the solvent, and, as van't Hoff has pointed out, such a relationship is only to be expected when it is possible to separate the purely kinetic influence of the solvent from its effect on the equilibrium. The solubility in a particular solvent of the reacting substances and the substances formed appear to be of great importance in determining the velocity.

The general question of the effect of temperature on the rate of chemical reactions is discussed, the recent work of Trautz and Volkmann (Abstr., 1908, ii, 824) being adversely criticised in some respects. The temperature-coefficient of unimolecular reactions appears in general to be higher than that of polymolecular reactions.

G. S.

Formation of Esters. ANTON KAILAN (*Zeitsch. Elektrochem.*, 1909, 15, 500—505. Compare this vol., ii, 129, 305).—Polemical.

T. E.

Proposed Solution of the Equation of Condition for Calculating Atomic Weights. GUSTAVE D. HINRICHS (*Compt. rend.*, 1909, 149, 124—125. Compare this vol., ii, 140).—The author objects to the solution of his equation of condition (Abstr., 1907, ii, 945) worked out by Dubrueil by the method of least squares (Abstr., 1908, ii, 937). Hinrichs' equation requires an inverse proportionality between x , the deviation of the atomic weight from a round-number value (X), and ΔX , the variation in atomic ratio when X is increased by 1/100,000 of its value. Dubrueil's solution of the equation requires a direct proportionality of x to ΔX . A careful study of the one hundred and twenty principal chemical actions used to determine atomic weights lends no support to Dubrueil's thesis.

R. J. C.

New Proof of the Existence of Molecules. III. THE SVEDBERG (*Zeitsch. physikal. Chem.*, 1909, 67, 249—256. Compare this vol., ii, 277, 561).—In connexion with the previous observations, it is now shown that the depth of colour of a colloidal solution of gold is increased by warming and by the addition of electrolytes; Na^+ ions have much less effect than Ba^{++} ions. In this case, also, increase in absorptive power corresponds with an increase in the size of the particles.

A solution of colloidal gold containing extremely fine particles has been prepared both in the presence and absence of gelatin as protective colloid, and it has been found that under equivalent conditions the depth of colour is less when gelatin is present, a result ascribed to the effect of gelatin in hindering the coagulation of the particles. This view is further supported by the observation that the time taken to obtain the same depth of colour is approximately proportional to the amount of gelatin added.

G. S.

Improved Form of Safety Valve. H. STOLTZENBERG (*Chem. Zeit.*, 1909, 33, 779. Compare Abstr., 1908, ii, 828).—The safety

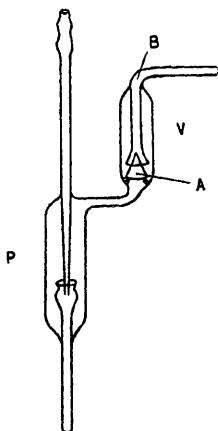
valve previously described (*loc. cit.*), being made in one piece, was difficult to clean, especially the internal ground-glass joint; this has been overcome by having the outside jacket made in two pieces, which are held together and kept air-tight by a stout, wide elastic band. This improvement allows of the valve being taken completely to pieces for cleaning purposes, and does not detract from its efficiency.

J. V. E.

New Safety Valve for Water Pumps. C. GERHARDT (*Zeitsch. anal. Chem.*, 1909, 48, 460—462).—To prevent any variation in the

water-pressure causing a backward flow of water, an automatic cut-off valve, indicated by *V* in the accompanying figure, is inserted between the pump and the vessel to be exhausted. *A* is a conical rubber washer, which fits closely into the enlarged end of tube *B* so as to close it completely when the pressure in the vessel being exhausted is less than in the pump *P*.

J. V. E.

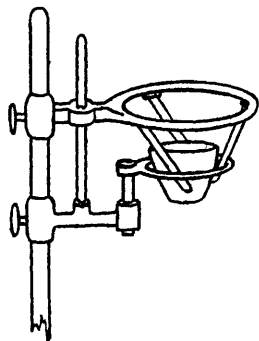


Automatic Regulator for the Pneumatic Agitation of Liquids. H. DENÈVE (*Bull. Soc. chim. Belg.*, 1909, 23, 315—318).—

Müller has devised a method of agitating liquids, depending on the alternate efflux and influx of air in wide tubes, the lower ends of which are immersed in the liquids. The author has modified Müller's apparatus in replacing the mercury pneumatic interrupter by an

electro-magnetic one. In the latter, a wide tube, the lower end of which is immersed in a beaker of mercury, carries two electrodes of different lengths, neither reaching the mercury level, and is connected with the vacuum pump (the action of which raises the liquids to be agitated in the wide tubes). As this tube becomes evacuated, the mercury rises, and when it covers both electrodes, a current passes through the coils of an electro-magnet, which, by depressing a lever, opens the pump to the atmosphere and at the same time completes another circuit which maintains the current round the electro-magnet until the mercury has fallen below both electrodes. This arrangement permits the agitated liquids to attain their original level before evacuation re-commences.

E. H.



Adjustible Crucible Support. CARL BORMANN (*Zeitsch. anal. Chem.*, 1909, 48, 462).—The arrangement described consists

of two rings, the upper one being somewhat larger than the lower, and from it three short porcelain rods are suspended. By raising the lower

ring, the porcelain rods are brought together, and form a convenient support for a crucible. As will be seen from the figure on p. 724, by raising or lowering the smaller ring this support may be made suitable for almost any size crucible.

J. V. E.

Inorganic Chemistry.

System Hydrogen Chloride and Water. FRANK F. RUPERT (*J. Amer. Chem. Soc.*, 1909, 31, 851—866).—The properties of aqueous solutions of hydrogen chloride, the vapour pressure of which does not exceed one atmosphere, have already been fully studied. Pickering (*Ber.*, 1893, 26, 277) has determined the f. p. of solutions containing from 0 to 48·8% of hydrogen chloride, and has shown the existence of two solid hydrates, namely, the dihydrate, m. p. $-17\cdot7^{\circ}$, and the trihydrate, m. p. $-24\cdot4^{\circ}$. The present investigation was primarily undertaken with the object of obtaining a solid monohydrate.

Solutions of a composition approximating to that of the monohydrate have a vapour pressure which is much greater than one atmosphere. The experiments, therefore, had to be carried out under pressure, and this was effected by the use of sealed tubes. The method adopted is described in detail.

Determinations of the densities of liquid and gaseous hydrogen chloride gave the following results. Density of the liquid (grams per c.c.): at 51° , 0·572; at 50° , 0·597; at 45° , 0·658; at 40° , 0·707; at 35° , 0·749; at 30° , 0·783; at 20° , 0·839; at 0° , 0·929; at -15° , 0·984; at -30° , 1·032; at -50° , 1·090. Density of the vapour (grams per c.c.): at 51° , 0·278; at 50° , 0·247; at 45° , 0·215; at 40° , 0·181; at 35° , 0·152; at 30° , 0·130; at 20° , 0·0974; at 0° , 0·0539; at -15° , 0·0543; at -30° , 0·0238; at -50° , 0·0125. The densities of solutions and of their vapours have also been determined up to the saturation point at -15° , 0° , 20° , and 35° .

The composition-temperature curve for the system hydrogen chloride and water has been constructed for all conditions in which the liquid and a solid, or two liquid phases, appear, the portion from 0 to 50% of hydrogen chloride being taken from Pickering's paper (*loc. cit.*). A eutectic point occurs at 57% hydrogen chloride and $-23\cdot5^{\circ}$, where the system is monohydrate-dihydrate-solution-vapour, and a maximum f. p. is found at about 66·9% and $-15\cdot35^{\circ}$. Near this point two liquid phases are formed, the new phase containing more than 99·9% of hydrogen chloride giving a quadruple point for the system monohydrate-solution-solution-vapour. The solubility of the hydrogen chloride phase in the water phase decreases as the temperature increases, whilst that of the latter in the former increases under these conditions. This relation continues up to $54\cdot5^{\circ}$, the critical

point of the hydrogen chloride phase. The portion of the curve showing the equilibrium between the monohydrate and the liquid hydrogen chloride phase was not investigated, owing to the difficulty of measuring such small quantities of water.

The monohydrate, the existence of which was confirmed by analysis, forms white crystals, has D 1.48, f. p. -15.35° , is very soluble in water, but only slightly so in hydrogen chloride, and has a vapour pressure at its m. p. which is approximately equal to that of pure hydrogen chloride, namely, 17.3 atmospheres. E. G.

Isomorphism between Tellurium and Sulphur. GIOVANNI PELLINI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 701—706).—The course of the solidification curve for mixtures of tellurium and sulphur indicates that these two elements do not unite to form compounds.

T. H. P.

Solid Hydrates of Ammonia. FRANK F. RUPERT (*J. Amer. Chem. Soc.*, 1909, 31, 866—868).—Although the monohydrate of ammonia, or ammonium hydroxide, is regarded as a compound, owing to the similarity of the properties of its solutions to those of the alkali hydroxides, the substance has not hitherto been obtained in the solid state. An investigation of the ammonia hydrates has therefore been carried out.

The f. p.'s of solutions of ammonia containing from 4.1% to 100% have been determined, and the results plotted as a curve which shows maximum f. p.'s at about 49%, f. p. -79° , and at 65%, f. p. -79° . The monohydrate theoretically contains 48.59% of ammonia, and the hydrate, $2\text{NH}_3 \cdot \text{H}_2\text{O}$, 65.40%. Eutectic points probably occur at 32% at about -115° , 57.5% at -86.5° , and 78.5% at -96° .

Ammonia monohydrate forms small, colourless crystals, whilst those of the hydrate, $2\text{NH}_3 \cdot \text{H}_2\text{O}$, are much larger, transparent, and needle-shaped. Solutions containing from 25 to 60% of ammonia are very viscous below -60° , whilst at -100° the 33% solution can hardly be stirred. E. G.

Allotropic States of Phosphorus. PIERRE JOLIBOIS (*Compt. rend.*, 1909, 149, 287—289).—When ordinary red phosphorus is heated in exhausted tubes at temperatures above 360° , its density increases from 2.18 to 2.37, and a new form, termed pyromorphic phosphorus, is obtained. The velocity of the transformation increases with the temperature, and although very slow at 360° , it can be observed even at 250° if iodine, which acts as a catalyst, is added in very small quantity. On examination of specimens of red phosphorus which had been partly transformed into the pyromorphic variety, it was found that these are always homogeneous, as if a solid solution had been formed.

Red phosphorus melts when heated to 725° ; the liquid has a violet colour and D 2.27. When the molten phosphorus is rapidly cooled, it is not transformed into yellow phosphorus, as has been stated by Chapman (*Trans.*, 1899, 75, 734). H. M. D.

Preparation and Properties of Solid Hydrogen Phosphide, $P_{12}H_6$. ALFRED STOCK, WILLY BÖTTCHER, and WALTER LINGER (*Ber.*, 1909, 42, 2839—2847).—The method of preparation depends on the observation that spontaneously inflammable hydrogen phosphide, P_2H_4 , on coming into contact with granulated calcium chloride is converted into the solid phosphide, $P_{12}H_6$, and phosphine. A yield of 8 grams of the solid from 1 kg. of calcium phosphide can be obtained as follows. A conical filtering flask, three-quarters filled with water, is immersed in a slanting position, with the side-tube pointing upwards, in a warm water-bath at 60° . The side-tube is connected to a short reflux condenser, the far end of which passes into the lower end of the first of a series of three wide glass tubes filled with granular calcium chloride; the third tube is attached to a wash-bottle containing hydrochloric acid, the other end of the wash-bottle being connected to the draught of a fume cupboard. After displacing the air in the apparatus by carbon dioxide, small lumps of calcium phosphide, 1 cm. thick, are introduced into the water in the filtering flask through a wide glass tube passing through the cork in the neck. The formation of appreciable quantities of solid phosphide in the wash-bottle is an indication that the efficiency of the calcium chloride is exhausted; a current of carbon dioxide is then again passed through the apparatus, and the calcium chloride with the solid phosphide is gradually added to dilute hydrochloric acid, cooled to 0° , and thoroughly shaken until all the calcium chloride has dissolved; rise of temperature and exposure to sunlight must be avoided. The solid phosphide is then repeatedly washed with ice-cold water, then with alcohol and dry ether, and finally filtered by the aid of a pump and dried in a vacuum over sulphuric acid and phosphoric oxide. The purity of the substance can only be ascertained by analysis, which is performed by measuring the hydrogen evolved when a known weight of the hydride is distilled over a heated copper spiral in a vacuous tube.

The freshly prepared substance is an odourless, canary-yellow, amorphous powder, which is neutral to litmus; after short exposure to the air, it acquires an acid reaction and an odour of phosphine. If kept in the dark, it is stable, but exposure for a few days to sunlight causes it to turn red and evolve a quantity of spontaneously inflammable gas. If heated suddenly to 200° it catches fire. The only substances in which it is appreciably soluble are liquid hydrogen phosphide and molten phosphorus; its specific gravity in a mixture of chloroform and bromoform was found to be 1.83 at 19° ; its physiological action is due to the phosphine produced by its decomposition. P. H.

A New Solid Hydrogen Phosphide, P_9H_2 . ALFRED STOCK, WILLY BÖTTCHER, and WALTER LINGER (*Ber.*, 1909, 42, 2847—2853).—When the solid hydrogen phosphide, $P_{12}H_6$, is heated in a vacuum it evolves phosphine and turns orange-red; the phosphine so formed is quite pure, and the method is therefore a convenient one for the preparation of the pure gas. The red substance which remains is a new compound of the formula P_9H_2 , produced according to the equation: $5P_{12}H_6 = 6P_9H_2 + 6PH_3$.

The substance forms either a flocculent powder or a vesicular mass,

according as the temperature is raised slowly or rapidly during the decomposition of the compound $P_{12}H_6$; it is stable in dry air, but in moist air it rapidly increases in weight, acquires an acid reaction, and becomes converted into phosphine and phosphoric acid; it is darkened by contact with alkalis in the cold, and, on warming, dissolves with evolution of phosphine, but it dissolves readily in dry liquefied ammonia without the formation of phosphine. Prolonged heating in a high vacuum at $340-360^\circ$ converts it into red phosphorus.

P. H.

Action of Liquefied Ammonia on the Two Solid Hydrides of Phosphorus. ALFRED STOCK, WILLY BÖTTCHER, and WALTER LINGER (*Ber.*, 1909, 42, 2853—2863).—The compound $P_{12}H_6$ dissolves readily in liquid ammonia to form a clear red solution, which, on keeping, changes its colour to a light yellowish-red; on evaporating off the ammonia, a quantity of phosphine escapes and a black solid remains; the same substance is also obtained by dissolving the hydride P_9H_2 in liquid ammonia and evaporating the solution, but in this case no phosphine is formed, and it is therefore concluded that the substance is not produced directly from $P_{12}H_6$, but from P_9H_2 , produced by the decomposition of the $P_{12}H_6$. The black solid is of the nature of a salt, formed by ammonia with the compound P_9H_2 , which has acid properties; its ammonia content varies between values corresponding to the two formulæ: $P_9H_2 \cdot NH_3$ and $2P_9H_2 \cdot NH_3$. The hydride P_9H_2 may be recovered from its ammonia compounds by warming them or by treatment with acids.

P. H.

Volatilisation of Boric Acid by Heating in a Current of the Vapours of Carbon Tetrachloride and Methyl Alcohol. PAUL JANNASCH and HENRY F. HARWOOD (*J. pr. Chem.*, 1909, [ii], 80, 134).—Boric anhydride is completely volatilised in one hour at a moderate red heat in a current of the vapours of carbon tetrachloride (4 vols.) and methyl alcohol (1 vol.), without any deposition of carbon on the boat or combustion tube (this vol., ii, 759).

C. S.

Separation of Argon from Nitrogen. JOSÉ R. CARRACIDO (*Anal. Fis. Quim.*, 1909, 7, 109—111).—The gas evolved from the mineral water of Urberuaga de Ubilla consists of 97% of nitrogen and 3% of carbon dioxide. This nitrogen is remarkable, inasmuch as it contains no argon; it probably, therefore, was not formed within the earth from atmospheric air. Moissan has stated that in order to absorb nitrogen by means of a mixture of quicklime and magnesium, it is necessary to pass the gas several times over the heated material; this may be true of nitrogen containing argon, but with nitrogen free from the latter gas absorption is instantaneous and complete.

W. A. D.

Tellurides. CHARLES AUSTIN TIBBALS, jun. (*J. Amer. Chem. Soc.*, 1909, 31, 902—913).—This investigation has been carried out with the object of studying the composition and reactions of the tellurides. A review is given of previous work on the subject.

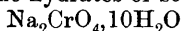
Sodium and potassium tellurides have been prepared by the direct union of the elements, whilst the tellurides of several of the heavy metals have been obtained by double decomposition between sodium telluride and metallic salts in aqueous solution. The alkali tellurides are immediately decomposed on exposure to the air with liberation of tellurium, and, for this reason, all experiments with their solutions have been carried out in an atmosphere free from oxygen. Sodium telluride, Na_2Te , forms colourless crystals containing a large amount of water of crystallisation. Tellurium dissolves in a solution of this salt with formation of the *polytelluride*, Na_4Te_3 . Potassium telluride, K_2Te , was obtained as a dark purple solid, which is very soluble in water and is precipitated in small crystals on the addition of alcohol to a strong solution. The following salts are also described: zinc telluride, $\text{ZnTe}, \text{H}_2\text{O}$; cadmium telluride, CdTe , nickel tellurides, $\text{Ni}_2\text{Te}_3, 4\text{H}_2\text{O}$ and NiTe ; cobalt tellurides, $\text{Co}_2\text{Te}_3, 4\text{H}_2\text{O}$ and CoTe ; lead tellurides, $\text{Pb}_2\text{Te}_3, 4\text{H}_2\text{O}$ and PbTe ; silver telluride, Ag_2Te , and copper tellurides, CuTe and Cu_2Te_3 . On adding sodium telluride to an aqueous solution of arsenious oxide, an arsenic telluride is precipitated, which is soluble in a solution of sodium polytelluride. Mercuric telluride is precipitated from mercuric chloride solution, but reacts rapidly with excess of mercuric chloride with formation of mercurous and tellurium chlorides. When sodium telluride is added to solutions of auric and platinic chlorides, gold and platinum respectively are precipitated and tellurium tetrachloride is produced. Sodium telluride reacts with ammonium molybdate to form dark coloured solutions which appear to contain telluro-salts.

E. G.

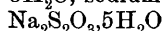
Nature of Change which Crystals of Sodium Sulphate Heptahydrate Undergo in Contact with Crystals of the Decahydrate. DÉSIRÉ GERNEZ (*Compt. rend.*, 1909, 149, 77—84).—A 66% solution of sodium sulphate cooled below 8° in absence of dust deposits crystals of heptahydrate, $\text{Na}_2\text{SO}_4, 7\text{H}_2\text{O}$, and the mother liquor remains supersaturated with respect to the decahydrate, $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$. On sowing the mother liquor with a crystal of the decahydrate, progressive crystallisation occurs until the solid heptahydrate is reached, and then an opacity spreads through the hitherto transparent crystals of $\text{Na}_2\text{SO}_4, 7\text{H}_2\text{O}$. The porcelain-like mass contains the decahydrate, since a fragment of it induces the crystallisation of $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$ from its supersaturated solutions; it is, therefore, not merely an allotropic modification of $\text{Na}_2\text{SO}_4, 7\text{H}_2\text{O}$. On the other hand, van't Hoff's suggestion that the solid heptahydrate has been transformed thus: $10\text{Na}_2\text{SO}_4, 7\text{H}_2\text{O} = 7\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O} + 3\text{Na}_2\text{SO}_4$, is unsupported by experimental evidence. The mass contains more water than the pure heptahydrate, and must therefore hold occluded mother liquor, the crystallisation of which as decahydrate would account for the rise in temperature observed. The author suggests that decahydrate crystallising in interstices between the crystals of heptahydrate gives rise to opacity. A solution was permitted to crystallise in a U-tube with a constricted bottom, and the heptahydrate crystals were rammed down into the constricted part until they completely blocked the tube so that the mother liquor could not be drawn through by the

pump. On sowing the mother liquor in one arm of the tube, crystals of the decahydrate grew down at a measurable rate, passed through the heptahydrate as an opacity at the same rate, and finally grew up into the mother liquor in the other arm of the tube.

The author shows that the hydrates of sodium chromate,



and $\text{Na}_2\text{CrO}_4, 4\text{H}_2\text{O}$, sodium acetate, $\text{NaOAc}, 3\text{H}_2\text{O}$ and $1\frac{1}{2}\text{H}_2\text{O}$, calcium nitrate, $\text{Ca}(\text{NO}_3)_2, 4\text{H}_2\text{O}$ and $3\text{H}_2\text{O}$, sodium thiosulphate,



and $2\text{H}_2\text{O}$, exhibit the same phenomenon as sodium sulphate, the lower hydrate in each case being rendered opaque by the subsequent crystallisation of the higher hydrate in its interstices. In all these cases, however, the higher hydrate can be melted by heating to a suitable temperature, and the lower hydrate appears in its original quantity and transparency. With sodium sulphate itself the hypothesis cannot be directly tested, because the heptahydrate is dehydrated on warming. It is shown, however, that transparent crystals of the decahydrate formed at -10° to -12° are rendered opaque by the subsequent crystallisation of the mother liquor (ice) in their interstices, and on warming slightly above 0° , the decahydrate crystals re-appear in the transparent condition. A dilute solution of sodium sulphate, on cooling, often deposits a mass of ice, and the mother liquor then solidifies in contact with a crystal of decahydrate. The decahydrate extends as an opacity through the mass of ice, which may often be melted away, leaving a deposit of small crystals of decahydrate.

R. J. C.

Normal Carbonates of Rubidium and Cæsium. ROBERT DE FORCRAND (*Compt. rend.*, 1909, 149, 97—100. Compare Abstr., 1908, ii, 256).—The heats of dissolution at 15° of potassium, rubidium, and cæsium carbonates are $+6.38$ Cal., $+8.75$ Cal., and 11.84 Cal. respectively. Saturated solutions at 20° contain 51.61 K_2CO_3 , 69.01 Rb_2CO_3 , 72.34 Cs_2CO_3 per 100 parts by weight of solution, so that saturated solutions have the composition $\text{K}_2\text{CO}_3, 7.20\text{H}_2\text{O}$; $\text{Rb}_2\text{CO}_3, 5.76\text{H}_2\text{O}$; $\text{Cs}_2\text{CO}_3, 7.59\text{H}_2\text{O}$. The rubidium salt appears to have an abnormal affinity for water. Heat is developed on diluting the saturated solution of rubidium carbonate only. When left in the desiccator, the saturated solutions deposit bulky crystals of hydrates, supposed to be $2\text{K}_2\text{CO}_3, 3\text{H}_2\text{O}$, $2\text{Rb}_2\text{CO}_3, 3\text{H}_2\text{O}$, and $2\text{Cs}_2\text{CO}_3, 7\text{H}_2\text{O}$, although analysis always revealed rather more water. When heated on the water-bath in dry air, potassium and cæsium carbonates are slowly but completely dehydrated, whereas the trihydrate, $2\text{Rb}_2\text{CO}_3, 3\text{H}_2\text{O}$ is converted into the monohydrate, $\text{Rb}_2\text{CO}_3, \text{H}_2\text{O}$, which is stable until the temperature is raised to 110 — 120° . Since the heats of addition of the last molecule of water to the hydrates $2\text{K}_2\text{CO}_3, 3\text{H}_2\text{O}$, $2\text{Rb}_2\text{CO}_3, 3\text{H}_2\text{O}$, and $2\text{Cs}_2\text{CO}_3, 7\text{H}_2\text{O}$ are practically equal (4.5 Cal.), these three salts have the same tendency to effloresce, whereas the monohydrate, $\text{Rb}_2\text{CO}_3, \text{H}_2\text{O}$, with heat of formation 7 Cal., is more stable. The anhydrous carbonates of rubidium and cæsium are more powerful dehydrating agents than potassium carbonate.

R. J. C.

Crystallisation of Ammonium Chloride. STEFAN KREUTZ (*Bull. Acad. Sci. Cracow*, 1909, 564—609).—Experiments were made on the growth of crystals of ammonium chloride from pure solutions, and from solutions containing cadmium chloride and various other substances. The presence of small amounts of cadmium chloride has a marked influence on the development of the crystals, these being rhombohedral in habit, owing to hindering of the growth in the direction of the cubic axes.
L. J. S.

Colloidal Silver Solutions obtained by the Action of Pure Distilled Water on Silver. MARGHERITA TRAUBE-MENGARINI and ALBERTO SCALA (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 542—545).—When heated for a long time with distilled water, silver dissolves to a slight extent, giving a solution exhibiting all the characters of colloidal solutions. Platinum is also attacked under these conditions, but to a less extent than silver.
T. H. P.

Variations in the Structure of Silver Coinage Alloys during Working. ERNESTO PANNAIN (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 523—525).—The author has studied metallographically the various changes in structure produced by the different processes employed in the manufacture of silver coins containing 83.29% of silver and 165.3% of copper. The most characteristic change is that wrought by lamination, which determines elongation of the crystals into the form of parallel fibres. Re-heating tends to give to the structure a regular aspect, whilst the compression produced by actual coining breaks the crystals and gives rise to a structure quite distinct from that of the fused alloy before mechanical treatment. False coinage may hence be detected by examining it metallographically.
T. H. P.

Bolognian Stones. LUDWIG VANINO and E. ZUMBUSCH (*J. pr. Chem.*, 1909, [ii], 80, 69—86).—Of the three methods of preparing the phosphorescent sulphides of calcium, strontium, and barium, it is known that the heating of the sulphates with carbon yields sulphide only, and the ignition of the thiosulphates gives a mixture of sulphide and polysulphide. It is now found that the heating of the oxides with sulphur at 1200° yields sulphides containing polysulphide, but no thiosulphate or free sulphur. The polysulphide plays an important part in producing luminescence, for a Bolognian stone prepared by igniting 13.5 grams of calcium sulphide (obtained from the sulphate and carbon, and therefore free from polysulphide), 0.3 gram of potassium sulphate, 0.3 gram of sodium sulphate, 0.7 gram of lithium carbonate, 0.7 gram of starch, and 0.7 c.c. of a solution of 0.8 gram of bismuth nitrate in 100 c.c. of alcohol, is found to be free from polysulphide and scarcely luminous, whereas a similar stone containing calcium sulphide produced from the oxide and sulphur is extremely luminous. The presence of a large sulphur content is not of great moment; just a slight amount of sulphur, present as polysulphide, is essential for the production of a good stone. Good strontium and barium stones are made by using the thiosulphates.

With regard to the metals, copper, lead, bismuth, thorium, and thallium, which are known to influence the colour and intensity of the luminescence, it is astonishing how little is necessary. A mixture of 40 grams of lime, 6 grams of sulphur, 1 gram of potassium sulphate, 1 gram of sodium sulphate, 0.5 gram of lithium carbonate, and 2 grams of starch, is treated with 1, 2, 3, 4, 5, and 6 c.c. of 0.8% alcoholic bismuth nitrate, and heated for one hour at 1200° ; the resulting stones are activated by burning magnesium for fifteen seconds. The most luminous stone is that corresponding with 2 c.c. of bismuth nitrate solution, and contains therefore 0.000135 gram of bismuth per 1 gram of stone.

Sodium sulphate (m. p. 880°) and lithium carbonate (m. p. 660°) have a greater effect than potassium sulphate (m. p. 1074°) in increasing the luminescence. It appears that salts of low m. p. are more efficient than those of high m. p.; too much of any one salt, however, is disadvantageous, a stone containing 2% of lithium carbonate being very luminous, whereas the same stone containing 12% of lithium carbonate was very much less so.

It has long been known that the luminosity of Bolognian stones increases with the temperature. The authors find that an extraordinary increase of intensity is produced when a stone, previously exposed to light, is covered with hot water, benzene, amyl alcohol, glycerol, acids, anhydrides, bases, and salt solutions; even unexposed calcium and strontium stones become luminous by this treatment. Hot sulphuric acid, in particular, produces magnificent effects, causing calcium stones to emit blue rays, strontium stones green rays, and barium stones orange-yellow rays, and also rise of temperature and evolution of hydrogen sulphide. Even cold acids cause an increased luminosity in exposed stones. When stones are treated with water and a reagent such as phosphoric oxide, quicklime, or anhydrous calcium chloride, which develops heat in contact with water, an increased luminosity is observed. Stones which have been prepared in the dark and never exposed to light do not become luminous by treatment with concentrated acids or by warming.

The paper concludes with a detailed account of the compositions of stones which give good blue, yellow, and red luminosities respectively.

C. S.

Action of Soluble Substances on Insoluble Substances.

WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1909, 295—297, 333—335. Compare this vol., ii, 668).—A solution of sodium chloride (2 mols.) in diffused daylight acts on finely powdered chalk (1 mol.), giving appreciable quantities of calcium chloride after two months, on tricalcium phosphate (1 mol.), giving a trace of the same salt, and on magnesium carbonate ($\frac{1}{4}$ mol.), giving an appreciable quantity of magnesium chloride. A solution of uranyl sulphate (large excess) in diffused daylight acts on tricalcium phosphate and on chalk, giving, after two months, notable amounts of calcium sulphate, and on magnesium carbonate, forming magnesium sulphate in one month. An appreciable amount of tricalcium phosphate is converted into chloride by heating on a water-bath at 95° daily for five hours

during six weeks, whilst the carbonate is similarly affected by lithium chloride solution.

Appreciable amounts of silver carbonate, chalk, magnesium carbonate, and barium and strontium carbonates are converted into the nitrate by boiling with concentrated sodium nitrate solution for respectively eleven minutes, thirty minutes, 2.5 hours, forty-five minutes, and thirty-five minutes. Under similar conditions, cobalt carbonate is only very slightly attacked after five hours, whilst basic lead carbonate remains unaltered.

E. H.

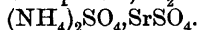
The Microscopic Structure of Portland Cement. ERNST STERN (*Zeitsch. anorg. Chem.*, 1909, 63, 160—167. Compare Abstr., 1908, ii, 589).—In the study of the action of water on Portland cement, the powdered cement has been mixed with water on a microscope slide, and kept in a moist chamber in a current of hydrogen. The formation of a colloidal substance, which often unites to form fibrous connexions between the cement particles, is observed. Slender needles of calcium silicate and aluminate, and of calcium hydroxide, form within the colloid.

The colloidal constituent may be dyed by means of 0.1—0.2% solutions of eosin dyes. Recently set cement dyes very rapidly, cement which has set for a year only very slowly. Alite and belite are not attacked. The process does not appear to be one of true dyeing, but rather of surface adsorption.

The disintegration of mixtures containing dicalcium silicate, $2\text{CaO} \cdot \text{SiO}_2$ (Day and Shepherd, Abstr., 1906, ii, 770), may be avoided by a very rapid cooling. Of the ternary lime-silica-alumina series, those mixtures disintegrate in which the primary crystals separating on cooling are those of dicalcium silicate. Within the cement region, the primary crystallisation is of mixed crystals of silicate and aluminate, separated from the former region by a eutectic line. The eutectic structure is well developed in the photo-micrographs.

C. H. D.

Double Sulphates. BARRE (*Compt. rend.*, 1909, 149, 292—295).—Strontium sulphate combines with potassium and ammonium sulphates to form the double sulphates, $\text{K}_2\text{SO}_4 \cdot \text{SrSO}_4$ and



The composition of the saturated solution in equilibrium with strontium sulphate and the double salt has been determined for a series of temperatures up to 100° . At 50° the solutions contain respectively 1.92 parts of potassium sulphate and 78.54 parts of ammonium sulphate per 100 parts of water. The ammonium double sulphate is therefore only stable in contact with nearly saturated solutions of ammonium sulphate.

Double sulphates of the same type are also formed by combination of lead sulphate with potassium and ammonium sulphates. The composition of the solutions saturated with respect to lead sulphate and the double salt has been ascertained at different temperatures. At 50° these solutions contain respectively 1.11 parts of potassium sulphate and 19.25 parts of ammonium sulphate for 100 parts of water.

H. M. D.

Reactions of Some Salts. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1909, 664).—No interaction has occurred between zinc carbonate and sodium chloride solution or between manganese carbonate and sodium nitrate solution after a further month's contact (compare this vol., ii, 668). A slight reaction has, however, been detected between sodium chloride and cadmium carbonate. The latter is thus distinguished from zinc carbonate. E. H.

Lead Chromate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1909, 665).—If a small quantity of lead chromate is boiled for one-half to one hour with a very concentrated solution of pure potassium nitrate and immediately filtered, the filtrate exhibits a well-marked red fluorescence and contains lead chromate. If, however, the filtrate after some moments is re-filtered, the filter retains the lead chromate, and the second filtrate is absolutely colourless. Sodium nitrate behaves similarly, but much more slowly. The conclusion is drawn that the lead chromate is rendered colloidal, but that the colloidal form re-polymerises very rapidly. E. H.

Purification of Mercury. JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1909, 31, 933—935).—A modification of L. Meyer's method (*Zeitsch. anal. Chem.*, 1863, 2, 241) for the purification of mercury, in which the mercury is allowed to fall in a fine stream through a long column of mercurous nitrate solution, is described.

The impure mercury is placed in a separating funnel, the delivery tube of which is slightly contracted at 0.5 cm. from the lower end. A piece of closely woven muslin is bound with twine over this end. The mercurous nitrate solution is contained in a glass tube, 1.5 metres long and 2 cm. in diameter, terminating at the lower end in a narrow delivery tube which is bent up to a height of 25 cm. The muslin-covered end of the delivery tube of the separating funnel should dip below the surface of the mercurous nitrate solution, so that the surface tension of the mercury may be diminished and the fine streams running through the muslin break up into very minute globules.

Experiments are described which show that mercury can be readily purified in this way to a degree of purity comparable with that of distilled mercury. E. G.

Bromates of the Rare Earths. II. Bromates of the Cerium Group and Yttrium. CHARLES JAMES and W. F. LANGELIER (*J. Amer. Chem. Soc.*, 1909, 31, 913—917*).—A method has been described by James (*Abstr.*, 1908, ii, 190, 498) for the separation of the yttrium earths which depends on the fractional crystallisation of the bromates.

In the present paper, an account is given of the preparation and properties of these bromates. They are usually prepared either by dissolving the oxide of the metal in bromic acid or, preferably, by the double decomposition of the sulphate of the metal and barium bromate.

Lanthanum bromate, $\text{La}_2(\text{BrO}_3)_6 \cdot 18\text{H}_2\text{O}$, m. p. 37.5° , is soluble to the extent of 416 parts in 100 parts of water at 25° . Cerous bromate,

* and *Chem. News*, 1909, 100, 85—86.

$\text{Ce}_2(\text{BrO}_3)_6, 18\text{H}_2\text{O}$, m. p. 49° , decomposes just above its m. p.; it readily undergoes decomposition in aqueous solution, and this property can be made use of for purifying the element. *Praseodymium bromate*, $\text{Pr}_2(\text{BrO}_3)_6, 18\text{H}_2\text{O}$, m. p. about 56.5° , is soluble to the extent of 190 parts in 100 parts of water at 25° . *Neodymium bromate*, $\text{Nd}_2(\text{BrO}_3)_6, 18\text{H}_2\text{O}$, m. p. about 66.7° , is soluble to the extent of 146 parts in 100 parts of water at 25° . Since the praseodymium salt is more soluble than that of neodymium, the latter can be obtained in the least soluble portion and a separation thus effected.

Samarium bromate, $\text{Sm}_2(\text{BrO}_3)_6, 18\text{H}_2\text{O}$, m. p. 75° , is soluble to the extent of 114 parts in 100 parts of water at 25° . *Yttrium bromate*, $\text{Y}_2(\text{BrO}_3)_6, 18\text{H}_2\text{O}$, m. p. 74° , is soluble to the extent of 168 parts in 100 parts of water.

All these salts crystallise in hexagonal prisms. When the normal hydrates of lanthanum, praseodymium, neodymium, and samarium bromates are heated at 100° , they are converted into lower hydrates containing $4\text{H}_2\text{O}$. The anhydrous salts are obtained by heating to 150° , with the exception of praseodymium bromate, which cannot be heated about 130° without decomposition.

E. G.

Extraction of Lutecium from Gadolinite Earths. GEORGES URBAIN, FRANÇOIS BOURION, and MAILLARD (*Compt. rend.*, 1909, 149, 127—129. Compare Abstr., 1907, ii, 956).—Crude yttrium earths of atomic weight 118, separated commercially from earths of the cerium group, were roughly fractionated as chromates to remove most of the yttrium. Fractional crystallisation of the hydrated nitrates from nitric acid gave a mother liquor containing mainly neoytterbium, lutecium, lanthanum, and cerium. Sufficient magnesium nitrate and bismuth magnesium nitrate were added to obtain on cooling a copious crystallisation of double nitrates of bismuth with magnesium, cerium, and lanthanum, the last two double nitrates being insoluble in saturated bismuth magnesium nitrate solution. Bismuth and magnesium were completely removed from the mother liquor, and the earths containing lutecium were precipitated by oxalic acid. The precipitate was converted into nitrate and fractionally crystallised to remove traces of erbium and yttrium and to separate the neoytterbium from the lutecium, which after 100 crystallisations was concentrated in the mother liquor. The lutecium earths, which were very feebly paramagnetic, were converted into chlorides by sulphur monochloride (compare Bourion, this vol., ii, 229). A certain amount of thorium and scandium chlorides sublimed in the process, and the lutecium chloride was heated in a stream of chlorine until it began to sublime also. Fractional sublimation of the chlorides appears to be a possible method of separating neoytterbium from lutecium.

R. J. C.

Action of Hydrogen Chloride on Aluminium. Method of Estimation of Metallic Aluminium. ÉMILE KOHN-ABREST (*Bull. Soc. chim.*, 1909, [iv], 5, 768—775. Compare Nilson and Pettersson, Abstr., 1888, 788; Stockhausen and Gattermann, Abstr., 1893, i, 161; Moissan, Abstr., 1894, ii, 450; Escales, Abstr., 1897, ii, 407).—The observations described were made during the course of an attempt

to prepare a chloride of aluminium other than AlCl_3 . Powdered aluminium is not acted on in two hours by cold dry hydrogen chloride, but is rapidly attacked if previously heated in hydrogen at 300° . Gattermann's observation that when once the action has commenced, it continues without further application of external heat, is confirmed. Aluminium powder is attacked more regularly than are the turnings, and the residue in the former case is voluminous and consists of small, grey tufts, whilst in the latter it is white and compact.

The residue from a quantity of aluminium powder is very hygroscopic, and almost completely soluble in hot dilute hydrochloric acid. It consists of hydrated alumina ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), neutral chlorides of foreign metals, traces of iron, and a small amount of insoluble matter (carbon, etc.), the amount of the first being almost identical with that previously estimated in the aluminium powder used. No trace of silicon or silica can be detected in either the residue or the volatilised chloride.

When powdered aluminium contained in a porcelain boat is heated in a current of dry hydrogen chloride at 500 — 600° , a very small quantity of minute spangles is formed on the glass above the boat after the aluminium chloride has volatilised.

At 1100° the action of hydrogen chloride is very rapid, and the sublimed aluminium chloride is found to contain appreciable quantities of calcium chloride, although calcium has not been detected in the ordinary analysis of the aluminium used. When powdered iron is heated at 300° in hydrogen chloride and hydrogen for twenty minutes, a sublimate of ferric chloride is formed, and a brown, amorphous mixture of ferrous chloride and unattacked iron remains. If the iron is mixed with an equimolecular amount of aluminium powder, the aluminium chloride sublimed is at first quite white, then the heated mass becomes covered with beautiful nacreous spangles, and finally the sublimate becomes yellow. Only 1% of the iron is volatilised, whilst the part of the residue soluble in water contains no aluminium. But when only small quantities of iron are present, as impurities in the aluminium, they are almost wholly volatilised in twenty-five minutes.

In order to estimate the aluminium in a sample of the powder, 0.3 gram contained in a porcelain boat is heated at 300° in a current of hydrogen, then for twenty-five minutes in hydrogen chloride, and cooled for ten minutes in hydrogen.

The residue is weighed, and the chlorine in it determined volumetrically, the amount of hydrated alumina being thence deduced.

E. H.

Hydrates, the Vapour Pressure of which varies continuously with the Composition. ERNST LÖWENSTEIN (*Zeitsch. anorg. Chem.*, 1909, 63, 69—139).—Whilst most crystalline hydrates have a vapour pressure which alters abruptly at a definite temperature, it has been shown by Tammann (Abstr., 1898, ii, 208) that the zeolites remain clear during dehydration, no new phase being formed, and their vapour pressure, like that of amorphous substances, varies continuously with the quantity of water present. Wyruboff has also observed that certain oxalates of the rare earths remain clear during dehydration

(Abstr., 1901, i, 7). These points have been more fully investigated by van Bemmelen's method (Abstr., 1897, ii, 137), the hydrates being kept at 25° over sulphuric acid of different dilutions and known vapour pressure, the loss of weight, and the water-content of the crystals being determined after equilibrium is reached.

The vapour pressure of the zeolites chabasite, desminite, and heulandite varies continuously with the water-content, and this is also true of the substitution products obtained by replacing the calcium by potassium, the crystals always remaining clear. The potassium zeolites contain less water than the calcium compounds, and their vapour-pressure for the same proportion of water is higher. Calcium chloride replaces the potassium by calcium, the products being identical with the original zeolites. Ammonium desminite behaves similarly.

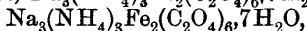
Silicic acids, prepared from different zeolites, olivine, and labradorite by the action of hydrochloric acid at 15°, also give continuous curves, indicating the absence of definite hydrates. Whether the silicic acids thus obtained are identical is uncertain, as the different vapour pressures observed may be due to changes in the colloids. Clays are found to contain water in two forms, one part being given off continuously over sulphuric acid of different concentrations, the other being retained even in presence of the concentrated acid. The examination of a large number of clays leads to their classification in the following groups, most of which correspond with the grouping proposed by Le Chatelier (Abstr., 1887, 785):

- I. Plastic fireclay, sedimentary clay, $2\text{SiO}_2, \text{Al}_2\text{O}_3, 2\text{H}_2\text{O}, \text{Aq.}$
- II. Halloysite, $2\text{SiO}_2, \text{Al}_2\text{O}_3, \text{H}_2\text{O}, \text{Aq.}$
- III. Kaolin, $4\text{SiO}_2, 2\text{Al}_2\text{O}_3, 3\text{H}_2\text{O}, \text{Aq.}$
- IV. Collyrite, $\text{SiO}_2, \text{Al}_2\text{O}_3, 2\text{H}_2\text{O}, \text{Aq.}$
- V. Pyrophyllite, $4\text{SiO}_2, \text{Al}_2\text{O}_3, \text{H}_2\text{O}.$
- VI. Montmorillonite, $4\text{SiO}_2, \text{Al}_2\text{O}_3, \text{H}_2\text{O}, \text{Aq.}$

The presence of anhydrous minerals and zeolites affects the vapour pressure of clays: they may be removed by fractional levigation.

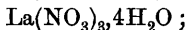
The oxalates of lanthanum, erbium, yttrium, cerium, thorium, and zirconium also yield continuous curves. A basic zirconium oxalate, $\text{Zr}(\text{C}_2\text{O}_4)_2, 2\text{Zr}(\text{OH})_4, \text{Aq.}$ forms doubly-refracting pyramids, 2 mm. high, which after dehydration re-absorb water, doubling their size without change of shape, remaining doubly-refracting.

Two double oxalates, $\text{Na}_3(\text{NH}_4)_3\text{Al}_2(\text{C}_2\text{O}_4)_6, 7\text{H}_2\text{O}$ and



give continuous curves for the loss of the first $2\text{H}_2\text{O}$, after which the vapour pressure remains constant until only $1\text{H}_2\text{O}$ remains: this is only driven off at a high temperature. Similar salts containing only two bases, such as $\text{Na}_5\text{Fe}_2(\text{C}_2\text{O}_4)_6, 9\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Fe}_2(\text{C}_2\text{O}_4)_6, 6\text{H}_2\text{O}$, behave like simple oxalates, the loss of water being discontinuous.

The nitrates of cerium, lanthanum, yttrium, and zirconium, the sulphates of cerium, lanthanum, yttrium, didymium, zirconium, and thorium, and uranyl nitrate form true hydrates, giving discontinuous curves. The following hydrates are new: $\text{Ce}(\text{NO}_3)_3, 4\text{H}_2\text{O}$;



$\text{La}(\text{NO}_3)_3, \text{H}_2\text{O}$; $\text{Y}(\text{NO}_3)_3, 5\text{H}_2\text{O}$; $\text{Zr}(\text{NO}_3)_4, 2\text{H}_2\text{O}$; $\text{UO}_2(\text{NO}_3)_2, 2\text{H}_2\text{O}$; $\text{La}_2(\text{SO}_4)_3, 3\text{H}_2\text{O}$. Cerium and lanthanum nitrates form similar hydrates,

that of yttrium is different. Yttrium sulphate, unlike cerium and lanthanum sulphates, does not lose water over sulphuric acid.

Boric acid does not lose water over sulphuric acid.

Continuous curves are given by zinc and copper ferrocyanides and by strychnine sulphate, $(C_{21}H_{22}O_2N_2)_2H_2SO_4 \cdot 6H_2O$.

The velocity with which equilibrium with the sulphuric acid is reached is greatest for those substances which give continuous curves. It depends on the rate of diffusion within the hydrate, which is greatest in zeolites and clays, and least in definite hydrates. The process of dehydration is reversible, and the crystals remain clear during the process, but silicic acids do not re-absorb the whole of the original proportion of water.

The form of the continuous vapour-pressure curve is different for the crystalline hydrates and for the amorphous substances, d^2p/dc^2 being positive in the former, and negative in the latter case. C. H. D.

Passivity of Iron. P. KRASSA (*Zeitsch. Elektrochem.*, 1909, 15, 490—500. Compare Abstr., 1907, ii, 598).—Iron assumes the active form in solutions of sodium or potassium hydroxide of greater concentration than $4N$ at temperatures below the boiling point of the solution. With weaker solutions higher temperatures are necessary (200° , for example, with $2N$ -solutions). When such active iron is used as cathode with a small current density it remains active, an oxide of iron being formed, which partly dissolves and partly adheres to the iron. The adhering layer gradually increases in thickness until, when a certain thickness is attained, the iron becomes passive and oxygen is evolved. The change is a gradual one, the potential (compared with the $N/10$ -calomel electrode) changing in boiling $10N$ -sodium hydroxide, for example, from -1.23 to $+0.27$ volt. If, on the other hand, a large current density is employed, the iron becomes passive at once, and no visible change occurs at its surface. Between these extremes any intermediate condition can be produced by taking a suitable current density and strength of solution. The author, therefore, draws the conclusion that in all cases the passivity is due to a skin of oxide.

The optical evidence against this view brought forward by Müller and Königsberger (Abstr., 1907, ii, 924) is discussed. The author comes to the conclusion that a layer of oxide of sufficient thickness to produce passivity might not change the reflecting power of the iron by more than 2%, and could, therefore, readily escape observation.

T. E.

Cementation of Iron by Carbon in a Vacuum. LÉON GUILLET and CH. GRIFFITHS (*Compt. rend.*, 1909, 149, 125—127).—Margueritte (1864) and, recently, Roberts-Austen believed that solid iron could absorb pure carbon whereas Caron (1864) disputed the point. Charpy has recently shown that iron can be carbonised by carbon monoxide (this vol., ii, 405). The authors have re-investigated the cementation of iron by pure carbon, special care being taken to exclude gaseous carbon compounds by maintaining a vacuum, and to ensure intimate contact between iron and carbon. Sugar-charcoal

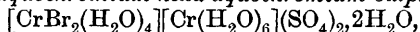
heated to 1000° in chlorine was employed. A mixture of carbon and iron was slowly heated to 450 — 500° in a long porcelain tube glazed inside, and the tube was then connected to a mercury pump. The temperature was raised to 800° , when a small quantity of gas was removed, and then to 1000° , which temperature was maintained during the whole experiment. Preliminary experiments without the vacuum showed that considerable carbonisation of the iron occurred with formation of pearlite. When gas was carefully excluded, no cementation occurred, but if the charcoal had been left in the air to absorb gases, some carbonisation of the iron occurred in spite of the vacuum. The mixture of iron and carbon was also heated in a cylinder pierced with small holes and provided with a screw stopper. If the stopper was left out and the mixture heated in a vacuum, there was no carbonisation, but when the material was rammed down tight by the screw, considerable carbonisation occurred. A sample of thin steel sheet with 0.05% of carbon contained 0.32% after five hours heating under these conditions. The mechanical pressure was sufficient to weld the steel fragments together at 1000° .

The authors conclude that, although when the contact is good carbonisation with pure carbon may occur, it is so slow that under manufacturing conditions direct cementation plays a very unimportant part.

R. J. C.

Halogenochromium Salts containing Aluminium, Iron, and Vanadium. NIELS BJERRUM and G. HIRSCHFELDT HANSEN (*Zeitsch. anorg. Chem.*, 1909, 63, 151—159. Compare following abstract).—Salts resembling Werner and Huber's dichlorotetra-aquochromium hexa-aquochromium sulphate, the second chromium atom of which is replaced by other metals, have been prepared. They are all very soluble in water, and are precipitated by sulphuric acid in the form of green leaflets with angles approaching 60° . They are not alums, although resembling alums in water-content and composition.

Dibromotetra-aquochromium hexa-aquochromium sulphate,



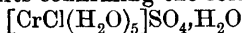
is prepared from violet hexa-aquochromium sulphate and dibromotetra-aquochromium bromide. *Dichlorotetra-aquochromium hexa-aquochromium aluminium sulphate* and the corresponding *dibromo-compound* are prepared from aluminium sulphate and the chromium halides. Ferric sulphate does not yield a chloro-compound, but the *dibromo-compound*, $[\text{CrBr}_2(\text{H}_2\text{O})_4][\text{Fe}(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, is readily obtained. Its colour is like that of the aluminium salts, but soon becomes brown. The *dichloro-vanadium* salt is obtained by the electrolytic reduction of vanadyl sulphate and addition of chromium chloride. The product is very stable. The corresponding *dibromo-compound* is prepared in similar manner.

It was not found possible to prepare similar salts containing titanium or tervalent cobalt or manganese.

Pentameta-aquochromium sulphate, $[\text{CrBr}(\text{H}_2\text{O})_5]\text{SO}_4 \cdot \text{H}_2\text{O}$, described by Werner and Huber (*Abstr.*, 1906, ii, 170) as an analogue of Recoura's salt, is best prepared from dibromochromium bromide and sulphuric acid.

C. H. D.

Physico-chemical Investigations of the Chromium Chloro-sulphates. NIELS BJERRUM (*Zeitsch. anorg. Chem.*, 1909, 63, 140—150. Compare Abstr., 1906, ii, 363).—The conductivity, velocity of transformation, and colour of the chromium chlorosulphates have been examined, the results confirming the formulæ



for Recoura's salt, and $[\text{CrCl}_2(\text{H}_2\text{O})_4][\text{Cr}(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ for Werner and Huber's salt.

The conductivity of both salts in 0.01 molar solution increases rapidly at first, then passes through a maximum, and falls asymptotically to a limiting value. The initial conductivity in each case is equal to that calculated from the corresponding chlorides, namely, λ 140 for the chlorochromium sulphate and λ 125 for the dichlorochromium chromium sulphate.

The first transformation, the ionisation of the chlorine, proceeds much faster than the second, the formation of a sulphate complex, and it is therefore possible to calculate the velocity constant of the former from the conductivity observations. The values $k = 0.008 - 0.0039$ and $0.0137 - 0.0065$ are found for the velocity constants of the two salts respectively.

The extinction coefficients for a number of rays have been measured for both salts, on the assumption that free and combined ions have the same colour, provided that complexes are not formed. Thus all hexa-aquochromium salts have the same colour in solution, whether dissociated or not. In the solutions examined, the hydrolysis was restrained by addition of acid. The extinction coefficients of Werner and Huber's salt agree within the limits of experimental error with those calculated from the mean of those for the dichlorotetra-aquochromium ion and the hexa-aquochromium ion, whilst Recoura's salt, on the other hand, gives values indicating a different constitution, as required by the hypothesis.

C. H. D.

Chromic Acid. GREGOIRE WYROUBOFF (*Bull. Soc. chim.*, 1909, [iv], 5, 765—767. Compare Walden, Abstr., 1888, 1008; Ostwald, Abstr., 1888, 1009; Miolati, Abstr., 1901, ii, 381; Abegg and Cox, Abstr., 1904, ii, 662; Sand and Kaestle, Abstr., 1907, ii, 178; Spitalsky, Abstr., 1907, ii, 338, 695; Lundberg, Abstr., 1907, ii, 967; Sherrill, Abstr., 1908, ii, 92).—When a solution of chromic acid is treated with an equimolecular quantity of calcium, strontium, zinc, copper, cerium, or lanthanum carbonate, effervescence ceases when half the carbonate has been added, whatever the concentration (3—30%) of the acid or the temperature (15—70°) of working, and from analysis of the resulting solution, chromic oxide and the basic oxide are always found present in the ratio $\text{CrO}_3 : \text{M}''\text{O} = 2 : 1$.

The sesquioxides of iron and aluminium behave less definitely. In the cold solution, ratios are found oscillating about the mean $\text{CrO}_3 : \text{M}_2\text{O}_3 = 5.2 : 1$, whilst if chromic acid solution is heated, the ratios approximate to 4.8 : 1, instead of the normal 6 : 1. Chromic hydroxide behaves peculiarly, giving insoluble chromium chromates of variable composition, whilst the liquid contains only a small quantity of chromium, depending on the concentration and temperature. The

conclusions drawn from these facts are, firstly, that physico-chemical methods are essentially incapable of determining the basicity of an acid, and, secondly, that chromic acid (a very weak acid) does not exist in the free state, but when liberated from its salts condenses to a polychromic acid, which again in the presence of strong bases is depolymerised, as are the polytungstic and polymolybdic acids. From the experiments cited, it seems to exist in solution as a dichromic acid, but in very concentrated solutions it may be much more condensed, since well crystallised compounds of tri- and tetra-chromic acids are known.

E. H.

Transformations of Iron and Steel. GRENET (*Bull. Soc. chim.*, 1909, [iv], 5, 758—764).—A theoretical consideration of the mutual solubility of iron and carbon, the transformation of pure iron, and the solution of iron in carbon, from which the conclusions are drawn that the phenomena exhibited by steels belong to the general case of phenomena produced in all alloys the constituents of which can form solid solutions decomposable into their elements at certain temperatures, and that the laws deduced from the study of steels probably apply to all alloys.

E. H.

Inorganic Salts of Titanium Peroxide. ARRIGO MAZZUCHELLI and ENRICO PANTANELLI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 608—613. Compare this vol., i, 631).—For the preparation of inorganic salts of titanium peroxide, which are very readily soluble and practically uncrystallisable, the author treats with alcohol the solution containing titanium sulphate, hydrogen peroxide, and an alkali sulphate in rather less amount than corresponds with the ratio $\text{TiO}_2 : \text{X}_2\text{SO}_4$.

In this way the following salts have been prepared :

$\text{TiO}_2(\text{KSO}_4)_2, 7\text{H}_2\text{O}$; $\text{TiO}_2(\text{NaSO}_4)_2, 10\text{H}_2\text{O}$; $\text{TiO}_2(\text{NH}_4\text{SO}_4)_2, x\text{H}_2\text{O}$;
 $\text{TiO}_2(\text{LiSO}_4)_2, 7\text{H}_2\text{O}$; $\text{TiO}_2\text{Cl}_2, 2\text{NaCl}, 9\text{H}_2\text{O}$; $\text{TiO}_3, \text{P}_2\text{O}_5, \text{Na}_2\text{O}, 3\text{H}_2\text{O}$, and
 $\text{O}(\text{TiO}_2, \text{P}_2\text{O}_5, \text{Na}_2\text{O})_2, 24\text{H}_2\text{O}$. T. H. P.

Hydrates of Thorium Chloride and Bromide. EDOUARD CHAUVENET (*Compt. rend.*, 1909, 149, 289—292).—When the hydrate, $\text{ThCl}_4, 8\text{H}_2\text{O}$, is dried at the ordinary temperature and pressure it yields $\text{ThCl}_4, 7\text{H}_2\text{O}$. When heated at 50° in a current of dry hydrogen or hydrogen chloride, $\text{ThCl}_4, 4\text{H}_2\text{O}$ is formed, and at 100° the product is $\text{ThCl}_4, 2\text{H}_2\text{O}$. Above 100° basic chlorides are formed. The heats of solution of the various hydrates are : $\text{ThCl}_4, +56.7$ cal. ; $\text{ThCl}_4, 2\text{H}_2\text{O}$, 41.08 cal. ; $\text{ThCl}_4, 4\text{H}_2\text{O}$, 26.23 cal. ; $\text{ThCl}_4, 7\text{H}_2\text{O}$, 14.7 cal. ; $\text{ThCl}_4, 8\text{H}_2\text{O}$, 11.45 cal.

When a solution of thorium hydroxide in alcoholic hydrogen bromide is evaporated at 100° , well formed needles of the dodecahydrate, $\text{ThBr}_4, 12\text{H}_2\text{O}$, are obtained. When dried at the ordinary temperature and pressure, this yields $\text{ThBr}_4, 10\text{H}_2\text{O}$; in an exhausted desiccator, $\text{ThBr}_4, 7\text{H}_2\text{O}$ is obtained. The heats of solution of the various hydrates are : $\text{ThBr}_4, +70.19$ cal. ; $\text{ThBr}_4, 7\text{H}_2\text{O}$, 22.55 cal. ; $\text{ThBr}_4, 10\text{H}_2\text{O}$, 9.84 cal. ; $\text{ThBr}_4, 12\text{H}_2\text{O}$, 2.30 cal.

A comparison of the two series of observations shows that the

oxybromides are formed at lower temperatures than the corresponding basic chlorides.

H. M. D.

Thorium Phosphates. A. COLANI (*Compt. rend.*, 1909, 149, 207—210. Compare Abstr., 1907, ii, 878).—The analogy between thorium and uranium is well shown by the parallelism existing between their phosphates. Troost's phosphates of thorium closely resemble those of uranium previously described by the author; the series has now been completed by the preparation of new thorium halogen phosphates and of double phosphates containing calcium and strontium. *Thorium chlorophosphate*, $3\text{ThO}_2, \text{ThCl}_4, 2\text{P}_2\text{O}_5$, prepared by heating thorium chloride with anhydrous thorium metaphosphate in a current of dry carbon dioxide, is a heavy, white, crystalline powder, insoluble in water and acids, but decomposed by boiling sulphuric acid or on fusion with alkali carbonates.

Thorium bromophosphate, $\text{ThBr}_4, (3\text{ThO}_2, 2\text{P}_2\text{O}_5)_3$, prepared in the same way as uranium chlorophosphate, but employing a very large excess of thorium bromide, occurs as a pearly-white, crystalline powder. This compound is very stable, and resists the action of molten alkali carbonates and of most acids. It was analysed after decomposition with boiling concentrated sulphuric acid. The existence of these halogen-phosphates throws light on the occurrence of fluorine in monazites. The following double phosphates were prepared in the same way as the corresponding uranium compounds. *Thorium calcium phosphate*, $\text{ThO}_2, \text{CaO}, \text{P}_2\text{O}_5$, forms brilliant needles, whilst the analogous *strontium* salt occurs in minute, colourless crystals. A well defined barium salt has not been obtained.

W. O. W.

Double Nitrate and Oxalate of Thorium. OTTORINO ANGELUCCI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 526—530. Compare Abstr., 1907, ii, 773).—In view of Ramsay's results on the disintegration of the copper ion into the lithium ion by the action of radium emanation and of the thorium ion into carbon by further resolution of thorium-C, the author has studied the properties of solutions of thorium nitrate in order to discover whether the carbon dioxide evolved from these solutions is due to disintegration of thorium-C, or to oxidation or to the decomposition of organic acids used in the isolation of the thorium and not completely eliminated in the subsequent purification.

A concentrated solution of thorium nitrate, D 2.25—2.30, placed in a dilatometer, showed, after a fortnight, a considerable increase in volume, indicating that decomposition had taken place. After some months, the solution deposited acicular crystals having a composition corresponding with the formula $6\text{Th}(\text{NO}_3)_4, \text{Th}(\text{C}_2\text{O}_4)_2, 48\text{H}_2\text{O}$.

The conclusion is hence drawn that the carbon dioxide evolved from solutions of thorium nitrate is formed by decomposition of the oxalate present in the form of a readily soluble complex salt, and is not a result of the degradation of radiothorium or of radioactive phenomena.

T. H. P.

Hydrolytic Decomposition of Bismuth Bromide. RENE DUBRISAY (*Compt. rend.*, 1909, 149, 122—124).—Bismuth bromide

solution, free from uncombined bromine, was diluted with variable amounts of water, and, after removing the precipitate, the ratio of bismuth to bromine in the liquid phase was determined. Contrary to the case of bismuth chloride, the extent of the hydrolysis of bismuth bromide is not appreciably altered by temperatures varying from 15° to 95°.

The variation of bismuth with bromine in the liquid phase follows a regular curve, whence the conclusion is drawn that within the limits of dilution studied only a single oxybromide is produced. The ratio of water to bromine in dilute solutions leads to the same result.

R. J. C.

Velocity of Hydrolysis of an Inorganic Salt, Potassium Ruthenium Chloride. S. C. LIND and F. W. BLISS (*J. Amer. Chem. Soc.*, 1909, 31, 868—885).—The velocity of hydrolysis of inorganic salts has not been much studied, since, in most cases, the hydrolysis is instantaneous, and, in cases in which the rate is measurable, the difficulties of measurement and the many factors influencing the hydrolysis have rendered it impossible to obtain a satisfactory kinetic equation.

Potassium ruthenium chloride, K_2RuCl_5 , rapidly undergoes hydrolysis in aqueous solution, the rate of which can be determined by the increase in electrical conductivity due to the hydrochloric acid formed. The solution, which is originally red, gradually becomes black, and when completely hydrolysed has the appearance of a colloid. On addition of alkali hydroxide, ruthenium hydroxide, $Ru(OH)_3$, is immediately precipitated.

The equilibrium of the hydrolysed solution is not altered by dilution, change of temperature, or addition of acid, and hence the conclusion is drawn that the reaction is irreversible and does not reach a homogeneous equilibrium. The hydrolysed product, probably $Ru(OH)_2Cl$, has a positive catalytic influence on the rate, resulting in a period of constant velocity, extending over the first half of the course of the reaction, which has been used with slight corrections to obtain a velocity constant. The rate of the reaction in a solution of the salt in hydrochloric acid (0.1*N*—0.4*N*) is approximately proportional to the concentration of the acid. It is suggested that this is best explained on the supposition that the rate of hydrolysis is determined by the hydroxyl-ion concentration. In aqueous solutions the velocity is at a maximum at the beginning of the reaction, whilst in acid solutions a distinct period of induction is exhibited similar to that observed by Goodwin (*Abstr.*, 1897, ii, 16) in the case of ferric chloride, which is likewise attributed to autocatalysis.

The temperature-coefficients between 22° and 30° are as follows: for 0.005 molar solution, 3.27; for a 0.0025 solution, 2.96; for 0.00125, 2.63; and for 0.0025 molar in 0.01*N*-hydrochloric acid is 5.40. The rate is also increased by dilution; the coefficient of dilution from 0.005 to 0.00125 molar is 2.23 at 22°, 2.17 at 25°, and 1.80 at 30°. The coefficient in a solution in 0.01*N*-hydrochloric acid is 1.08 at 25°, or, in other words, dilution has practically no effect when the acid concentration remains constant. When, however, the concen-

trations of both salt and acid are diminished from 0.005 molar in 0.04*N*-hydrochloric acid to 0.00125 molar in 0.01*N*-hydrochloric acid, the dilution coefficient at 25° is 5.15. From these results, and the fact that the reaction is slower in the more concentrated solutions, the general conclusion is drawn that the accelerating influence of either increase in temperature or dilution has the greater effect on the slower reaction. The acceleration produced by doubling the dilution is about the same as that effected by an increase of 3° in temperature. Sunlight has no influence on the rate of the reaction. Both platinum and platinum-black electrodes have a positive catalytic influence on the rate of hydrolysis, amounting for the latter to 50% in the Ostwald form of cell.

E. G.

Mineralogical Chemistry.

Nature and Origin of Gases Forming Volcanic Fumaroles or Issuing from Craters of Ancient Volcanoes. ARMAND GAUTIER (*Compt. rend.*, 1909, 149, 84—91. Compare this vol., ii, 674).—The gases given off by lavas of Vesuvius three and eighteen months after the eruption of 1906 are, in general, those which are obtained by vacuum distillation at red heat of such igneous rocks as basalt or granite. Recent lavas, which are hottest, emit chlorides of sodium, potassium, ammonium, iron, copper, lead, and arsenic, excess of hydrogen chloride, water vapour, and various permanent gases. As the lava cools, the less volatile substances condense in fissures, until finally only gases and very volatile products are emitted. The three months old lavas of Vesuvius were at 300°, and the gases issuing contained 62·5 to 77% of water vapour, which apparently, as in many other instances, could not have originated in rain or the moisture of the soil. Hydrogen chloride, which is very abundant in fresh lava, had almost disappeared. It is suggested that it had been used up in reconvertng into chlorides the oxides and oxychlorides formed by the action of water at higher temperatures. Carbonyl sulphide, carbon monoxide, sulphur, and boron compounds had also almost entirely disappeared. The permanent gases from lava contain 12 to 17% of oxygen and rather more than four times as much nitrogen by volume. Argon and helium are present in notably greater ratio to the nitrogen than in air. It is remarkable that free hydrogen is found in admixture with oxygen issuing from the hot crater.

The hydrogen is supposed to originate in decomposition of water at great depths, whereas the oxygen is drawn in as air through fissures in the base of the volcano by the up-draught in the central shaft. Carbon dioxide, which was present to the extent of 34% after three months, but only 3% after eighteen months, certainly appears to come from the deep-seated reservoir of volcanic activity. The Solfatare of Naples gives water vapour and permanent gases, of which 96 to 97% is carbon

dioxide. The gases given off by the hot springs of Agnano also contain at least 96% of carbon dioxide, as well as methane, nitrogen, helium, argon, and neon.
R. J. C.

Methods for the Collection and Preservation of Gases from Fumaroles and Volcanic Springs or Soils. ARMAND GAUTIER (*Compt. rend.*, 1909, 149, 245—250).—Two simple arrangements of apparatus which the author has employed for the collection of volcanic gases are described. In the second arrangement, which is designed for use in the case of gases consisting almost entirely of carbon dioxide, the latter is to a large extent absorbed before the gas is placed in communication with the exhausted collecting tube. By this means the volume of gas which has to be preserved for analysis is enormously reduced.
H. M. D.

Manganese and Iron Minerals from the Crystalline Schists of Brosteni, Roumania. VASILE C. BUȚUREANU (*Ann. sci. Univ. Jassy*, 1909, 6, 7—23. Compare Abstr., 1908, ii, 955).—Further analyses of carbonates and of "brostenite" from other localities are given. The massive, reddish-grey carbonates give the formula $5\text{MnCO}_3, \text{FeCO}_3$ after deducting variable amounts of admixed rhodonite (MnSiO_3). The compact, grey carbonate from Rarău, which is of sedimentary origin, gives, however, the formula $2\text{FeCO}_3, \text{MnCO}_3$. The several analyses of "brostenite" lead to the formulæ

$\text{RO}, 2\text{MnO}_2, 2\text{H}_2\text{O}$,
 $\text{RO}, 3\text{MnO}_2, 2\text{H}_2\text{O}$, $\text{RO}, 3\text{MnO}_2, 3\text{H}_2\text{O}$, and $\text{RO}, 5\text{MnO}_2, \text{H}_2\text{O}$, where $\text{R} = \text{Mn}, \text{Fe}, \text{Ca}, \text{Mg}$. Except for the presence of water, these formulæ correspond with those of various manganites which have been prepared artificially.
L. J. S.

Hopeite. GIUSEPPE CESÀRO (*Bull. Acad. roy. Belg.*, 1909, 567—593).—The paper consists mainly of a criticism of a communication by Spencer (Abstr., 1908, ii, 397) on the same mineral.

For the index of refraction of hopeite the author obtains the value 1.6, and points out that Des Cloizeaux's value, 1.471, is that of the oil used. The mineral has the axial angle $83^\circ 13'$, and the birefringences $n_m - n_p$ 9.3, $n_g - n_m$ 2.2, and $n_g - n_p$ 11.5, whilst the respective constants obtained by Buttgenbach for the Broken Hill hopeite are $51^\circ 42'$, 9.7, 0.8, and 10.5.

The minerals from the two sources also have a different optical appearance in convergent polarised light.

Parahopeite forms anorthic crystals (optically positive) having D 3.31. Tarbuttite is orthorhombic ($a:b:c = 0.95832:1:1.32037$), optically negative, has an axial angle of 90° (approx.), index of refraction β 1.7, and D 4.12.
E. H.

Natural Ferrous Sulphate. JUAN CALAFAT Y LEÓN (*Anal. Fis. Quim.*, 1909, 7, 214—216).—In the neighbourhood of the station of Fuente Santa (Almeria) large masses of crystalline ferrous sulphate exist. The mineral is found in veins between slaty rocks, and is associated with alum and other substances, such as ferric oxide. The

neighbourhood is situated geologically at the transition from Triassic to Cambrian ; the Triassic rocks are limestones and dolomites, and the Cambrian rocks, ferruginous clays and slate. Gypsum, alum, and other sulphates also occur abundantly in the neighbourhood, the sulphates probably having been formed from prior existing carbonates.

W. A. D.

Alterations in the Oxygen in Sea-water Collected in the Dark. HANS WINTERSTEIN (*Biochem. Zeitsch.*, 1909, 19, 425—433).

—The gases of sea-water depend not only on physical conditions, but on the presence of living organisms, and the effect of those which specially contain chlorophyll. According to Pütter, water collected in the dark, for instance, from the depths of the ocean, shows on exposure to light an increase of oxygen at the expense of carbon dioxide. This was not confirmed in the present research. Any change which does occur in the light results in a loss of oxygen.

W. D. H.

Physiological Chemistry.

Blood Gases of Invertebrate Marine Animals. HANS WINTERSTEIN (*Biochem. Zeitsch.*, 1909, 19, 384—424).—The animals specially investigated were those which contain respiratory pigments in their blood, such as hæmoglobin, hæmocyanin, chlorocruorin, etc. The hæmocyanin-containing blood of *Octopus* contains 4.2 to 5% of oxygen, of *Maja* and *Palinurus* about 1%; the hæmoglobin-containing blood of *Glycera* from 2 to 3%, and of *Cardita* and *Pectunculus*, 1 to 2%; the hæmoerythrin-containing blood of *Sipunculus*, 2%. In invertebrates, when respiratory pigments are absent (*Patella*, *Pinna*, *Ascidia*, etc.), the amount of both oxygen and nitrogen depends on purely physical conditions. The differences between venous and arterial blood, except in the *Octopus*, are small. It is regarded as doubtful whether the function of the pigments is wholly or even chiefly respiratory. The amount of carbon dioxide in the blood is extraordinarily small; this probably depends on the low intensity of gaseous metabolism, and on the readiness with which carbon dioxide is excreted. Full analytical details are given. W. D. H.

The Rate of Digestion in Cold-blooded Vertebrates. OSCAR RIDDLE (*Amer. J. Physiol.*, 1909, 24, 447—458).—The experiments were performed with fish, frogs, and turtles, and the results indicate that within certain not very wide ranges of temperature, van't Hoff's rule applies to their digestive processes, the average of eight valid coefficients being 2.62. The range of temperature within which the speed of digestion is doubled with a rise of 10° differs in different classes of vertebrates, the range

being most restricted in amphibians. Temperatures, however, have an influence quite apart from this, for sometimes low, and sometimes high, temperatures inhibit or destroy ferment activity. W. D. H.

Action of Pancreatic Juice on Esters. L. MOREL and ÉMILE TERROINE (*Compt. rend.*, 1909, 149, 236—239. Compare this vol., ii, 497).—The action of the pancreatic juice on the esters of aliphatic mono- and di-basic acids has been examined, and it is found that the hydrolytic action is feeble except in the presence of biliary salts. In many cases hydrolysis proceeds in a manner different from that induced by chemical agents; thus, in the series of ethyl esters of saturated fatty acids the speed of hydrolysis increases until it reaches a maximum at ethyl butyrate. The same phenomenon is noticed in the alkyl acetates, the maximum occurring at the butyl term. The presence of an ethylenic linking, or a ketonic or hydroxyl group, diminishes the rate of hydrolysis. *iso*Butyric and methylmalonic esters are only slightly attacked. The author considers that his experiments do not support the theory of the specific action of diastases. W. O. W.

Diastatic Decomposition of α - and β -Methyl-*d*-glucosides. H. BIERRY (*Compt. rend.*, 1909, 149, 314—316).—The intestine of dogs contains a ferment, *α -glucosidase*, which decomposes α -methyl-*d*-glucoside. Aqueous macerations of the intestinal mucus have very slight action on β -methyl-*d*-glucoside. The pancreatic juice of dogs and horses is without action on either compound. The gastrointestinal juice of *Helix pomatia* attacks both the α - and the β -glucoside, but especially the latter.

The results, and those of other investigations, indicate that the field of action of diastases is very limited, and that each diastase attacks only derivatives of the same sugar, or even only α - or β -derivatives. N. H. J. M.

Variation of some Diastases during the Metamorphosis of a Caddis-fly, *Limnophilus flavicornis*. XAVIER ROQUES (*Compt. rend.*, 1909, 149, 319—321).—The digestive activity in the larva was found to be greatest during the period preceding the formation of the pupa; it diminishes considerably in the young pupæ. The invertine increases until the second half of the life of the pupa, and then remains unchanged. N. H. J. M.

Absorption of Fats Stained with Sudan III. LAFAYETTE B. MENDEL (*Amer. J. Physiol.*, 1909, 24, 493—496).—When fat stained with dyes insoluble in water, such as Sudan III, is administered to animals, the pigment readily passes into the lymph and blood stream. Since these pigments are soluble in free fatty acids as well as in neutral fats, their presence in the lymph cannot be taken as evidence either for or against the possibility of the digestion of the fat prior to absorption. The conclusions thus differ from those recently drawn by Whitehead (this vol., ii, 498) from similar experiments. W. D. H.

Cytolysis in *Paramœcium*. ROSALIND WULZEN (*Quart. J. exp. Physiol.*, 1909, 2, 293—301).—The same agents which cause cytolysis in the sea-urchin egg and in red-blood corpuscles produce also cytolysis in *Paramœcium*. As in the other cases, the formation of a membrane is a preliminary essential step in cytolysis. This membrane resists lipid solvents so greatly that it probably contains but little lipid.

W. D. H.

Lipoids. VI. SIGMUND FRÄNKEL (*Biochem. Zeitsch.*, 1909, 19, 254—285).—This research deals with methods of extraction from the brain. The following are the results with human brain; the dry residue amounts to 23%, and of this the following percentages occur in successive extracts:

Acetone extract (cholesterol).....	10.96
„ (unknown extractive and phosphatides)	9.64
Light petroleum extract.....	27.84
Benzene extract	13.53
Alcohol „	6.25
Ether „	0.91
Residue (protein, etc.)	31.63

In round numbers the dry material consists of two-thirds lipoids and one-third protein. About 48% of the lipoids are unsaturated compounds.

W. D. H.

The Interfibrillar Substance of the Dermis. E. H. B. VAN LIER (*Zeitsch. physiol. Chem.*, 1909, 61, 177—187).—The main constituent of the ground substance of the true skin is a mucoid of very similar nature to that found in other connective tissues, but contains more carbon and nitrogen. This conclusion is opposed to that of Reimer and Körner, who deny the mucoid character of this substance. The name coriin is suggested; among its decomposition products, Levene's glucothionic acid was found, but the exact chemical nature of this material is still unknown.

W. D. H.

Hydrolysis of Ox-muscle. THOMAS B. OSBORNE and D. BREESE JONES (*Amer. J. Physiol.*, 1909, 24, 437—446).—This is work similar to that previously carried out with other kinds of flesh, the various cleavage products being estimated and compared with those already found. The table shows considerable differences, among other points brought out being the increase in glycine, alanine, valine, leucine, and proline on passing from the lower to the higher forms of life.

W. D. H.

Neutrality of the Tissues and Tissue-fluids. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1909, 6, 313—320).—It is suggested that the proteins of the plasma and tissues play a part in maintaining their neutrality; and that the liberation of carbon dioxide from the blood in the lungs is accompanied by a transfer of sodium from the carbonic acid to the proteins of the plasma, the reaction proceeding in the

reverse direction in the tissues. The amount of sodium bound by protein is probably more than enough to bind the excess of carbon dioxide in venous over that in arterial blood. W. D. H.

Uricolysis. H. GIDEON WELLS and HARVEY J. CORPER (*J. Biol. Chem.*, 1909, 6, 321—336).—The tissues of the human body possess no uricolytic power, such as is found in other mammals; the same is true for human foetal tissues. The presence of urate deposits in the kidneys of new-born infants cannot therefore be due to the tardy appearance of the uricolytic enzyme. The deposition is probably due to the high proportion of uric acid in the urine of the new-born, and favoured by local kidney conditions. The placenta possesses no uricolytic activity, and the statement that allantoin occurs in the urine of pregnant women and new-born children is doubted. Uricolysis was found in the liver of the guinea-pig, and absent in the organs of the turtle, spleen, bone-marrow leucocytes, and serum of the dog. W. D. H.

Uricase in Animal Tissues. FR. BATTELLI and Mlle. LINA STERN (*Biochem. Zeitsch.*, 1909, 19, 219—253).—The destruction of uric acid by animal tissues is probably a complex process, and the name uricase is given to an enzyme which oxidises it to allantoin, according to the equation: $C_5H_4O_3N_4 + H_2O + O = C_4H_6O_3N_4 + CO_2$. In free oxygen the reaction is most energetic, especially at 50—55°. The enzyme is precipitated with the nucleo-protein. Its amount is estimated by the quantity of carbon dioxide produced. In many tissues, inhibiting substances delay its action, and these can in large measure be removed by alcohol. It is present in most mammalian organs, and is particularly abundant in the liver and kidney. It is, however, entirely absent in man, and also in the duck. W. D. H.

Relation of Ions to Contractile Processes. IV. RALPH S. LILLIE (*Amer. J. Physiol.*, 1909, 24, 459—492).—The present experiments deal with *Arenicola* larvæ. They lose contractility gradually in isotonic solutions of non-electrolytes (dextrose, sucrose), and more rapidly in solutions of magnesium salts. The effect resembles anæsthesia, and contractility is readily restored on return to seawater, or to various solutions of electrolytes. The action of various electrolytes and ions in this direction is described at length, and this is discussed in connexion with alterations in permeability of plasma membranes. W. D. H.

Allantoin in Normal Urine and its Metabolic Significance. WILHELM WIECHOWSKI (*Biochem. Zeitsch.*, 1909, 19, 368—383).—Although allantoin occurs in the urine of other mammals, it has never yet been identified with certainty in human urine, and the opinion has been held that in man uricolysis does not occur, or at any rate that the destruction of uric acid if it takes place pursues a different course in man from what it does in other mammals. It is now shown that allantoin is present in human urine, and is therefore

probably an intermediate stage in uric acid catabolism. Its amount, however, indicates that it is far less than in other mammals.

W. D. H.

Colloids in Urine. I. LICHTWITZ and OTTO ROSENBAACH (*Zeitsch. physiol. Chem.*, 1909, 61, 112—118).—Colloid substances occur in normal human urine and exert a protective influence on gold solution. They can be precipitated by dialysis, by shaking with benzene, or by alcohol. They are not affected by boiling, freezing, or drying, and consist of the protein-precipitating substances and the nitrogenous carbohydrate complex of Salkowski.

W. D. H.

Biological Importance of Lecithin. II. W. GLIKIN (*Biochem. Zeitsch.*, 1909, 19, 270—273. Compare Abstr., 1908, ii, 120).—In degenerative diseases of the central nervous system (dementia paralytica and tabes) the amount of lecithin in the bone-marrow is usually diminished and often altogether absent. The same is true for iron.

W. D. H.

Narcosis and Deficiency of Oxygen. I. G. MANSFELD (*Pflüger's Archiv*, 1909, 129, 69—81).—A discussion of the Meyer-Overton theory of narcosis and the part played by lipoids. Oxygen is much more soluble in fats and lipoids than in aqueous fluids, and the physiological importance of the latter is believed to be the conveyance of oxygen into the interior of the cells, and narcosis is due to interference with this function.

W. D. H.

The Degradation of Amino-acids in the Organism under Normal and Pathological Conditions. OTTO NEUBAUER (*Deut. Archiv. klin. Med.*, 1909, 95, 211—256).—Experiments were made by administering various possible intermediate products between phenylalanine and tyrosine, on the one hand, and homogentisic acid, on the other, to an alcaptonuric patient. The subject of the experiment was kept on a fixed diet, and determinations of the ratio of homogentisic acid to total nitrogen were made. The following substances caused no relative increase in the acid: *p*-hydroxyphenyl-lactic acid, tryptophan, *o*-hydroxyphenylpyruvic anhydride, *p*-hydroxy- β -phenylpropionic acid, *dl*- α -aminophenylacetic acid, acetanilide, *p*- and *m*-hydroxyphenylpyruvic acids, *p*-hydroxyphenyl-lactic acid, phenylethyl alcohol, and *o*-, *p*-, and *m*-hydroxyphenyl-lactic acid. The following substances, on the other hand, caused an increase in the homogentisic acid output: tyrosine, *p*-hydroxyphenylpyruvic acid, quinol-lactic acid, quinolpyruvic acid, homogentisic acid, and phenyl-lactic acid.

dl- α -Aminophenylacetic acid was administered to a dog, rabbit, and human being. The *l*-acid was excreted unchanged, whilst the *d*-acid underwent deamination, giving through phenylglyoxylic acid, by optically active reduction, *l*-mandelic acid. A small portion of both *d*- and *l*-acids was converted into benzoic acid, which was excreted in the conjugated form as hippurate.

From the experiments on normal and alcaptonuric individuals, both by the author and others, the following conclusions were drawn as to

the fate of amino-acids in the organism. The amino-acids undergo oxidative deamination, yielding keto-acids. The aliphatic keto-acids lose carbon dioxide, and yield fatty acids, which are subject to the known laws of destruction in the organisms. Of the aromatic keto-acids, tyrosine undergoes a corresponding change into a keto-acid, which is oxidised to the corresponding quinol, which later undergoes isomeric change, yielding quinolpyruvic acid; the latter by loss of carbon dioxide yields homogentisic acid, which in the normal individual undergoes further oxidation, yielding finally carbon dioxide and water, but which in the alcaptonuric individual is excreted without further change. Phenylalanine yields *p*-hydroxyphenylpyruvic acid, which is then oxidised as above. The method of tryptophan degradation in the organism is unknown. S. B. S.

Behaviour of Glucosphenetide and of Tetra-acetylglucosphenetide in the Animal Organism. ST. MOSTOWSKI (*Bull. Acad. Sci. Cracow*, 1909, 641—651).—Contrary to statements in the literature, glucosphenetide does not possess toxic properties. It does not affect the normal temperature of the body, and when administered in milk to dogs whose temperature has been increased by the subcutaneous injection of diphtheritic toxin, it does not produce any marked lowering, passes through the organism unchanged, and can be recovered from the urine.

Tetra-acetylglucosphenetide, $O \begin{array}{l} \text{CH} \cdot [\text{CH} \cdot \text{OAc}]_3 \cdot \text{CH}_2 \cdot \text{OAc} \\ \text{CH} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt} \end{array}$, m. p.

132°, prepared from tetra-acetyl- β -bromodextrose and phenetidine (2 mol.) in dry ether, crystallises in white needles. Its antipyretic action in dogs is slow and insignificant, and is probably due to phenetidine produced by partial hydrolysis in the intestines, for about two-fifths of the acetate is recovered from the faeces, scarcely a trace in the urine, and the ratio of free to combined SO_3 is very largely diminished, due probably to combination with the liberated phenetidine. C. S.

Physiological Action of *l*- and *d*-Suprarenine. IV. EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1909, 61, 119—123).—In mice the subcutaneous administration of *d*-suprarenine confers a considerable amount of immunity towards *l*-suprarenine. The similar power of the latter is not so easy to demonstrate, on account of the smallness of the lethal dose. Further experiments, using larger animals, are in progress. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Humus on the Development of Yeast and on Alcohol Fermentation. ADAM DZIERZBICKI (*Bull. Acad. Sci. Cracow.*, 1909, 651—660).—Soil humus has a very favourable effect

on the development of yeast and on alcoholic fermentation in solutions containing dextrose, asparagine, and mineral nutrients, especially when small amounts of yeast are employed for inoculation; with large amounts the favourable effect is less marked.

In absence of asparagine, fermentation becomes comparatively feeble, so that the action of humus cannot be attributed to its direct utilisation as food by the yeast, and is probably similar to its effect on the development of *Azotobacter* (Krzemieniewski, this vol., ii, 335).

N. H. J. M.

Paralysing Action of Acids on Alcoholic Fermentation.

M. ROSENBLATT and Mlle. M. ROZENBAND (*Compt. rend.*, 1909, 149, 309—312).—The smallest amounts of acids which (a) completely inhibited fermentation, and (b) the highest amounts without effect were, in gram-mol., as follows:

Acid.	a.	b.	Acid.	a.	b.
Dichloroacetic	M/100	M/2000	Lactic	2M	M/200
Benzoic	M/60	M/1000	isoButyric	3M	M/100
Salicylic	M/60	M/2000	Propionic	4M	M/200
Monochloroacetic	M/50	M/5000	Butyric	5M	M/200
Trichloroacetic	M/25	M/4000	Sulphuric	M/10	M/8000
Nitric	M/9	M/3000	Oxalic	M/10	M/1000
isoValeric	M/5	M/200	Malonic	5·6M	M/200
Hydrochloric	M/5	M/3000	Arsenic	2M	M/500
Formic	M/4	M/1000	Phosphoric	3M	M/2000
Benzenesulphonic	M/3	M/3000	Citric	3M	M/200
Acetic	M/2	M/100	Methylarsenic	3M	M/1000
Ethylsulphuric	2M	M/4000			

In the case of *p*-hydroxybenzoic, tartaric, boric, and arsenious acids there was appreciable fermentation in saturated solutions; the highest amounts without effect were M/60, M/200, M/4, and M/2000 respectively.

N. H. J. M.

Action of Ultra-violet Rays on Fermenting Cider. MAURAIN and WARCOLLIER (*Compt. rend.*, 1909, 149, 155—157).—The ultra-violet light from a quartz-tube mercury arc is absorbed by passing through 1 mm. of cider to such an extent that two to three minutes' exposure is required to blacken silver citrate paper instead of the few seconds when the cider is replaced by water. With cider diluted to 1 in 20, one minute's exposure is necessary.

A drop of cider 0·24 mm. thick exposed to the rays of the quartz light through 5 mm. of quartz lost its power of fermenting malt extract containing sugar and tartaric acid when the time of exposure exceeded three minutes. An exposure of two minutes or less was not sufficient to kill the yeast. A layer of cider 1 mm. thick whether exposed directly to the lamp at 4 cm. distance or through 5 mm. quartz could not be sterilised in fifteen minutes. Cider diluted to 1 in 20 and exposed in a layer 1·7 mm. thick was sterilised in one to two minutes. Whenever the layer of liquid was so thick that yeast escaped the action of the rays, it is supposed that the ultra-violet light was all absorbed by the first layers of liquid encountered.

R. J. C.

Action of Ultra-violet Rays on Acetic Fermentation in Wine. VICTOR HENRI and JOSEPH SCHNITZLER (*Compt. rend.*, 1909, 149, 312—314).—The ultra-violet rays above 3021 check the acetic fermentation in wine in presence of air.
N. H. J. M.

Chemical Effect of Quartz Mercury Lamp on Water. JULES COURMONT, TH. NOGIER, and A. ROCHAIX (*Compt. rend.*, 1909, 149, 160—161).—A powerful quartz mercury lamp immersed in clear water destroys ordinary microbes and the coli bacillus to a range of 30 cm. in one minute. After the lamp had been burnt for ten minutes in 1½ litres of water containing 5 c.c. of dissolved oxygen, no trace of ozone could be detected. There was in some waters a slight reduction in the oxidisable organic matters present. Ammonia and nitrites were scarcely affected, nitrates not at all. The bactericidal action of ultra-violet rays is therefore not traceable to chemical changes in the water.
R. J. C.

Toxicology of Chlorates. JUAN FAGES VIRGILI (*Anal. Fis. Quim.*, 1909, 7, 104—109*).—The methods for detecting and estimating small quantities of chlorates described in former papers (this vol., ii, 179, 432, 433) have been utilised in studying the rate of destruction of chlorates in presence of flesh undergoing putrefaction. For this purpose 0·5 gram of potassium chlorate was dissolved in 500 grams of water containing 250 grams of chopped meat, which was then allowed to putrefy. The temperatures varied between $-1\cdot8^{\circ}$ and $33\cdot8^{\circ}$. The quantity of chlorate present was found to be practically the same as in the beginning during the first ten days. On the tenth day it had fallen to 0·43 gram, on the thirty-first to 0·33 gram, on the forty-fifth to 0·15 gram, and on the sixty-fifth, chlorate could not be detected under the conditions, that is, less than 0·015 gram was present.
W. A. D.

Influence of Radium Radiations on Chlorophyllic and Respiratory Functions of Plants. ALEXANDRE HÉBERT and ANDRÉ KLING (*Compt. rend.*, 1909, 149, 230—232).—Radium radiations have no appreciable influence on the composition of the atmosphere in which plants are growing. Chlorophyll does not exercise its functions under the influence of the radiation when light is excluded. The cells, however, appear to undergo alteration, since respiration and assimilation are considerably diminished in the case of leaves which have been exposed to the radiation before being placed in daylight. The ratio between respired oxygen and carbon dioxide assimilated is not affected by preliminary exposure to radium.
W. O. W.

Retardation of Vegetal Assimilation during Cloudy Weather. ACHILLE MÜNTZ and H. GAUDECHON (*Compt. rend.*, 1909, 149, 190—191).—By determining the amount of oxygen liberated by the leaves of wheat during respiration, it has been found that the assimilation of carbon takes place about five times more rapidly when the sky is clear than when it is cloudy.
W. O. W.

* and *Ann. Chim. anal.*, 1909, 14, 289—294.

Elaboration of Phosphorus-containing Material and Saline Substances in the Leaves of Living Plants. GUSTAVE ANDRÉ (*Compt. rend.*, 1909, 149, 45—48. Compare this vol., ii, 693).—This communication contains the results of monthly analyses of the ash of chestnut leaves and of estimations of total mineral phosphates and of organic phosphorus between May and October. The conclusion is drawn that the soluble phosphates migrate towards the organs of reproduction during the period of fertilisation, and that the amount of lecithin in the leaves reaches a maximum during efflorescence. The amount of silica in the leaves is very small, and remains constant.

W. O. W.

Sodium as a Partial Substitute for Potassium. BURT L. HARTWELL and F. R. PEMBER (*21st Ann. Rep. Agric. Exper. Stat. Rhode Island*, July, 1907, to June, 1908, 243—285. Compare Abstr., 1908, ii, 423).—Experiments with millet and oats showed that the yield was increased by addition of sodium when the amount of potassium present was insufficient for the maximum growth. Rye was less benefited than wheat (*loc. cit.*) and barley by addition of sodium.

In cultures containing too high an amount of magnesium in relation to the calcium, there was a very marked reduction in transpiration and in root growth, whilst the weight of leaf and stem was less affected. Addition of calcium increased the development of roots. Sodium had less effect on root production.

The results indicate that, whilst the principal functions of potassium cannot be performed by any other element, there are other functions which, in some plants at least, may be performed by sodium.

N. H. J. M.

Soluble Carbohydrates and Hemicelluloses in the Seeds of *Cicer arietinum*. NICOLA CASTORO (*Gazzetta*, 1909, 39, i, 608—625).—From the seeds of *Cicer arietinum*, the author has isolated (1) sucrose; (2) lecithin; (3) dextrose or lævulose, or both; (4) a polysaccharide, to which he gives the name γ -galactan, which does not reduce Fehling's solution or form a phenylosazone, but, after hydrolysis by means of dilute mineral acid, strongly reduces Fehling's solution and yields phenyldextrosazone; the $[\alpha]_D^{18}$ of γ -galactan is $+134.2^\circ$, the value after hydrolysis being $[\alpha]_D^{17.6} + 52.56^\circ$; when oxidised by means of nitric acid (D 1.15) it gives 37.98% of mucic acid; with hydrochloric acid and resorcinol, it gives Seliwanoff's reaction. The hemicelluloses of the seeds comprise probably a paragalacto-araban and a levulan.

T. H. P.

Unsaponifiable Constituents of Parsley Oil. HERMANN MATTHES and W. HEINTZ (*Ber. Deut. pharm. Ges.*, 1909, 19, 325—328).—Vongerichten and Köhler (this vol., i, 454) have given an account of an investigation of the fatty acids obtained from a solid fat which was separated from the fixed oil of parsley seed. The unsaponifiable matter contained in this fat has now been examined, and the following substances isolated: (1) a saturated hydrocarbon, *petrosilane*, $C_{20}H_{42}$, m. p. 69° , which crystallises in lustrous, white leaflets, and closely

resembles the hydrocarbon obtained by Étard (Abstr., 1892, 746) from *Bryonia dioica*; (2) melissyl alcohol; (3) a substance, probably a mixture, which gave the phytosterol reaction, but crystallised in a form resembling that of sitosterol rather than that of phytosterol, and (4) a yellowish-brown liquid.

The fixed oil of parsley seed contains about 14% of unsaponifiable constituents.

E. G.

Analytical Chemistry.

Solvents for Use with the Munroe Crucible. OTIS D. SWETT (*J. Amer. Chem. Soc.*, 1909, 31, 928—932).—The author gives a list of those precipitates which may be advantageously collected in a Munroe crucible, and also a list of forty-five solvents useful for removing the various precipitates from the felt. The list includes neutral solvents, acids, alkalis, and a large number of saline solutions. L. DE K.

Estimation of a Dissolved Substance in Presence of Suspended Material. WARREN RUFUS SMITH (*J. Amer. Chem. Soc.*, 1909, 31, 935—937).—A definite volume of the clear supernatant liquid is withdrawn, and the amount of material contained is determined (m). The solution is then again made up to the original volume, and, when clear, the operation is repeated (n). The total amount of material (x) in the solution will then be represented by the equation $x = m^2/m - n$. L. DE K.

Estimation of Mineral Matters in Vegetable Substances. HENRI PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1909, 26, 1145—1148).—A reply to Vuafart (this vol., ii, 182). The author when estimating mineral constituents in such substances as beetroot, wheat, etc., finds that accurate results are obtained by the process of carbonisation and extracting the soluble salts with water. No advantage is obtained by the sulphuric acid combustion method. L. DE K.

Analysis of Combustible Gases. GEORGES DE VOLDERE and GUILLAUME DE SMET (*Bull. Acad. roy. Belg.*, 1909, 622—663. Compare Abstr., 1908, ii, 425).—From a mathematical consideration of the amount of oxygen required for the complete combustion of different gases and the total contraction produced by such combustion, the authors have formulated a series of rules, some of which have been previously discovered by experiment, indicating what mixtures of gases can be analysed by a single complete combustion. These mixtures include (1) a mixture of two known hydrocarbons of one series and one (known) of another; (2) three known hydrocarbons belonging to different series and a known nitrogenous gas (or two of the hydrocarbons may belong to the same series); (3) a mixture of (a) ammonia, hydrogen cyanide, and nitrogen, or (b) ammonia,

hydrogen cyanide, and nitrous oxide, or (c) ammonia, nitrous oxide, and nitrogen, or (d) hydrogen cyanide, nitrous oxide, and nitrogen, with a known hydrocarbon or oxyhydrocarbon (CH_2O , etc.) other than methane or acetylene with (a), ethylene with (b), hydrogen or oxygen with (c), hydrocarbon containing C_2 with (d); (4) a mixture of the four gases nitrogen, ammonia, hydrogen cyanide, and nitrous oxide; (5) a mixture of two known hydrocarbons or oxyhydrocarbons with a known nitrogenous gas; and (6) a mixture of a known hydrocarbon or oxyhydrocarbon with two known nitrogenous gases, except the two mixtures nitrogen, hydrogen cyanide, acetylene (or acetaldehyde) and nitrous oxide, hydrogen cyanide, ethylene (or methyl ether).

By a single complete combustion it is also possible to determine the respective volumes of a group of hydrocarbons and a known hydrocarbon, not belonging to the group, in a mixture containing no other gas.

By a single complete combustion, however, it is not possible (1) to analyse a mixture of hydrocarbons (with which are included hydrogen, oxygen, carbon monoxide, and dioxide) containing more than (a) two members of the same series (both known); (b) three members of different series (all known); (2) to determine (in a mixture of hydrocarbons) the volume of more than two known series; (3) to analyse a mixture of more than three known hydrocarbons or oxyhydrocarbons, alone or mixed; (4) to analyse a mixture of three known hydrocarbons of the same series with a known nitrogenous gas, or (5) to analyse a mixture of an oxyhydrocarbon with the corresponding hydrocarbon (C_2H_4 "corresponds" with Me_2O , since the latter is separable, thus: $\text{C}_2\text{H}_4, \text{H}_2\text{O}$).
E. H.

Estimation of Total Sulphur in Animal Charcoal. ETTORE SELVATICI (*Bull. Assoc. chim. Sucr. Dist.*, 1909, 26, 1164).—About 0.5 gram of the sample is fused as usual with potassium nitrate and sodium carbonate for about fifteen minutes. The mass is boiled with water, and the filtrate is evaporated with excess of hydrochloric acid to separate silica and to remove the nitric acid. The residue is dissolved in water, and to the filtrate is added magnesia mixture (prepared from the chloride) and ammonia, so as to precipitate any phosphoric acid.

The filtrate is then acidified with hydrochloric acid, and the sulphuric acid precipitated with barium chloride as usual.

L. DE K.

Determination of the Free Acid in Electrolytic Copper Baths. MAURICE DEBAISIEUX (*Bull. Soc. chim. Belg.*, 1909, 23, 310—314).—The method proposed by Sims (Abstr., 1907, ii, 574) for the volumetric estimation of sulphuric acid in the presence of copper sulphate suffers the disadvantage of being affected by the concentration of the latter. The author finds that the change from red to yellow of a sulphuric acid solution containing methyl-orange becomes in the presence of copper sulphate a change to bright green. It is shown by titrations of a $N/2$ -sulphuric acid solution with $N/2$ -sodium hydrogen carbonate solution that the change of the methyl-orange to

yellow in the absence of copper sulphate coincides with the change to green in the presence of this salt. The colour of the solution initially varies from rose to violet as the concentration of copper increases, and when this is considerable, the solution during neutralisation becomes colourless or blue before finally turning green. Accordingly, the amount of free sulphuric acid in a copper sulphate solution can be very accurately estimated by titration with sodium hydrogen carbonate solution, using methyl-orange as indicator.

Attempts to estimate the copper in the neutralised solution by titration with sodium hydroxide in the presence of phenolphthalein failed, owing to the precipitation, not of the hydroxide, but of a basic salt. This is corroborated by determination of the change of electrical conductivity of the solution, curves of which are given.

E. H.

Some Modifications of Kjeldahl's Nitrogen Estimation

JOHN SEBELIEN, A. BRYNILDSEN, and O. HAABYDASHOLM (*Chem. Zeit.*, 1909, 33, 785, 795—796).—The process has been devised for the estimation of nitrogen by Kjeldahl's process in laboratories where electricity, but not gas, is at disposal, and where it is necessary to conduct a large number of analyses simultaneously.

The heating of the substance with sulphuric acid is carried out by means of a specially constructed Heraeus electric furnace. The expulsion of the ammonia formed is carried out by adding excess of alkali and passing at once a current of purified air through the solution; the ammonia is then absorbed in standard acid as usual. The current of air may be kept up for a considerable time, and the "distillation" requires no special attention.

L. DE K.

A Sensitive Reagent for Ammonia. FRIEDRICH TRETZEL (*Pharm. Zeit.*, 1909, 54, 568).—The reagent is simply an improved Nessler solution. Five grams of mercuric chloride are dissolved in an Erlenmeyer flask in 80 c.c. of water at a gentle heat. Meanwhile, 30 grams of potassium hydroxide are dissolved in 60 c.c. of cold water and put aside. Ten grams of potassium iodide are now dissolved in a 300 c.c. Erlenmeyer flask in 10 c.c. of hot water, and the hot mercuric chloride solution is poured in with constant shaking until the liquid becomes just turbid; on no account should more mercury solution be added. The solution is now filtered, and the potassium hydroxide solution added. After diluting to 200 c.c., another 1 c.c. of the mercuric chloride is added, and the solution is allowed to settle.

L. DE K.

A Rapid Clinical Method for Determining the Ammonia Coefficient of Urines. RAYMOND F. BACON (*Philippine J. Sci.*, 1909, 4, 153—162).—The ammonia coefficient of a urine, that is, the percentage of the total nitrogen which is present as ammonia or ammonium salts, is of importance in clinical work. The author recommends a simple process for estimating the ratio $\text{NE}_3/\text{NH}_3 + \text{urea}$, as this ratio is a sufficiently close approximation to the true ammonia coefficient. The method is based on two reactions: (a) Millon's reagent,

whereby the urea is converted into carbon dioxide and nitrogen, whereas the ammonia is unaffected; (b) alkaline solution of hypobromite, when both ammonia and urea yield nitrogen. A special form of apparatus is described. The following formula, in which allowance is made for the fact that the reactions are not quantitative, serves for the calculation of the ammonia coefficient: $A = 100(H - M/2.05)/H$, where A is the coefficient, M = number of c.c. of gas from Millon's reagent, and H = number of c.c. of gas from the hypobromite.

The results are only approximate, for example, they vary 10%, but are sufficiently accurate for clinical work, and the determination can be carried out in a very short time. J. J. S.

Volumetric Estimation of Hydroxylamine. ARTHUR STÄHLER (*Ber.*, 1909, 42, 2695—2696).—An aqueous solution of hydroxylamine hydrochloride is reduced by a strongly acid solution of titanium trichloride or sesquisulphate until the solution has a persistent faint rose coloration. The ammonia is liberated, distilled, and titrated in the usual way. The method is applicable to such organic nitrogen compounds as yield volatile amines on reduction by tervalent titanium. C. S.

Estimation of Small Quantities of Nitrates. L. FARCY (*Bull. Soc. chim.*, 1909, [iv], 5, 775—779 *).—It has been shown previously that Grandval and Lajoux's method of estimating nitrates is inaccurate in the presence of halide salts (this vol., ii, 344, 615).

MacGowan (*Trans.*, 1891, 59, 530), making use of the reaction $\text{KNO}_3 + 4\text{HCl} = \text{NOCl} + \text{Cl}_2 + \text{KCl} + 2\text{H}_2\text{O}$, discovered by Koninck (*Abstr.*, 1891, 618) based a method of estimating nitrates on the determination of the iodine liberated from potassium iodide by the mixture of chlorine and nitrosyl chloride. On the other hand, Frerichs' method (*Abstr.*, 1903, ii, 328), based on the same reaction, consists in estimating the chlorine in the residue by titration with silver nitrate solution. Utz (*Abstr.*, 1905, ii, 283) and Drawe (*Abstr.*, 1906, ii, 490) find the latter method sufficiently accurate for ordinary purposes, but Müller (*Abstr.*, 1903, ii, 690) states that the results given are too high, and the author finds that the ratio of the nitrate found to that present is about 1.05. Both MacGowan's and Frerichs' methods, however, are more accurate than that of Grandval and Lajoux in the presence of chlorides. The presence of ammonium salts, however, by reacting thus: $\text{NOCl} + \text{NH}_4\text{Cl} = 2\text{HCl} + \text{N}_2 + \text{H}_2\text{O}$ with nitrosyl chloride, renders both of the former methods inaccurate, the first by loss of nitrosyl chloride, the second by loss of ammonium chlorides. In fact it is found experimentally that the loss of nitrosyl chloride in MacGowan's method, and that of ammonium chloride in Frerichs' method, correspond almost exactly with those deduced from the above equation.

The conclusions drawn are that MacGowan's and Frerichs' methods are useless in the presence of ammonium salts, although unaffected by chlorides, and that Grandval and Lajoux's method as modified by Perrier and Farcy is preferable in the presence of the former.

E. H.

* and *Ann. Chim. anal.*, 1909, 14, 338—342.

Estimation of Nitric Acid with "Nitron." CARL PAAL and AUGUST GANGHOFER (*Zeitsch. anal. Chem.*, 1909, 48, 545—555).—Experiments are adduced showing the influence of organic substances on the accuracy of the "nitron" process. Dextrin, even if present to the extent of 2%, does not interfere with the complete precipitation of "nitron nitrate" if only enough time is allowed. Peptone interferes to some extent, but its influence may be neutralised by adding a sufficiency of sulphuric acid. It may be removed from the solution by heating with addition of formaldehyde on the water-bath for several hours, and the results of the "nitron" precipitation are then quite satisfactory for practical purposes.

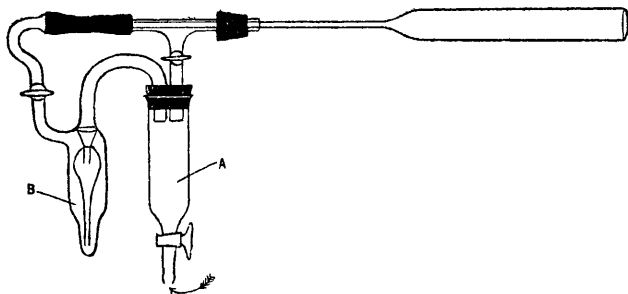
Gelatin, if present to the extent of less than 0.5%, does not interfere. It may be removed from the solution by means of tannin, the excess of which is then precipitated by means of normal lead acetate. The results are fairly accurate. A cold-water extract of meat may be analysed for nitrates after removing the interfering substances by adding normal lead acetate to the boiling solution; if alkaline, some acetic acid should be added. L. DE K.

Volatilisation of Phosphoric Acid and its Quantitative Separation from Phosphates of the Metals of the Ammonium Sulphide Group. PAUL JANNASCH and W. JILKE (*J. pr. Chem.*, 1909, [ii], 80, 113—127).—The separation and the estimation of the phosphorus in the phosphates of iron, chromium, uranium, zinc, nickel, cobalt, and manganese has been accomplished as follows. The phosphate, contained in a silica boat in a combustion tube, the forward end of which is loosely packed with glass-wool, is heated in a current of the vapour of carbon tetrachloride, first at a dull and finally at a bright red heat. The metal, in the form of the chloride, is retained by the glass-wool, whilst the phosphorus, probably in the form of phosphoryl chloride, is collected in a receiver, kept at 90°, and is estimated as magnesium pyrophosphate. It is advisable to mix the phosphate with powdered silica. For some undiscovered reason, the phosphorus in aluminium phosphate cannot be quantitatively separated by this method. C. S.

Estimation of Alkali Phosphates by Direct Titration. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1909, 26, 1162—1163).—Ten c.c. of the solution are mixed with two drops of 0.2% solution of helianthin and five drops of 1% phenolphthalein, and dilute sulphuric acid is added until a red coloration appears, which is then removed by cautious addition of dilute alkali solution. The liquid is now titrated with normal or decinormal alkali until a slight rose coloration is visible; 1 c.c. of *N*-alkali = 0.071 gram of phosphoric anhydride. The process applies to alkali phosphates only. L. DE K.

Improvements in the Apparatus for Elementary Analysis. MAX DENNSTEDT (*Chem. Zeit.*, 1909, 33, 769—770. Compare *Abstr.*, 1908, ii, 321, 984; this vol., ii, 270).—Several improvements in construction of the apparatus for elementary analysis are described, the chief

being that indicated in the accompanying sketch, which represents a more convenient and more compact arrangement for supplying a slow current of oxygen to the combustion tube. *A* contains calcium chloride and



B a small quantity of sulphuric acid, which serves to indicate the rate at which the oxygen is passing. Other minor improvements are suggested for which the original must be consulted. J. V. E.

Some Precipitation Reactions with *p*-Sulphobenzeneazodimethylaniline. M. EMMANUEL POZZI-ESCOT (*Bull. Soc. chim. Belg.*, 1909, 23, 299—303).—The micro-chemical reactions given by *p*-sulphobenzeneazodimethylaniline (helianthin) with a number of metals are described. Mercury gives a slight precipitate of slender needles. Gold is simply reduced. In the cold, copper gives an amorphous, yellow precipitate, which gradually becomes semi-crystalline, especially on warming. Palladium almost immediately gives an abundant precipitate of small, rod-like crystals. Lead gives an amorphous precipitate, which dissolves on warming, and, on cooling, crystallises in very small, hexagonal crystals. Tin readily gives an abundant precipitate of small, square crystals. Silver, especially on warming, forms a felted mass of prismatic crystals. Cadmium salts are precipitated immediately as lozenge-shaped crystals. Zirconium gives a thick, felted mass of slender, prismatic crystals, and also some orange-yellow prisms. The chromium precipitate is a mixture of needles and orange-yellow, prismatic tablets felted together. In the cold, thallium gives a crystalline precipitate of small, rod-like crystals, whilst when heated the product is a conglomeration of prismatic needles. The reaction with uranium is clear and characteristic, the precipitate crystallising readily in large, rectangular, yellow crystals. Cobalt, even in the presence of large quantities of nickel, forms long, violet, prismatic needles grouped in stars and surrounded by smaller needles. Nickel gives an amorphous, green precipitate, which redissolves on warming, and then crystallises in voluminous, yellow, nacreous crystals. Lanthanum is precipitated in amorphous, yellow flocks, soluble on heating, and then crystallising in slender needles. The reaction with manganese is very characteristic, the precipitate being composed of black needles and orange-yellow prisms. Iron and zinc give valueless reactions, small needles in the former, and an amorphous precipitate in the latter case. Erbium also gives an amorphous, yellow precipitate, which is gradually transformed

into sheaves of badly defined, prismatic crystals. The precipitate given by glucinum consists of small, highly refracting prisms. With cerium the reaction is very clear and characteristic, a mixture of long, black, prismatic needles and dichroic tablets being produced. Strontium forms large, indefinite, yellow needles. Calcium forms large, golden-yellow needles. Magnesium gives a yellow precipitate, transformed immediately into small, well defined needles, and, on heating, into voluminous, hexagonal tablets. The precipitate with aluminium consists of small, very abundant, violet-black prisms. Didymium gives an amorphous precipitate, becoming crystalline with difficulty on heating. Rubidium forms almost immediately a mass of small, lozenge-shaped crystals. Drawings are given of a number of the crystals described. E. H.

Estimation of the Alkalis in Drinking Waters. ERICH KOCH (*Zeitsch. angew. Chem.*, 1909, 22, 1442—1444).—A fully tabulated paper showing that in accurate analysis the indirect methods for the estimation of potassium and sodium in waters are not trustworthy, and that the platinic chloride process should be employed.

L. DE K.

Estimation of Alkalis in Silicates. G. STARCK (*Zeitsch. anal. Chem.*, 1909, 48, 415—428).—The silicate is treated according to the old Berzelius method with hydrofluoric and sulphuric acids, and the alkalis are finally weighed as sulphates. Assuming it to be all sodium sulphate, it is dissolved in water so as to yield an approximately $N/0.03$ solution, and hydrochloric acid is added so as to obtain a $N/0.15$ acidity. The solution is then boiled and precipitated with a calculated amount of barium chloride. When cold, the liquid is diluted to a definite bulk and filtered. An aliquot part of the filtrate is evaporated with excess of platinic chloride. The mass is slightly moistened with water, and left until apparently dry, when the sodium platinichloride, together with the small amount of barium chloride, is removed by means of 80% methyl alcohol. The potassium platinichloride is then collected in an asbestos filter tube, dried at 130° , and weighed. It is advisable to test it for any barium chloride it may still contain, although this is not likely to occur to any extent.

L. DE K.

Assay of Sodium Sulphide. M. TSCHILIKIN (*Zeitsch. anal. Chem.*, 1909, 48, 456—458).—Fifteen grams of the sample are dissolved in air-free water, and, after twelve hours, any iron sulphide is collected and the filtrate diluted to 1 litre; 10 c.c. of the solution are added to 50 c.c. of $N/10$ -iodine previously diluted with 200 c.c. of water, the liquid is then acidified with 10 c.c. of $N/10$ -sulphuric acid, and titrated with $N/10$ -thiosulphate; the result = sulphide + thiosulphate.

In order to estimate the thiosulphate alone, 10 c.c. of the solution are added to 5 grams of cadmium carbonate digested with 100 c.c. of water and 10 c.c. of $N/10$ -sulphuric acid. After fifteen minutes the solution is filtered, the insoluble matter washed, and the thiosulphate estimated by adding 25 c.c. of $N/10$ -iodine, 10 c.c. of $N/10$ -sulphuric acid, and then titrating with thiosulphate. As a check on the sulphide

estimation, 10 c.c. of the solution may be added to 10 c.c. of a copper sulphate solution (17.3195 grams of crystals in 500 c.c.). After acidifying with *N*/10-hydrochloric acid, the copper sulphide is collected and weighed as such. Thiosulphate is not precipitated. L. DE K.

Detection of Small Quantities of Sodium Carbonate in Waters. J. FLAMAND (*Bull. Soc. chim. Belg.*, 1909, 23, 296—299).—Dilute solutions of the chlorides and sulphates of calcium and magnesium when boiled with hops give a bright green coloration, whilst the carbonates of the same metals give a brownish-rose colour. The alkali carbonates and hydrogen carbonates under the same conditions give a red coloration. The production of the latter is prevented by the addition of gypsum when the amount added is sufficient to react with all the alkali carbonate present. To a solution containing 20 grams of gypsum and 14.71 grams of calcium carbonate per hectolitre, 10 grams of sodium carbonate must be added to give the coloration, whilst in a solution of 4.95 grams of gypsum, 21.42 grams of calcium carbonate, and 3.99 grams of magnesium carbonate per hectolitre, only 1 gram of sodium carbonate is necessary.

Relying on this reaction, quantities of sodium carbonate in natural waters can be detected, which would remain unnoticed in the ordinary methods of analysis.

Seyffert (*Zeitsch. ges. Brauwesen*, 1908) has devised a method of estimating alkali carbonates in water. The amount of combined carbon dioxide is estimated by evaporating the water to half its bulk with a known volume of *N*-sulphuric acid and titrating the excess with standard alkali. To the quantity of sulphuric acid theoretically necessary to transform the chlorides, silicates, and nitrates (previously estimated) into sulphates are added the quantity of sulphuric acid found originally in the water and that required to convert the carbonates into sulphates; from this sum is deducted the amount of sulphuric acid required to convert all the estimated bases present, and the remainder gives the weight of acid combined with alkalis (calculated as Na_2O). Knowing the amount of the latter present as chloride, that combined with carbon dioxide can be deduced, if sodium carbonate has been detected in the manner described. E. H.

Volumetric Estimation of Di-ammonium Hydrogen Phosphate. P. B. DALLIMORE (*Pharm. J.*, 1909, [iv], 29, 69—70).—To the solution is added a definite volume of *N*/10-sodium hydroxide, and the liquid is boiled in order to expel the ammonia. It is then titrated with *N*/10-sulphuric acid, using methyl-orange as indicator. The difference in alkalinity represents half the sodium hydroxide used in the conversion of the di-ammonium salt into the di-sodium compound. Addition of sodium chloride in the titration cannot be recommended.

Many commercial samples are not, however, pure di-ammonium hydrogen phosphate, being deficient in ammonia. L. DE K.

Microchemical Analysis. VI. Alkali Earths Group (Barium, Strontium, Calcium). NICOLAAS SCHOORL (*Zeitsch. anal. Chem.*, 1909, 48, 401—415. Compare this vol., ii, 521).—Barium may

be separated from strontium and calcium by means of potassium dichromate. The precipitate on strong ignition yields chromic and barium oxides, from which the latter can then be extracted with dilute acetic acid. From this solution the barium is precipitated with ammonium silicofluoride, and the precipitate, which has a characteristic appearance, is then examined microscopically.

The strontium and calcium are reprecipitated as carbonates by ammonium carbonate, redissolved in nitric acid, and evaporated to dryness. The nitrates are then treated with absolute alcohol, which leaves the strontium undissolved. This is then identified under the microscope after being converted either into chromate or iodate.

Calcium may be tested for even in the presence of barium and strontium by evaporating the acetic acid solution with excess of sulphuric acid. The mass is treated with a little water, which is then evaporated with addition of a little acetic acid. Characteristic crystals of calcium sulphate are thus obtained.

L. DE K.

Attempt to Separate the Alkaline Earths in the Electrolytic Way. JACOB S. GOLDBAUM and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1909, 31, 900—902).—The authors succeeded in estimating with a fair degree of accuracy the metals barium, strontium, and calcium in their mixtures by taking advantage of their different decomposition potential.

The principle of the rotating silver anode and mercury cathode was employed, and the decomposition cell and apparatus were arranged identically in the way described under the separation of alkali metals (*Abstr.*, 1908, ii, 1072). The halogen was also determined by re-weighing the anode.

L. DE K.

Separation of Calcium from Magnesium. WALTER C. BLASDALE (*J. Amer. Chem. Soc.*, 1909, 31, 917—922).—Calcium may be separated from an excess of magnesium by a single precipitation under the following conditions. The solution representing about 0.6 gram of the mixed carbonates and containing 3.5 grams of ammonium chloride is diluted to 300 c.c. and heated to boiling. One gram of oxalic acid is added, and, after five minutes, the liquid is neutralised with 1% ammonia. If very much magnesium is present, the oxalic acid is not added all at once, but at first a little, enough to combine with the calcium; after neutralising the liquid, the remainder is added and the solution again neutralised. After an hour, or not quite so long if there is very much magnesium, the calcium oxalate is collected as usual.

If, however, the magnesium exceeds the calcium by 10 to 1, no satisfactory result can be obtained by a single precipitation.

L. DE K.

Estimation of Clay in Limestone. ANDREA ARCHETTI (*Boll. Chim. Farm.*, 1909, 48, 409—411).—The ordinary method of estimating clay in limestone, if the latter is rich in magnesium carbonate, yields high results, owing to partial precipitation of the magnesium along with the aluminium. The following procedure avoids such error. Two grams of the powdered limestone are treated with 10%

hydrochloric acid, mixed with one-tenth of its volume of 10% nitric acid, and, when solution is complete, excess of ammonium chloride and slight excess of ammonium hydroxide are added. The precipitate is washed until the washings give no precipitate either with silver nitrate or with sodium phosphate. T. H. P.

Estimation of Lead in the Solder and Plating of Tins used for Tinned Foods. V. DELLA CROSE (*Ann. Chim. anal.*, 1909, 14, 245—248).—About 0.5 gram of the solder is oxidised with nitric acid, about 5 grams of clean sand are added, and the whole is evaporated to dryness. The lead nitrate is then extracted with water, and to the solution is added an excess of standard dichromate solution. In a portion of the filtrate the dichromate is then estimated as usual by means of ferrous sulphate. If the solder contains iron, it is best to dissolve it in boiling hydrochloric acid, and, after diluting largely with boiling water, to precipitate both lead and tin with hydrogen sulphide. The filtrate is examined for iron, the weight of which is then deducted from the solder taken. The mixed sulphides are then digested with ammonium sulphide, and the undissolved lead sulphide redissolved in hot dilute nitric acid. After neutralising the excess of acid with ammonia, the lead is estimated by means of dichromate as directed. Of plating, 1 gram is scraped off carefully, and then treated in the same manner. If, however, but little lead is present, this may be precipitated from the hydrochloric acid solution by neutralising the free acid and then adding 20 c.c. of dilute sulphuric acid (1 : 20). The lead sulphate is then collected with the usual precautions and weighed. The iron is estimated in the filtrate after removing the tin with hydrogen sulphide. L. DE K.

Volumetric Estimation of Lead and of Sulphuric Acid in their Salts. BERNARDO ODDO and ANTONIO BERETTA (*Gazzetta*, 1909, 39, i, 671—675).—In the titration of lead salts with potassium chromate or dichromate solution, the authors use *s*-diphenylcarbazide as indicator, a violet coloration being obtained with a solution, acidified with acetic or hydrochloric acid, containing 1 part of chromate per million. Sufficient ammonium acetate must be added to the lead solution to ensure the absence of free mineral acid. A short time after the chromate solution has been added, a small drop of the liquid and one of an acetic acid solution of *s*-diphenylcarbazide are placed on filter paper so that they intersect without the lead chromate precipitate coming into contact with the indicator.

For the estimation of $\text{SO}_4^{''}$ ions, the hot solution is precipitated by excess of standard lead nitrate solution, the liquid being then boiled with a few drops of hydrochloric acid and filtered. The excess of lead in the combined filtrate and washings is determined by titration with potassium chromate solution after removal of the free acid by means of ammonium acetate. T. H. P.

Rapid Electro-analysis. H. ALDERS and ARTHUR STÄHLER (*Ber.*, 1909, 42, 2685—2695).—The rapid electrolytic estimation of several metals in the form of liquid or solid amalgams is described. The

apparatus consists of a Jena flask, 75—100 c.c. capacity, with an injecting bottom, through which are sealed three short platinum wires resting externally on a sheet of copper. An annular ring of mercury just covering the platinum points serves as the cathode, whilst the anode is a flat coil of platinum-iridium wire, the straight axis of which, passing through a filter funnel resting on the neck of the flask, is attached to a stirrer making 400—600 revolutions per minute. With this apparatus and a current of 3—4 amperes at 5—6 volts, good estimations of the metal in copper, silver, and mercury salts are obtained in ten to fifteen minutes, but not with salts of lead, iron, or zinc, since the liquid amalgams suffer oxidation during the washing. Mercury has been estimated in the presence of an arsenate in dilute nitric acid solution, but the rapid estimation of lead in the presence of arsenic or of phosphoric acid cannot be accomplished in the form of a liquid amalgam. When, however, a known quantity of mercuric chloride solution is added to that of the lead salt, and the electrolysis is conducted in the presence of a little 33% phosphoric acid (to prevent the formation of peroxide at the cathode) and nitric acid, which are neutralised by sodium hydroxide towards the end of the analysis, the lead is quantitatively separated as a solid amalgam in fifteen to twenty minutes. In the same way, lead can be estimated in the presence of potassium arsenate if mercurous nitrate is used instead of mercuric chloride.

C. S.

Improved Process for the Iodometric Estimation of Copper. E. V. VIDEGRÉN (*Zeitsch. anal. Chem.*, 1909, 48, 539—545).—The deposit of metallic copper formed by treating the copper solution obtained in the usual way with aluminium is not redissolved in nitric acid, but dissolved in hydrochloric acid with addition of potassium chlorate. After adding dilute sulphuric acid, the solution is evaporated to expel the chlorine and most of the hydrochloric acid, and the residual liquid is then at once ready for the usual titration with potassium iodide and sodium thiosulphate. If, however, antimony or arsenic should be present, it is necessary to neutralise the mineral acids by addition of a sufficiency of sodium acetate.

Supposing about 0.5 gram of copper to be present, the liquid before titration should be diluted to about 20 c.c., and 8 c.c. of 50% potassium iodide solution should be added. If the thiosulphate contains 39.3 grams of the salt per litre, 1 c.c. = 0.01 gram of metallic copper. The solution should be standardised occasionally, starting from pure metallic copper.

L. DE K.

Cuprous Acetylide in Analysis. JOHANNES SCHEIBER (*Zeitsch. anal. Chem.*, 1908, 48, 529—538).—Copper is precipitated quantitatively by acetylene in presence of hydroxylamine in ammoniacal solution. If the precipitate is collected on a Gooch filter and washed first with water and then with alcohol and ether, it may be converted into cuprous carbide by heating for about two hours at 100° in a current of absolutely dry carbon dioxide.

As the precipitate is credited with explosive properties, it may be converted into sulphide by digesting with weak ammonium sulphide

(free from polysulphide) or with a boiling solution of sodium sulphide. The sulphide is then heated with a little sulphur in a current of hydrogen, and finally weighed as cuprous sulphide. The precipitate may also be heated with dilute sulphuric acid on the water-bath, and oxidised by means of permanganate. After adding excess of sulphurous acid, the solution is filtered and neutralised with ammonia; it is then slightly acidified with hydrochloric acid, and the copper precipitated by means of ammonium thiocyanate. The cuprous thiocyanate is dried at 120—130° and weighed as such. L. DE K.

Use of *s*-Diphenylcarbazine in Volumetric Analysis. **Estimation of Mercury in Mercurous Salts.** BERNARDO ODDO (*Gazzetta*, 1909, 39, i, 666—671. Compare Abstr., 1903, ii, 758).—With mercurous salts, *s*-diphenylcarbazine yields an intensely blue diphenylcarbazon, which is stable towards nitric acid. This coloration may be used as an indication in the volumetric estimation of mercurous salts. To a solution of mercurous nitrate, rendered almost neutral by means of sodium carbonate, *N*/10-sodium chloride solution is added from a burette until a drop of the supernatant liquid gives no coloration with *s*-diphenylcarbazine paper.

This method is also applicable to the estimation of mercurous mercury in presence of mercuric salts. In this case a known volume in excess of standard sodium chloride is added, and the precipitated mercurous chloride removed by filtration. The mercuric mercury is then precipitated as sulphide and the liquid filtered, and, after expulsion of the hydrogen sulphide by evaporation, titrated with a mercurous nitrate solution of known titre to determine the excess of sodium chloride employed. T. H. P.

Electrolytic Estimation of Nickel in Nickel Ores, Steel, Etc. C. S. TATLOCK (*Zeitsch. anal. Chem.*, 1909, 48, 433—437).—This process has the advantage that not a single filtration is required. 0.5 Gram of the ore is dissolved in nitro-hydrochloric acid, and the whole is evaporated to dryness. The mass is then dissolved in hydrochloric acid and diluted with hot water to about 200 c.c. When cold, bromine water is added and then a slight excess of ammonia; the precipitate is redissolved in hydrochloric acid, and the iron and manganese again precipitated with bromine water and ammonia.

When the precipitate has fully settled and does not adhere to the sides of the beaker, the liquid is ready for electrolysis. A current of 2—4 amperes is used, and the operation is continued until the platinum electrode no longer increases in weight. If the amount of nickel is very large, it may be advisable to dissolve the metal of the electrode and to continue the electrolysis until the separation is complete.

The deposit should afterwards be examined for cobalt. This is best separated by means of ammonium phosphate from ammoniacal solution (Clark's process), and finally weighed as pyrophosphate. L. DE K.

Separation of Nickel from Iron by means of Ammonia. V. HASSREIDTER (*Zeitsch. angew. Chem.*, 1909, 22, 1492).—The author states that nickel may be freed completely from ferric iron by a single

precipitation with ammonia. In seven experiments there were used, respectively, 1 gram of iron and 0.25 gram of nickel, 1 gram of iron and 0.5 gram of nickel, 1 gram of iron and 0.75 gram of nickel, 1 gram of iron and 1 gram of nickel, 0.25 gram of iron and 1 gram of nickel, 0.5 gram of iron and 1 gram of nickel, and 0.75 gram of iron and 1 gram of nickel.

In each case the solution, measuring 50 c.c., was mixed with 200 c.c. of ammonia, D 0.92, and the nickel was then determined electrolytically in an aliquot part of the filtrate.

The results showed that practically no nickel had co-precipitated with the iron.

L. DE K.

Indirect Volumetric Method for the Estimation of Chromium, Copper, Nickel, Cobalt, Zinc, and Lead. A. BACOVESCU and E. VLAHUTA (*Ber.*, 1909, 42, 2638—2642).—When solutions of chromium, copper, nickel, cobalt, zinc, or lead salts are treated with an excess of freshly precipitated manganous carbonate, $\text{MnCO}_3 \cdot \text{H}_2\text{O}$, or manganous hydroxide, the carbonate or hydroxide of the given metal is precipitated, and an equivalent quantity of manganous salt goes into solution. The precipitate can be removed and washed, and the manganous salt determined in the filtrate and washings by titration with potassium permanganate, using Volhard's method (*Abstr.*, 1880, 141). It is essential that the metallic salts used should be soluble and also normal, and not acid or basic salts. The small amount of oxidation of the manganous hydroxide does not interfere with the reaction.

The following practical method is recommended. One or two drops of nitric acid are added to a mixture of equal volumes of *N*-solutions of manganous sulphate and potassium hydroxide (or carbonate). After the precipitate has settled, the clear liquid is run off, the precipitate removed to a filter, thoroughly washed until free from sulphate, and then introduced into an Erlenmeyer flask by means of the wash-bottle. The solution of the salt (chromium, copper, etc.) is added, care being taken that an excess of the manganous hydroxide or carbonate is present, and the mixture boiled for a few minutes. The precipitate is removed and washed, and the manganese estimated in the combined filtrate and washings.

When manganous carbonate is used, the method lends itself to the estimation of copper, chromium, and lead only.

J. J. S.

Quantitative Volatilisation of Vanadic Acid from its Compounds by Heating in a Current of Carbon Tetrachloride Vapour. PAUL JANNASCH and HENRY F. HARWOOD (*J. pr. Chem.*, 1909, [ii], 80, 127—134).—An apparatus is used similar to that described for phosphoric acid (this vol., ii, 759), the receiver containing dilute nitric acid and the tubulated safety-trap water. Ammonium metavanadate is decomposed at a moderate red heat in a current of carbon tetrachloride vapour, the distillate in the receiver is evaporated to dryness, the residue is dissolved in dilute sulphuric acid, and the vanadium, obtained in the form of divanadyl sulphate by passing sulphur dioxide, is titrated with potassium permanganate after the

removal of the excess of sulphur dioxide in a current of carbon dioxide. The vanadium in sodium ortho-vanadate can be estimated in the same way, the salt being dehydrated previously at 150—200° in a current of carbon dioxide.

The analysis of vanadinite and endlichite is carried out in a similar manner; the lead remaining as lead chloride in the boat and combustion tube is estimated as sulphate, the distillate in the receiver is evaporated, and the solution of the residue in dilute sulphuric acid is freed from arsenic by hydrogen sulphide and treated as above for the estimation of the vanadium. The chlorine in the minerals is estimated separately.

	PbO.	PbCl ₂ .	V ₂ O ₅ .	As ₂ O ₅ .	Gangue.	Total %.
Vanadinite	66·58	10·23	17·34	5·67	0·54	100·36
Endlichite	69·31	10·57	20·23	0·56	—	100·63

The method is also very convenient for the complete analysis of carnotite, only the moisture and carbon dioxide requiring separate estimation.

The vanadium in sodium vanadate is removed completely, whilst the phosphorus in sodium phosphate is unaffected, when the salts are heated separately in a current of carbon tetrachloride vapour. When a mixture of the two salts is treated in a similar manner, the vanadium is not quantitatively removed. When, however, the mixed salts and four times the amount of sodium chloride are heated in the current of vapour at the highest temperature the combustion tube can withstand, both vanadium and phosphorus are completely removed. C. S.

Estimation of Chlorine in Presence of Palladium, and Estimation of Palladium by Reduction with Alcohol in Alkaline Solution. ALEXANDER GUTBIER and FERDINAND FALCO (*Zeitsch. anal. Chem.*, 1909, 48, 555—559).—A modification of Frenkel's method (Abstr., 1893, ii, 195). The palladochloride is dissolved in water, and pure aqueous sodium hydroxide is added until the precipitate formed has redissolved. Excess of alcohol is added, and, after covering the beaker with a watch-glass, it is placed in a boiling water-bath until the alcohol has evaporated. The addition of alcohol and its removal by evaporation are then repeated at least once, and after boiling the solution on an asbestos plate for some time, the slightly cooled liquid is poured through a filter and the precipitated palladium is washed with boiling water by decantation until every trace of alkali is removed, and then it is collected on the filter, dried, and ignited, first in the air, then in hydrogen, and finally in a current of oxygen-free carbon dioxide.

The filtrate and washings are evaporated to a small bulk, and, after acidifying with nitric acid, the chlorine is estimated gravimetrically in the usual manner as silver chloride. L. DE K.

Detection of Ethyl Alcohol in Chloroform. ARNALDO RUSCONI (*Arch. Farmacol. sper. Sci. affini*, 1909, 8).—The presence of as small a proportion of alcohol as 0·1% in chloroform may be detected as follows. To 10—15 c.c. of the chloroform in a thick-walled test-tube are added 1 c.c. of 10% potassium dichromate solution and 1 c.c. of

2*N*-sulphuric acid. The tube is closed by a perforated cork, through which passes a tube leading into 3 to 5 c.c. of water contained in a test-tube. About one-third of the chloroform is then distilled off by means of a water-bath, and to the distillate are added 2 to 3 drops of about 1% sodium nitroprusside solution and 1 to 2 drops of dimethylamine solution. A blue coloration is obtained if the original chloroform contains 0.1% or more of alcohol. If the chloroform is to be tested for acetaldehyde, it is distilled directly and tested without oxidising.

T. H. P.

Iodometric Estimation of the Oxygen in Quinols and in Chromic Acid. ANGELO CASOLARI (*Gazzetta*, 1909, 39, i, 589—594).—It has been shown by Valeur (*Abstr.*, 1900, ii, 57) that quinones derived from benzene may be estimated by treating them with potassium iodide in presence of hydrochloric acid and alcohol, the iodine liberated being then measured by titration with standard sodium thiosulphate solution. In presence of an alkali instead of an acid, this reaction may be constrained to proceed in the opposite sense, thus: $C_6H_4(OH)_2 + I_2 + 2KHCO_3 = C_6H_4O_2 + 2KI + 2H_2O + 2CO_2$, and may thus serve for the estimation of quinols. The estimation is carried out as follows. To a known volume of a 0.1*N*-solution of the quinol, diluted with 5 to 6 times its volume of water, are added a few c.c. of 0.1*N*-potassium hydrogen carbonate solution; 0.1*N*-iodine solution is then run from a burette into the liquid until the latter gives a persistent coloration with starch paste. Further, the amount of iodine in a solution may be estimated by adding a known volume in excess of standard quinol solution, and determining the excess of the latter by titration either with 0.1*N*-iodine solution or with the iodine solution under examination.

Chromic acid in solution may be estimated by acidifying with hydrochloric or sulphuric acid and treating with a known volume in excess of 0.1*N*-quinol, the excess of the latter being measured by adding potassium hydrogen carbonate and titrating with 0.1*N*-iodine solution.

T. H. P.

Reaction of Pyrogallol. OTTORINO CARLETTI (*Boll. Chim. Farm.*, 1909, 48, 441—442).—When treated with sulphuric acid and alcoholic tartaric acid in the manner described previously (compare this vol., ii, 528), pyrogallol yields a liquid which exhibits violet striæ and ultimately assumes a uniform, intense violet colour; this colour disappears on dilution of the solution with water. If lactic acid is used in place of the tartaric acid, the coloration obtained is orange-red, and does not disappear when the liquid is diluted.

Tartaric acid solutions are readily attacked by moulds, with formation of aldehydic compounds. Such altered solutions give colorations with various reagents without the heating necessary to obtain Möhler's reaction and its modifications. Thus such a solution gives with guaiacol a bluish-violet, and with phenol a distinct rose-red, coloration.

T. H. P.

Estimation of Acetone in Urine by means of Extraction. WILHELM VAUBEL (*Zeitsch. öffentl. Chem.*, 1909, 15, 241—243).—An

attempt to extract acetone from its solutions by means of chloroform previous to titration with iodine. Although dilute aqueous solutions to which sodium chloride has been added yield about 90% of the acetone present to the chloroform, the process fails with urines owing to the presence of urea, ammonia, and phosphates; sugar and albumin also interfere.

L. DE K.

Detection of Sugar in Urine. GÖSTA BOHMANSSON (*Biochem. Zeitsch.*, 1909, 19, 281—290).—By shaking urine with animal charcoal and hydrochloric acid, or alcohol, no sugar is absorbed, but other substances are, which give a false Almén's reaction, and among these is urochrome. Pflüger's conclusion that the copper test for sugar in urine is the only trustworthy one is therefore disputed.

W. D. H.

Esterification of Certain Fatty Acids on Evaporation of their Alcoholic Solutions. WILLIAM H. EMERSON and H. N. DUMAS (*J. Amer. Chem. Soc.*, 1909, 31, 949—951).—Experiments showing that a considerable esterification takes place on prolonged boiling of stearic and palmitic acids with alcohol. A slight esterification takes place even on merely evaporating the alcoholic solution of these acids. When titrating the free acids in alcoholic solution, tetrachlorophenolphthalein is recommended as being superior to phenolphthalein.

L. DE K.

Simple Fat Extraction Apparatus. L. T. BOWSER (*J. Amer. Chem. Soc.*, 1909, 31, 947—949).—A combination of Dubois' flask (*Abstr.*, 1908, ii, 641) and Hopkins' condensing arrangement (*J. Amer. Chem. Soc.*, 1898, 20, 965).

The mercury cup differs somewhat from that used by Dubois in the internal shape of the maple ring, and in that a flat cork is used instead of a rubber stopper. The flask containing the fat is well wiped and dried, and cooled for at least 30 minutes before weighing. The fat is then removed by repeated washing with ether, and, after drying and cooling, the flask is re-weighed.

L. DE K.

Estimation of Camphor in Official Spirit of Camphor. ERNST DEUSSEN (*Arch. Pharm.*, 1909, 247, 307—313).—The authorised tests of the % of camphor in spirit of camphor are not altogether satisfactory, and do not determine whether natural or synthetic camphor has been used. The author recommends the adoption of a polarimetric examination, and also the following method of estimation. Five grams of spirit of camphor, 20 grams of a cold saturated solution of ammonium sulphate, and 30 grams of ice in small pieces are shaken together until the ice is nearly melted. The precipitated camphor is collected, thoroughly washed with water at 0°, dried, and weighed; it is then oxidised by nitric acid, when *d*-camphoric acid, m. p. 187°, or *i*-camphoric acid, m. p. 204—205°, is obtained, according as the camphor is the natural or the synthetic product.

C. S.

Coniine, Conhydrine, ψ -Conhydrine, γ -Coniceine, and a New Isomeride of Coniine. WALTER J. DILLING (*Pharm. J.*, 1909, [iv], 29, 34—36, 70—72, 102—104).—A detailed account and critical examination of the chemical reactions of these alkaloids.

A new characteristic reaction for coniine is given. To the solution of the alkaloid or its salts is added a little sodium carbonate and a few drops of alcohol and carbon disulphide. The liquid is boiled, and, after adding excess of water and some drops of uranium nitrate solution, it is shaken with toluene. If coniine is present, the toluene turns red. The other related alkaloids do not give the reaction. The reaction may be confirmed by means of Nessler's reagent, which, in very dilute solutions, only precipitates the coniine.

The conhydrine and ψ -conhydrine are characterised by the crystalline appearances of the ethereal residues and of their sublimates.

L. DE K.

New Reaction to Distinguish between α - and β -Eucaines. Distinction from Cocaine and its Substitutes. UMBERTO SAPORETTI (*Boll. Chim. Farm.*, 1909, 48, 479—482).—With a solution of iodine in potassium iodide solution, both α - and β -eucaines give precipitates, the first a chestnut-yellow and the second a rust-coloured precipitate (compare Candussio, this vol., ii, 450); such slight difference between the colours of the two precipitates does not admit of a definite distinction between the two compounds being made in this way.

For this purpose, however, saturated aqueous bromine solution may be used. With a 1% solution of β -eucaine, this reagent gives an abundant yellow precipitate, which partly dissolves on heating, and, on boiling the solution, is replaced by a white precipitate containing the bromine. With α -eucaine, on the other hand, the yellow precipitate formed by bromine water dissolves completely on boiling the solution, and similar behaviour is shown by cocaine, novocaine, stovaine, alypine, and nirvanine; in the case of the last, the liquid, on boiling, turns almost red and emits a pleasant fruity odour.

The reactions of these various anæsthetics with mercurous chloride, potassium iodide, solution of iodine in potassium iodide, mercuric chloride, sodium hydroxide, and potassium permanganate are described and tabulated.

T. H. P.

A Reaction of the Methylenic Ether Group in the Aromatic Series. A. LABAT (*Bull. Soc. chim.*, 1909, [iv], 5, 745—746).—The reactions of guaiacol, catechol, and morphine with hydrastine, hydrastinine, and narcotine (this vol., ii, 710) are not given by berberine and narceine; but the gallic acid reaction is given by the latter two alkaloids, and also by heliotropine, piperine, apiole, safrrole, and *isosafrole*. In the case of the last four substances, however, very dilute solutions must be used to avoid masking the green by the intense red colour they produce with sulphuric acid alone. The author points out that the one common group in these substances is the ortho-methylenic ether group, and suggests that the reaction may be characteristic of this function.

E. H.

New Adulteration of Pyramidone. UMBERTO SAPORETTI (*Boll. Chim. Farm.*, 1909, 48, 367—370).—A sample of commercial pyramidone examined by the author was found to contain 50·8% of acetanilide. The latter may be approximately estimated by treating the sample with a known weight of benzene, drying the insoluble residue at 50°, and weighing; an allowance should be made for the amount of acetanilide dissolved by the benzene employed. T. H. P.

Estimation of Urinary Indican. T. IMABUCHI (*Zeitsch. physiol. Chem.*, 1909, 60, 502—519).—The copper sulphate method as recommended by Salkowski and others for the estimation of urinary indican is found to be more accurate than Obermayer's ferric chloride method. It gives higher results than Obermayer's reagent, but the overplus is not always constant. W. D. H.

Modification of Grimbert's Process for the Detection of Urobilin in Urines. BLANC and RAMEAU (*Ann. Chim. anal.*, 1909, 14, 217—219).—The authors recommend Grimbert's process (*Abstr.*, 1904, ii, 460), but find that the quantity used for the test (30 c.c.) should vary according to the amount of urine passed during twenty-four hours, the normal amount being taken as 1500 c.c.

The quantity taken for the test in c.c. should be $30 \times \text{vol. passed}$ in twenty-four hours /1500; 20 c.c. of Denigès' reagent are added, and, after ten minutes, the liquid is filtered and treated according to Grimbert's directions. L. DE K.

Preservation of Urine [for Analysis] by Thymol and Refrigeration. F. W. GILL and HARRY S. GRINDLEY (*J. Amer. Chem. Soc.*, 1909, 31, 695—710).—Winchester quart bottles are rinsed with a 10% alcoholic solution of thymol, drained, and dried, with the result that a thin layer of thymol covers the entire inner surface of the bottle. From 0·2 to 0·3 gram of powdered thymol is also placed in the bottle, into which the human urine is discharged directly. The bottles are kept in refrigerators at 5° to 18°. The chlorine, phosphorus, total sulphur, inorganic sulphur, total nitrogen, and urea nitrogen in normal urines, thus preserved for thirty-two days, can be estimated as accurately and as satisfactorily as in fresh urine, and the same is true for the uric acid content after sixteen days' preservation. The quantitative change in the creatinine content is insignificant, but the results of the experiments are not conclusive as to the influence of the preservation on the organic sulphur, the total acidity, and the ammonia-nitrogen determinations. C. S.

Animal Fæces. II. Estimation of Fatty Matter in Animal Fæces by Ether and Carbon Tetrachloride. A. D. EMMETT (*J. Amer. Chem. Soc.*, 1909, 31, 693—695. Compare this vol., ii, 528).—The promiscuous use of ether or carbon tetrachloride for the extraction of the fatty matter in animal fæces is not permissible, for experiments on swine-dung show that carbon tetrachloride extracts in twelve hours 17·9 to 33·8% more of the fatty matter than does dry ether in twenty-four hours. C. S.

General and Physical Chemistry.

Variation of the Magnetic Double Refraction of Aromatic Compounds with Temperature. Supercooled Substances and Substances in the Vitreous Condition. A. COTTON and HENRI MOUTON (*Compt. rend.*, 1909, 149, 340—342. Compare Abstr., 1907, ii, 727; 1908, ii, 2, 745).—The magnetic double refraction of nitrobenzene falls with rise of temperature from 128·6' at 6·4° to 90·9' at 53·9°. The rate of fall is nearly constant, but diminishes slightly as the temperature rises. In the case of salol the variation of the double refraction with the temperature between -17° and +50° can be represented by $\beta = \beta_0 (1 - 0\cdot002t)$, in which β_0 is the value of the double refraction at 0°. The behaviour of the salol, which is in the supercooled condition below 41·5°, is therefore quite normal. Experiments with betol in the vitreous condition show also that this has a very considerable magnetic double refractive power. H. M. D.

Anomalous Dispersion by Metallic Vapours. P. V. BEVAN (*Phil. Mag.*, 1909, [vi], 18, 407—411).—There being no special property of sodium which would lead one to suppose that its vapour alone should give anomalous dispersion, the author has made experiments with lithium and potassium. The apparatus was similar to that used by Wood for sodium, and each of the above metals exhibited the phenomenon in question.

In the case of lithium, a considerably higher temperature is required than for sodium. The anomalous dispersion takes place in the region of the red lithium line, λ 6705, and there is no trace of anomalous dispersion in the region of the other lithium lines in the visible spectrum. It cannot yet be decided whether anomalous dispersion takes place near the other lines of the primary series for lithium, as is the case with sodium and potassium, since these lines are in the ultra-violet.

The temperature required for potassium is not as high as in the case of sodium. The chief region of anomalous dispersion is about the first pair of the primary series (λ 7699, 7665); it also appears at the pair of lines λ 4047, 4044, which are the second pair of the primary series.

In all experiments the gas present in the tube was hydrogen, and the effect showed very clearly both at a low pressure and at a pressure somewhat greater than one atmosphere.

In the case of potassium the dispersion spectrum is unsymmetrical about the mean position of the two red lines, one of the lines being more intense than the other in the emission spectrum. The same phenomenon occurs in the case of sodium, and the same seems to be true of the dispersion due to lithium, indicating that the lithium line is a double line with one component stronger than the other.

T. S. P.

Constitution of the Spectral Lines of the Elements. I. L. JANICKI (*Ann. Physik*, 1909, [iv], 29, 833—868).—The spectra were produced by means of an electric arc formed between a Wehnelt cathode and an anode of the metal under examination, and an echelon spectroscope of high resolving power was used in the determination of the structure of the lines. The elements examined were aluminium, magnesium, silver, zinc, tin, cadmium, cobalt, copper, lead, manganese, calcium, chromium, thallium, and mercury. The detailed measurements are compared with previous observations relating to the structure of the spectral lines. H. M. D.

Influence of the Medium on the Lines of Spark Spectra. HEINRICH FINGER (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1909, 7, 329—356; *Ber. Deut. physikal. Ges.*, 1909, 11, 369—376).—The spectra of the spark discharge under water between poles of various metals have been photographed and compared with the spectra obtained when the spark discharge took place in air. The following metals were used: silver, aluminium, calcium, cadmium, cobalt, chromium, copper, iron, mercury in the form of copper amalgam, magnesium, nickel, lead, platinum, tin, tantalum, thallium, and zinc.

The measurements were confined, in most cases, to that part of the spectrum lying between the wave-lengths 2000 and 4700. For each element, details are given of the effect of the water on the lines of the air spectrum, as to whether they are weakened, enhanced, reversed, suppressed, etc. In one case only, that of tantalum, does water have practically no effect. T. S. P.

Method of Producing an Intense Cadmium Spectrum, with a Proposal for the use of Mercury and Cadmium as Standards in Refractometry. T. MARTIN LOWRY (*Phil. Mag.*, 1909, [vi], 18, 320—327).—The essential properties for a standard source of light are: (1) that it should be of sufficient intensity to be used for all the various types of optical measurements, so that, for instance, refractive indices and optical and magnetic rotatory powers may be determined for the same wave-lengths; (2) that it should be strictly monochromatic and as far as possible free from satellites; and (3) that it should be produced with sufficient readiness to render it generally available. These requirements are only partly fulfilled by sodium light, which possesses the drawbacks inseparable from the use of a doublet, and fail completely in the case of the hydrogen spectrum.

It is suggested that mercury and cadmium should replace sodium and hydrogen. The enclosed mercury arc gives a very strong source of light, and of the six chief mercury lines, the green (5460·97) and violet (4358·58) have already proved to be of the utmost use in polarimetry. The green line can be read with a considerably smaller half-shadow angle, and gives readings about 15% larger than the sodium doublet; the violet line can be read with a half-shadow angle of only 6°, the readings only differing from one another by a hundredth of a degree.

For obtaining the cadmium spectrum, the author uses an arc burn-

ing between two rods rotating in opposite directions; the rods consist of an alloy of silver and cadmium. It is suggested that the three cadmium lines, 6438 (red), 5086 (green), 4800 (blue), should be used. The green line is even brighter than that of mercury, and can be read with a half-shadow angle of 3° or less.

Finally, it is suggested that the mercury line Hg 5461 should be used as chief standard in optical work of all kinds, and that dispersion should be measured from this line to Hg 4359. T. S. P.

Band Spectrum of Barium and the Structure of the Bands in the Compound Spectra of Barium Halogen Compounds. LUDWIG BÖRSCH (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1909, 7, 297—326).—Detailed measurements of the lines in the band spectrum of barium between $\lambda=5000$ and $\lambda=7200$ are recorded and the data compared with those of previous observers. The source of light in the author's experiments was a coal-gas oxygen flame, into which barium nitrite was introduced. An arrangement is described by means of which a highly luminous flame can be obtained by allowing the dry finely powdered salt to fall into the flame through a narrow funnel tube provided with an electrical tapper. The bands which are observed in these circumstances are attributed to molecules of the metal. Bands attributed to barium halogen compounds were obtained in experiments with barium halides. The formation of these bands was found to be facilitated by the addition of the corresponding ammonium salt, the effect of this being to diminish the dissociation of the barium compound. H. M. D.

Effect of Pressure on the Band Spectra of the Fluorides of the Metals of the Alkaline Earths. R. ROSSI (*Proc. Roy. Soc.*, 1909, 82, 4, 518—523).—The bands of the fluorides of the alkaline earth metals, which exhibit a marked Zeeman effect, have been investigated with the object of ascertaining whether they also show a large pressure-shift effect. The fluorides examined were placed in the positive carbon of an arc lamp contained in a pressure cylinder. The data show no obvious relationship between the magnitudes of the two effects, for whereas in the case of the calcium fluoride bands the displacements due to pressure are proportional to the magnetic separation, the greater Zeeman effect corresponds with the smaller pressure-shift in the case of the barium fluoride bands. H. M. D.

Absorption Spectra of Certain Salt Solutions. HARRY C. JONES and W. W. STRONG (*Physikal. Zeitsch.*, 1909, 10, 499—503).—A summary of observations previously recorded. H. M. D.

Absorption Spectra of Solutions of Neodymium. BORIS STAHL (*Le Radium*, 1909, 6, 215—219).—Owing to the uncertainty which still exists as to the elementary nature of neodymium and praseodymium, the author has investigated the absorption spectra of solutions of their salts.

Starting with a complete set of fractions of the nitrates which had been obtained in the separation of the neodymium from praseodymium,

the bismuth, magnesium, and greater part of the manganese present were first eliminated. The last traces of manganese were extremely difficult to remove; one or other of the two following methods was used, although neither was absolutely satisfactory. 1. The metals were precipitated as oxalates, and the precipitate dried and ignited. The resulting oxides were treated with a solution of potassium chlorate in concentrated nitric acid. The praseodymium and neodymium dissolved as nitrates, the manganese remaining as peroxide. 2. The solution of the nitrates was evaporated to dryness on the water-bath, and the residue heated for two hours at $260-280^{\circ}$. The nitrate of manganese forms the peroxide under these conditions, whilst the nitrates of neodymium and praseodymium are unaltered.

After treatment in either of the above ways, the amount of manganese remaining was extremely small, and did not interfere with the measurement of the absorption spectra.

In order to obtain the solutions for spectroscopic examination, the oxides were prepared by calcination of the oxalates, and then either the nitrate or the chloride prepared from the oxide. The solution of the nitrates was unsatisfactory for the purposes of the investigation, since the absorption spectra of the neutral solution was altered considerably by the addition of free nitric acid. The chlorides gave the same spectra, however, both in neutral and hydrochloric acid solution.

A 10% solution of neodymium chloride, 1 cm. thick, shows 20 bands ranging from λ 742 to λ 347; as the solution is diluted, a number of these bands split up into their components, while concentration of the solution causes a number of the bands to coalesce. Taking into account these facts, the complete absorption spectrum of neodymium is found to consist of 29 bands, ranging from λ 742 to λ 328.

The absorption spectrum of praseodymium contains only five bands, ranging between λ 597 and λ 444. Dilution has no effect on these bands, except to render them more feeble.

Examination of the fractions intermediate between neodymium and praseodymium showed that only the bands λ 482 and λ 444 are eliminated as the fractions become poorer in praseodymium. The bands λ 597 and λ 589 of praseodymium are close to the bands λ 579 and λ 572 of neodymium, and at certain concentrations they cannot be distinguished from each other. The band λ 469 is the same for both elements, and because of this it has been supposed that both praseodymium and neodymium contain another element which cannot be separated from them. The spectra of the intermediate fractions show, however, that at no point does this band become enhanced, and consequently it cannot be due to a third element. This shows the necessity, in all such investigations, of examining the intermediate fractions.

Both neodymium and praseodymium are to be considered as elementary substances.

T. S. P.

Absorption Spectrum of *p*-Xylene in the Ultraviolet.
WILHELM MIES (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1909, 7, 357—368).—Former investigators (Abstr., 1906, ii, 410; 1908, ii, 243) having made reference to the regular band spectrum

of *p*-xylene in the ultraviolet, the author has investigated the absorption in the ultraviolet of *p*-xylene vapour and also of solutions of *p*-xylene in alcohol. The source of light was the spark discharge between aluminium electrodes immersed in water.

The absorption spectrum of *p*-xylene vapour was measured under atmospheric pressure at 3°, 15°, 30°, 40°, 70°, and 90°, with the following results. In no case is there an alteration in the selective absorption. Neither temperature, nor thickness of the absorbing layer, nor pressure have any influence on the heads of the bands. There is no evidence of broadening of the bands. With a constant thickness of the absorbing layer, rise in temperature appears to increase the intensity of the heads of the bands of the longest waves.

The general absorption increases with the temperature and with the thickness of the absorbing layer. It is most marked towards the red end of the spectrum, and gradually decreases in the direction of shorter wave-lengths, until at $\lambda = 2389$ it becomes zero.

The spectrum is a very pronounced band spectrum, in which the individual bands are not resolved. All the bands have their edges towards the violet, and become diffuse towards the red. The spectrum is a very regular one, and tables are given in which the regularities existing between the bands of the various series are brought out.

The concentrations of the alcoholic solutions of *p*-xylene of which the absorption was measured were 50%, 20%, 10%, $\frac{1}{2}\%$, and $\frac{1}{50}\%$. As the concentration increases, there is a marked displacement of the absorption towards the red. This displacement is not connected with a broadening of the bands.

The liquid spectrum is displaced 10–14 Ångström units towards the red with respect to the vapour spectrum.

T. S. P.

Behaviour of the Phosphorescent Sulphides of the Alkaline Earths at Various Temperatures, and Particularly at very low Temperatures. PHILIPP LENARD, H. KAMERLINGH ONNES, and W. E. PAULI (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 157–174. Compare also Abstr., 1905, ii, 565; this vol., ii, 283; ii, 630).—Previous investigations have shown that the phosphorescence bands of “phosphors” (phosphorescent sulphides) become narrower and sharper as the temperature is lowered, the lowest temperature used being -180° . The experiments have now been extended to a temperature of -259° , using liquid and solid hydrogen. The phosphors used contained (1) calcium, copper, and lithium; (2) calcium, sodium, and manganese; (3) calcium, nickel, and fluorine; (4) calcium, sodium, and bismuth; (5) strontium, zinc, and fluorine; (6) strontium, sodium, and manganese; (7) strontium, sodium, and bismuth; (8) barium, copper, and lithium; and (9) barium, bismuth, and potassium. Phosphorescent zinc sulphide, the double fluoride of uranyl and ammonium, and uranyl nitrate were also examined.

It is found that the sharpness of the bands continually increases as the temperature is lowered. To each band of the phosphorescent light there belong three phases, which succeed each other in the following order as the temperature falls: (1) the upper momentary phase, or heat phase; (2) the permanent phase; (3) the lower momentary cr

cold phase. The temperature of solid hydrogen (-259°) is low enough to bring all bands of the phosphors of the alkaline earths into the lower momentary phase. When a phosphor is warmed after excitation by light, those bands appear in succession the temperature ranges of whose permanent phase succeed each other on the scale of temperatures.

The response to ultra-red at these low temperatures is very marked. As a general rule, the actual lighting up is far more striking than the subsequent extinction.

The excitation-distribution corresponding with the various phosphorescence bands is independent of the temperature.

Other experiments deal with the momentary and permanent parts of the spectral excitation, with the non-resolution of bands in amorphous substances, and with the upper temperature limits to the excitation of phosphorescence by light and on the glow of phosphors when heated in flames, or when crushed at high temperatures. T. S. P.

Decomposition of Carbon Dioxide by Ultraviolet Rays. H. HERCHEFINKEL (*Compt. rend.*, 1909, 149, 395—396).—Thiele has shown that exposure to ultraviolet light brings about combination of carbon monoxide with oxygen (Abstr., 1908, ii, 79); the present author finds that the action is reversible, considerable quantities of carbon monoxide being formed when dry carbon dioxide is exposed in quartz vessels, in the presence of mercury, to the action of the light. The author confirms Cameron and Ramsay's observation that this decomposition is also effected by radium emanation (Trans., 1908, 93, 981).

W. O. W.

Sterilisation by Ultraviolet Rays. Application to Butter. DORNIC and DAIRE (*Compt. rend.*, 1909, 149, 354—356).—Experiments on the sterilisation of the water employed for washing butter from pasteurised cream by means of ultraviolet rays showed that the number of colonies per c.c. was reduced to a tenth or less. Butter which had been washed with the partly sterilised water remained fresh for two to three weeks longer than butter washed with ordinary water.

The direct sterilisation of butter by ultraviolet rays is probably impossible, owing to its opacity, and the butter acquires an unpleasant odour and taste, due to the ozone produced by the lamps.

N. H. J. M.

Ionisation of Gases by Light. JOHANNES STARK (*Physikal. Zeitsch.*, 1909, 10, 614—623).—From the standpoint of the theory previously put forward (Abstr., 1908, ii, 545, 574, 746, 911, 1007), the author discusses the conditions which are necessary for photo-ionisation, and also the methods which can be used to detect such ionisation. It is shown that the absorption of light in bands of long wave-length will not cause ionisation of the absorbent atom or molecule, whereas ionisation will take place in bands of short wave-length if the radiation is sufficiently concentrated.

Three methods are discussed by means of which ionisation by light may be detected, namely: 1. From photoelectric experiments. 2. By conductivity measurements. 3. From experiments with canal rays.

The second method, which can only be used when the increase in conductivity of a gas due to illumination is large compared with the ordinary conductivity, is discussed in detail, and it is shown that photo-ionisation may be detected as follows: The gas is submitted to a potential which is less than the ionisation potential, and the current flowing is measured while the gas pressure is diminished from a high to a low value; at the same time the gas is illuminated by light belonging to the region of its bands of short wave-length. If the current strength is a maximum at some particular gas pressure, again diminishing after the maximum has been reached, photo-ionisation has been produced.

Experiments were carried out on the vapours of anthracene, diphenylmethane, α -naphthylamine, and diphenylamine, which were contained in quartz vessels illuminated by the light from a mercury lamp, so that the light used varied between 185 and 380μ . The pressure of the vapour undergoing examination was varied by varying the temperature.

The vapours of these four substances show the following behaviour: At a potential of 2 volts between the electrodes, and high pressure, the current flowing is small; as the pressure falls, the current increases to a maximum, then falls to a minimum, and finally begins to increase once more. This is indicative of photo-ionisation.

For each substance the pressure (calculated to be 50 mm.) at which the ionisation was a maximum was kept constant for some time, and the potential submitted to cyclic variations from 0—12·6—0 volt in steps of 2·1 volts, the current being measured at the same time. At potentials greater than 2 volts, the current increases less rapidly than at lower potentials, but even at 10 volts there is no sign of saturation. This result is explained in the light of the author's theory of valence electrons.

The negative valence electrons, which are separated by the photo-ionisation, are supposed to come from the carbon atoms of the condensed benzene rings.

The vapours of benzene and naphthalene were not found to be suitable for the present investigation. T. S. P.

Radioactivity of Ordinary Matter. MAX LEVIN and RUDOLF RUER (*Physikal. Zeitsch.*, 1909, 10, 576—579).—With the object of ascertaining whether radioactivity is exhibited by other than the recognised active substances, the authors have examined compounds of nearly all the known elements. The photographic method was used in the investigation, the plates being exposed to the action of the various compounds for about six months. The results obtained indicate that potassium and rubidium are the only two elements which have an undoubted specific activity. In most other cases the observed photographic effect is shown to be probably due to radium or thorium products. This explanation could, however, not be given to the positive, although feeble, results obtained in the case of antimonite, niobite, and tantalite acids (compare following abstract). H. M. D.

Radioactivity of Rubidium Compounds. ERNST H. BÜCHNER (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 154—157).—Previous

investigations (compare Abstr., 1907, ii, 597; 1908, ii, 448; this vol., ii, 288) have shown that potassium salts are either radioactive or else contaminated with a radioactive substance. In the latter case the impurity is probably one of the alkali metals, since it has been shown that it is not one of the known active substances. As a first step in the elucidation of the matter, the author has investigated whether other alkali salts have the same property as the potassium compounds. Cæsium, lithium, and sodium have been proved inactive by other investigators (Abstr., 1907, ii, 217; 1908, ii, 750), and the author has consequently only investigated rubidium salts, and for the sake of comparison, potassium and sodium salts. The photographic method was used, the radiations from the salts having to pass through air only, or through aluminium foil 0.001 mm. thick. Using the anhydrous sulphates in each case, an effect was obtained with rubidium sulphate only, the exposures lasting from 81 to 117 days. In no case was there an effect with potassium sulphate, a result which does not agree with that of previous observers.

The same result was obtained when rubidium sulphate was used which had been prepared by evaporating a solution in the dark, showing that the effect was not due to previous exposure of the salt to the light (compare preceding abstract).
T. S. P.

Radium Content of Sea-Water. JOHN JOLY (*Phil. Mag.*, 1909, [vi], 18, 396—407).—The discrepancies between the author's and Eve's results (this vol., ii, 633) for the radium-content of sea-water are discussed, and a table is given summarising all the results obtained by the author. It is pointed out that in the determination of the radium content it is necessary to state the quantity of acid added to the sea-water under examination (compare Abstr., 1908, ii, 246). The effect of acidification is to increase the quantity of emanation liberated, but beyond a certain degree of acidification, small additions of acid seem ineffective in producing further change. In cases where much organic matter is present, the emanation may be retained to a considerable extent even after prolonged boiling.

The radium content varies from 2 billionths of a gram of radium per litre in the Mediterranean to 34 billionths of a gram on the coast round Ireland, and in discussing this distribution of the surface radioactivity of the ocean, the author comes to the conclusion that the carriage of radium-rich water from beneath upwards takes place. This surface radioactivity cannot be ascribed to the atmosphere, neither can it be due to the diffusion of emanation from the radium contained in the globigerina ooze.
T. S. P.

Expulsion of Radioactive Matter in the Transformations of Radium. SIDNEY RUSS and WALTER MAKOWER (*Physikal. Zeitsch.*, 1909, 10, 568).—Polemical against Hahn and Meitner (this vol., ii, 634).
H. M. D.

Atomic Weight of Radium from Spectroscopic Data. W. MARSHALL WATTS (*Phil. Mag.*, 1909, [vi], 18, 411—413).—Runge and Precht's rule, that the separations of homologous pairs of lines are pro-

portional to some power of the atomic weight, although nearly true in many families of allied elements, is not strictly true in any one case. The diagram, in which the logarithms of atomic weights are plotted as ordinates and logarithms of separations as abscissæ, shows that the lines joining the points in each family of elements are not exactly straight, and this vitiates the calculation of the atomic weight of radium by Runge and Precht (Abstr., 1903, ii, 346), who made use of the straight line: $\log(\text{at. wt.}) = 0.02005 + 0.5997 \log x$, where x is the separation.

The line of slight curvature which passes through Mg, Ca, Sr, and Ba is represented almost exactly by the formula:

$$\begin{aligned}\log(\text{at. wt.}) = & 1.886242 + 0.623179 (\log x - 2.813121) \\ & - 0.080391 (\log x - 2.813121)^2 \\ & - 0.0374175 (\log x - 2.813121)^4,\end{aligned}$$

and this gives 226.56 for the atomic weight of radium, which number is consistent with that obtained by chemical methods. It also gives the following atomic weights: Mg, 24.32; Ca, 40.08; Sr, 87.62; Ba, 137.41.

T. S. P.

The Diffusion of Radium Emanation. L. CHAUMONT (*Le Radium*, 1909, 6, 106).—The author has determined the coefficient of diffusion of radium emanation in dry air at 0° and 760 mm., which he finds to be 0.1015. From this the molecular weight is calculated to be 80.

F. M. G. M.

The Diffusion of Actinium and Thorium Emanations. S. RUSS (*Le Radium*, 1909, 6, 109).—Polemical against G. Bruhat (this vol., ii, 300).

F. M. G. M.

Ionisation by Chemical Means. LÉON BLOCH (*Compt. rend.*, 1909, 149, 278—279. Compare Reboul, this vol., ii, 718).—Certain unpublished observations of the author's appear to cast doubt on the results recently obtained by Reboul. The interaction of nitric oxide and oxygen, the dissociation of arsine in Marsh's apparatus, the production of sulphur trioxide by the contact process, the synthesis of hydrogen sulphide from its elements, and the phosphorescence of sulphur are all actions which appear to be unaccompanied by ionisation, whereas the phosphorescence of phosphorus is accompanied by ionisation. Moreover, according to several authors the formation of ammonium chloride fumes is not accompanied by ionisation. Further research will be necessary to test the theory that ionisation produced chemically originates in a splashing action at the interacting surfaces.

R. J. C.

Charge of Gaseous Ions. J. FRANCK and W. WESTPHAL (*Ber. deut. physikal. Ges.*, 1909, 276—280).—The fact that positive ions with a double electric charge are produced in gases by the action of Röntgen rays has led the authors to examine whether such ions are generated by other ionising agents. The results of diffusion measurements indicate that singly charged positive ions only are produced by α - and β -rays and by the discharge of electricity from points. For

γ -rays the same experimental observations were made, but the authors consider that the experimental errors in this case are too large to permit of the definite conclusion that no doubly charged ions are produced.

Amongst the ions generated in point discharge, slowly moving positive and negative ions can be differentiated by the diffusion experiments.

H. M. D.

Diffuse Reflection of the α -Particles. HANS GEIGER (*Proc. Roy. Soc.*, 1909, 82, A, 495—500; *Le Radium*, 1909, 6, 201—203).—It has been found that a small fraction of the α -particles which fall on a metal plate have their directions changed to such an extent that they emerge again at the side of incidence. For plates of gold, platinum, tin, silver, copper, iron, and aluminium, the diffuse reflection diminishes with the atomic weight of the metal, but more rapidly than this. The reflected fraction in the case of lead is less than would be expected according to this relationship.

Since the diffuse reflection is due to scattering, it follows that the number of particles reflected must vary with the thickness of the reflecting plate, and this was examined in the case of gold. The relationship between the two quantities is similar to that already obtained in the case of the reflection of β -particles. Compared with the thickness of gold which an α -particle can penetrate, the effect is confined to a relatively thin layer, about half the reflected particles coming from a layer equivalent to about 2 mm. of air.

From experiments with the α -particles from radium-C, it follows that of the incident particles about one in 8000 is reflected under the described conditions. This ratio is more or less independent of the angle of emergence. In the case of grazing incidence, however, the number of particles reflected at a very small angle to the reflector is largely in excess of the number corresponding with this ratio.

H. M. D.

Ionisation Produced by an α -Particle. HANS GEIGER (*Proc. Roy. Soc.*, 1909, 82, A, 486—495; *Le Radium*, 1909, 6, 196—200).—Radium-C was used as a source of homogeneous α -rays, and the ionisation due to the whole number of α -particles expelled from a known quantity of this substance was measured at low pressure in such a way that only a small definite portion of the range of each α -particle was effective. In a further experiment, the ratio of the ionisation produced within this small portion of the range to the ionisation produced along the whole path was determined. As the mean result of several measurements, it is found that the average number of ions produced in air by an α -particle from radium-C along its whole path is 2.37×10^5 .

On the assumption that all α -particles produce the same ionisation at the same velocity, the number of ions produced by the different α -particles from the radium family has been calculated. For radium, radium emanation, radium-A, and radium-F, the numbers of ions are respectively 1.53, 1.74, 1.87, and 1.62×10^5 .

H. M. D.

Primary and Secondary Gamma Rays. A. S. EVE (*Phil. Mag.*, 1909, [vi], 18, 275—291).—The author has examined the incident and emergent secondary radiations from a reversible pair of dissimilar metals traversed by the gamma rays (compare Bragg, *Abstr.*, 1908, ii, 556). A rectangular brass electroscope was used, both ends of which had been removed and covered with thin aluminium foil. When using the primary γ -rays, the radium bromide was placed sometimes entirely inside a closed hollow cylinder of iron or lead of the desired thickness, and sometimes in a cylinder with an open end, which was then screened by plates of suitable metal (iron or lead). Plates of various substances were then placed at the ends of the electroscope, two at either end, and the ionisation current observed when they were interchanged in the four possible arrangements. When using the secondary γ -rays a somewhat similar arrangement was devised, the electroscope and plates being well screened from the radium by much lead; the secondary radiator generally consisted of four bricks on end, or a tinned iron pail filled with iron filings. The plates used consisted of lead, silver, zinc, copper, iron, aluminium, and carbon.

Change of hardness of the γ -rays makes little difference in the relative intensities of the incident corpuscular secondary radiation from various elements, and the intensities follow the order of atomic weights of the radiators. On the other hand, there is a marked difference in the relative intensities of the emergent corpuscular secondary radiation; such radiations do not follow the order of atomic weights, the curve, plotted with atomic weights as abscissæ and intensities of secondary radiation as ordinates, roughly resembling a parabola with the vertex downwards.

Hardening of the γ -rays is readily produced by lead screens, but not by iron screens of great thickness. On hardening the γ -rays the emergent radiation from carbon and aluminium is increased relatively to heavier substances; on softening, decreased.

With various radiators, and with the secondary rays due to the primary γ -rays from radium-*C*, the values of λ and λ/d , and the emergent corpuscular secondary radiations, were observed. These all indicate the soft character of the secondary γ -rays.

The γ -rays from uranium-*X* caused emergent radiation of a character, showing that these rays are softer than those from radium-*C*, and harder than the secondary γ .

When the plates are interchanged, as mentioned above, the four readings obtained are nearly in proportion. T. S. P.

The Influence of Cathode Rays on the Activity of Metallic Uranium. J. OLIE, jun. (*Chem. Weekblad*, 1909, 6, 683—689. Compare this vol., ii, 10).—The author has repeated Jorissen and Ringer's experiments on the effect of cathode rays on the activity of metallic uranium, using an induction coil of 35 cm. spark. Contrary to their experience, he finds that the activity of the metal is not appreciably augmented by exposure to the rays. A. J. W.

Effect of Light on the Conductivity of Nitrogen Tetroxide Vapour. MARIO TENANI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 16—18).—The presence of nitrogen tetroxide facilitates the discharge

of an insulated, positively charged platinum disk, but impedes that of a negatively charged disk. The explanation of the latter observation is that the nitrogen tetroxide absorbs the light and prevents it from reaching the metallic disk, the conduction being effected only by the ions formed by the action of the absorbed light in the body of the gas.

T. H. P.

Electric Conductivity of Saline Flames. U. GOUTTEFANGEAS (*Ann. Chim. Phys.*, 1909, [viii], 17, 515—525).—Solutions of various salts were atomised by means of a spray, and the particles were carried forward by a stream of air, which was mixed with coal gas and burnt under a constant pressure. The current passing at constant voltage between two platinum electrodes at a fixed distance from the blue cone of the flame is a measure of the ionisation produced by the salt. The experimental error when all precautions are taken to ensure standard conditions of flame, voltage, etc., appears to be about 3%. The values obtained were corrected by subtracting the galvanometer reading when distilled water was employed instead of salt solution. Measurements were made with alkali and alkali earth chlorides, bromides, iodides, nitrates, sulphates, monohydrogen phosphates, formates, acetates, and benzoates in solutions of equimolecular strength. In general, salts of almost equal molecular weight produce almost equal conductivities, and the conductivity increases with increase of molecular weight. The author considers the acid group to have an effect which is small relative to the effect of the metal. The effect of potassium and sodium alone was approximately estimated by spraying their alkyl-oxides dissolved in alcohol into the gas, it being assumed that the ethoxy-group has no conductivity of its own. The acid group appears to account for less than 1/10 of the total conductivity.

Concentration of the solution employed leads to a corresponding increase in the conductivity imparted to the flame. The conductivity increases less rapidly than the concentration (compare Wilson, *Abstr.*, 1899, ii, 722), but more rapidly than the square root of the concentration (Arrhenius, 1891). The theory put forward by Arrhenius that

the salt is dissociated in the flame, thus: $MR + H_2O = \overset{+}{M} + \overset{-}{OH} + RH$, necessitates that all salts of the same metal should give the same conductivity, whereas the author claims that the acid group has a distinct, although small, influence. The salts of organic acids impart slightly lower conductivities to the flame than inorganic salts. It is suggested that, in addition to cathodic decomposition of the metal on the hot electrode, a certain amount of electrolytic dissociation occurs (compare Moreau, *Abstr.*, 1903, ii, 125).

R. J. C.

Electrochemical Behaviour of Nickel. A. SCHWEITZER (*Zeitsch. Elektrochem.*, 1909, 15, 602—610).—The potential of a cathode on which nickel is being deposited was determined in an atmosphere of hydrogen at various temperatures and current densities for normal solutions of nickel chloride and sulphate. The potentials were measured against the normal calomel electrode, the potential of which was taken as -0.283 volt. The potentials of a nickel anode were also measured in a similar way. The numerous results are given in tables

and curves which show that the cathode potential becomes more positive as the current density increases and as the temperature falls, and the anode potential more negative at higher current densities and lower temperatures. The equilibrium potential between nickel and solutions of its sulphate and chloride was also determined. The results are (at 16°): nickel powder, charged with hydrogen in *N*-sulphate, 0.33 volt; in *N*/10 sulphate, 0.35 volt. Pure nickel sheet in *N*-sulphate, 0.307 volt; in *N*/10 sulphate, 0.336 volt. Nickel powder in *N*-chloride, 0.31 volt; in *N*/10 chloride, 0.36 volt. The potential required to deposit nickel, even with the smallest current density, is considerably higher than this. Possibly a nickel-hydrogen alloy is formed which gives higher potentials; on the other hand, the potential corresponding with the change $\text{Ni} + 2F \rightarrow \text{Ni}^{++}$ cannot, apparently, be measured if traces of oxygen are present. The potential measured in an atmosphere of hydrogen is therefore apt to err on the high side, whereas that obtained without hydrogen is probably too low. It is therefore probable that the real value for nickel in a normal sulphate solution lies between 0.2 volt (Schoch, this vol., ii, 370) and 0.33 volt.

T. E.

Electric Forces at the Junction of Two Phases. FRITZ HABER and K. KLEMENSIEWICZ (*Zeitsch. physikal. Chem.*, 1909, **67**, 385—431).—The paper contains a theoretical and experimental examination of the differences of potential at the boundary of two electrolytically conducting phases containing the same substance or substances. Such differences of potential are probably important in connexion with the action of muscle. Muscle in action is negatively charged with reference to resting muscle, and, further, active muscle has an acid reaction. It is considered that the difference of potential between the two states of muscle is connected with this formation of acid; as the fluids of the body are mostly nearly neutral, the formation of traces of acid in one phase would produce a considerable difference of potential at the boundary of this phase with another. These differences of potential are doubtless also connected with surface-tension effects.

Expressions are obtained for the boundary differences of potential between phases containing water, one phase being an aqueous solution of an acid or alkali, the other an electrolytically conducting water phase; for example, ice or a liquid or solid solution of water. The formulæ obtained show that the *E.M.F.*'s in question vary with the acidity or alkalinity of the aqueous solution on either side of the neutral point, and their applicability has been proved by direct experiment, glass, benzene, toluene, and *m*-xylene being used as solvents for water.

For the measurements with glass, a tube of common Thuringian glass was blown out to a bulb at the end, the walls being 0.06 to 0.1 mm. thick; it was heated in steam for some time, and then kept in water until thoroughly soaked. It was then partly immersed in the acid or alkaline solution against which the difference of potential was to be measured, one electrode was placed in a conducting solution in the interior of the tube, the side-tube of a calomel electrode in the acid or alkaline solution, and the difference of potential measured in the

ordinary way with an electrometer. In general, the concentration of the aqueous solution was progressively altered from $N/10$ -acid to $N/10$ -alkali, or vice versa, and the gradual alteration of potential with reference to the glass-water layer measured. The curves obtained by plotting the observed $E.M.F.$ against the amount of alkali added to the originally acid solution, or vice versa, are double hyperbolas, one on either side of the neutral point. In the case of Thuringian glass, the total difference of potential was nearly 0.7 volt at 20° , and rather over 0.7 volt at 90° , in agreement with the theoretical value, but was less for Jena glass, and depended greatly on the treatment to which the glass was subjected.

In one series of measurements in which organic liquids were used as solvents for water, the aqueous solution (acid or alkaline) was placed in a quartz vessel, above this floated the organic liquid saturated with water, and the measurements were made by dipping the quartz side-tubes of normal electrodes into the lower and upper layers respectively. An $E.M.F.$ in the required direction was observed, but the results were considerably affected by experimental error. G. S.

Electrical Stimulation of Catalytic Pulsations. GEORG BREDIG and J. W. KEBB (*Verh. Naturhist. Med. Vereins Heidelberg*, 1909, 10, 23—29).—Nernst has recently shown (*Pflüger's Archiv*, 1908, 122, 275) that in physiological systems there is a quantitative relationship between the strength, i , of the alternating current required to produce a certain stimulus and the frequency, n , of the current, which may be represented by the equation $i/\sqrt{n}=k$, where k is a specific constant depending on the nature of the stimulus and the form of current used. It has already been shown that, when a fairly concentrated aqueous solution of hydrogen peroxide is poured on a clean surface of mercury, the system performs catalytic pulsations. These spontaneous pulsations can be stopped by addition of a trace of acid, but they commence again when the system is connected with an alternating current, and it is shown that, within the moderate range of frequency attainable with the available apparatus, the equation of Nernst holds for this case also. G. S.

Electromotive Force of Zinc Amalgams. ERNST COHEN and W. TOMBROCK (*Proc. K. Akad. Wetensch. Amsterdam.*, 1909, 12, 98—104).—If the Clark cell is to be used as a standard of electromotive force, it is necessary that the behaviour of zinc amalgams of varying concentrations should be investigated. The present communication gives an account of some measurements of electromotive force which have been made with this object in view.

In the first set of experiments the electromotive forces of combinations of a 10% amalgam with amalgams varying in concentration from 0.103% to 2.268%, and also with two rods of pure zinc which were two halves of the same rod, were measured. The electrolyte was an unsaturated solution of zinc sulphate, and the temperature, 0.5° . The results obtained with cells containing the zinc rod as one pole varied irregularly, showing that zinc in this form is unfit for potential measurements (compare Richards and Lewis, *Abstr.*, 1899, ii, 267).

The *E.M.F.* of the amalgam cells gradually decreases as the concentration of the one amalgam increases, being 0.0285 volt with the 0.103% amalgam, and becoming zero with amalgams varying in composition from 1.34—2.268%. In all cases where there is an *E.M.F.*, the 10% amalgam forms the negative (solution) pole.

In the second set of experiments the electromotive forces of combinations of a 10% amalgam and amalgams varying in concentration from 2.57—60% were measured, and also the effect of time on the electromotive force. With amalgams up to 38.82%, the final electromotive force is of the order of a tenth of a millivolt; with the 60% amalgam it is 0.0009 volt.

The results show that where a potential between zinc and zinc amalgams does exist, it is always of such a nature that the zinc forms the negative pole. No further discussion can be given until the freezing-point curve of zinc amalgams has been investigated.

T. S. P.

Electrolysis with Magnesium Cathodes. FR. SCHMIDT (*Chem. Zeit.*, 1909, 33, 911).—When a neutral solution of sodium chloride is electrolysed with a magnesium cathode, a thin film of magnesia forms on the surface of the cathode which entirely prevents the reduction of the hypochlorite which is formed at the anode. At high current densities the film breaks up, to some extent, exposing fresh surfaces of the metal, but with low current densities the consumption of magnesium is very small. Owing to the resistance of the magnesia film, a higher *E.M.F.* is required than with a platinum anode, but this can be compensated by using a lower current density. The concentration of hypochlorite which can be attained is no higher than it is with a platinum cathode; in both cases it is limited by the formation of chlorate.

In the electrolytic preparation of iodates or bromates, the loss by reduction at a platinum cathode is much larger than in the case of hypochlorite, and here the use of a magnesium cathode is of very marked advantage.

In the electrolytic oxidation of ammonia to alkali nitrite, the presence of iron (or other heavy metal) in the solution makes the artifice in question of no use, because the heavy metal is deposited on the surface of the magnesium.

T. E.

Absorption and Mobility of Didymium Ions. ADOLFO CAMPETI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 53—58).—According to Lenard's results (*Abstr.*, 1905, ii, 565), the ions of didymium in solution must be regarded as free, and not loaded with molecules of the solvent, since the characteristic vibrations observed with didymium glass, many solid didymium salts, etc., are also exhibited by solutions of didymium salts.

The author has determined the mobility of the didymium ion, both by conductivity measurements and by determination of the coefficient of transport.

Taking the mobility of the chlorine ion at 18° as 65.4, the conductivity measurements give the value 59.8 for the mobility of the

didymium cation, whilst the transport experiments give the numbers 68.9 and 56.3 for the mobilities at 18° of the chlorine and didymium ions respectively.

The conclusion is drawn that, in solutions of didymium salts, a small proportion of the didymium ions are in a state of absolute freedom, and hence capable of exhibiting their characteristic vibrations, whilst the greater number of the ions are united with molecules of the solvent, so that the mean mobility bears no relation to the absorption produced by the solution.

T. H. P.

Magnetic Properties of Carbon and Organic Compounds.

P. PASCAL (*Compt. rend.*, 1909, 149, 342—345. Compare this vol., ii, 487).—Sugar charcoal is diamagnetic, and its magnetic susceptibility is -5.2×10^{-7} when that of water is taken as -7.5×10^{-7} .

From the measurement of magnetic susceptibility of a number of organic compounds, it has been found that the values for isomeric substances of similar constitution are very nearly the same. The data indicate that the molecular magnetic susceptibility is approximately equal to the sum of the atomic susceptibilities. In open-chain compounds, double linkings diminish the diamagnetism; a measurable effect is, however, only produced by the two first double linkings. Aromatic compounds behave as if they contained tertiary carbon atoms, an observation which is in favour of Claus's formula.

The data for oxygen compounds require the assumption of different values for the susceptibility of oxygen according to its mode of combination.

H. M. D.

Effect of Mechanical Vibration on Carbon Dioxide Near the Critical Temperature. II. WALTER P. BRADLEY, ARTHUR W. BROWN, and C. F. HALE (*Physical Review*, 1908, 26, 470—482).—Further details are given of the production of fog in carbon dioxide under the conditions described in a previous paper (*Abstr.*, 1905, ii, 75). A distinction is drawn between dynamic fog, which clears up at once when the vibrations are interrupted, and the more persistent residual fog, which clears away in part by settling. The sensitiveness of the system to vibrations depends greatly on the width of the tube, which must be at least 5 mm. in internal diameter, and on the temperature. When the carbon dioxide is in thermal equilibrium, residual fog practically cannot be produced below 30°; the system is most sensitive at 31.1—31.2°, and above the latter temperature the sensitiveness diminishes rapidly. The critical temperature is 31.26°.

The effect of rising and falling temperature on the fog has been investigated. Minute changes of temperature were brought about by sudden slight alteration of the volume of the carbon dioxide, as well as by the slower method of changing the temperature of the bath. When the temperature is very near the critical and the gas is slightly compressed, new liquid is after a time formed, and this is at first not allied in sensitiveness to the liquid existing previously, but to what remains of the vapour phase. Under equilibrium conditions, fog tends to thicken towards the meniscus, and the phenomena may be used to define the boundary between phases when the meniscus is no longer visible.

G. S.

Liquid above the Critical Temperature. WALTER P. BRADLEY, ARTHUR W. BROWNE, and C. F. HALE (*Physical Review*, 1908, 27, 90—106).—When carbon dioxide is progressively compressed in a Cailletet apparatus just below the critical temperature, at a certain point liquid begins to run down the glass, forming “ripples,” which adhere to the wall until they reach the level of the meniscus, when they leave the wall and mix with the remainder of the liquid. The same phenomenon may, however, be observed above the critical point, even up to 38° , the ripples run down the glass for some distance, and then spread out as though they had reached a “liquid” and were mixing with it. An increase in the volume of this localised “liquid” results, above the critical temperature, in ripples or striæ, which flow upwards, without any tendency to adhere to the glass, until they reach the localised vapour. Below the critical temperature, these ripples are replaced by bubbles, rising to the meniscus. For these and other reasons, it is considered that liquid exists above the critical temperature.

The paper concludes with a discussion of the nature of the critical state. G. S.

Examination of the Laws of Radiation of the Bunsen Flame. HANS SCHMIDT (*Ann. Physik*, 1909, [iv], 29, 971—1028).—It has been found that the radiation of a Bunsen flame, investigated for the bands at 2.7μ and 4.4μ , is determined by the same quantitative laws which regulate the radiation of a black body. Although it is not possible to conclude from this that the radiation is a pure temperature effect, the author supposes that, although the origin of the radiation is a luminescence phenomenon, the intensity is determined by the temperature of the surrounding medium.

The mean temperature of the Bunsen flame, examined by the author at a height of 2.5 cm. above the mouth of the burner, was found to be 1670° . H. M. D.

The Specific Heats of Argon, Steam, Nitrogen, and Hydrogen at Very High Temperatures. MATHIAS PIER (*Zeitsch. Elektrochem.*, 1909, 15, 536—540).—Electrolytic gas, mixed with one of the other gases, was exploded in a spherical bomb of 35 litres content, and the pressure measured by means of a corrugated steel diaphragm fixed in the side of the bomb. The maximum movement of the centre of the diaphragm was about 0.8 mm.; this was transmitted by a lever to a silver mirror, from which a spot of light was reflected on to a rapidly moving photographic film. In this way the rise and subsequent fall of pressure due to the explosion and cooling of the gases is registered. The moving parts of the manometer weighed less than 1 gram, and the curves obtained showed a sharp maximum and were free from the waves due to the inertia of the manometer which previous observers have obtained. The mean molecular heats of the gases between 0° and t° found are :

Steam	$6.065 + 0.0005t + 0.2 \times 10^{-9} t^3$
Argon	2.977
Nitrogen	$4.900 + 0.00045t$
Hydrogen	$4.700 + 0.00045t$

These formulæ hold good for values of t lying between 1300° and 2500° . The close agreement between the value found for argon and the theoretical value is regarded as proving the accuracy of the results.

T. E.

Calorimetric and Cryoscopic Constants of Mercuric Bromide. JOSEPH GUINCHANT (*Compt. rend.*, 1909, 149, 479—481. Compare Abstr., 1907, ii, 667; Beckmann, *loc. cit.*, 739).—Mercuric bromide melts at 235° and has a latent heat of fusion (L) of 12.8 cal. The solid has specific heat 0.052, and the liquid, 0.068. Application of van't Hoff's formula, $K = 0.0198T^2/L$, gives the value 403 for the cryoscopic constant of mercuric bromide, where T is the absolute melting point. Experimental determinations of the cryoscopic constant with various solutes show a decrease in the value obtained as the concentration of the solutions increased. The author therefore calculates the limiting value of the cryoscopic constant for infinitely dilute solutions. The results obtained are: β -dibromonaphthalene 407, anthraquinone 380, mercurous bromide, Hg_2Br_2 , 378, antimony bromide, SbBr_3 , 350, ammonium bromide 345, potassium bromide 323, silver bromide 320, thallium bromide 283. Bromides of lead, lithium, sodium, and calcium are insoluble in fused mercuric bromide. Solutions of mercurous bromide in mercuric bromide are anomalous, for as the concentration of the solutions increases, the cryoscopic constant increases. This is due to the formation of a cryohydrate containing 4.69% of mercurous bromide and melting at 231° . The increase of K from 378 at infinite dilution to 431 in a solution of 3.533% strength corresponds with a compound of formula $\text{Hg}_2\text{Br}_2 \cdot 6\text{HgBr}_2$.

Since the experimental cryoscopic constant (mean 340) is markedly less than the theoretical (403), it is suggested that mercuric bromide, like benzene in some instances, does not completely separate the solute into single molecules.

R. J. C.

cycloHexane as a Cryoscopic Solvent: Behaviour of Piperidine. LUIGI MASCARELLI and A. CONSTANTINO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 104—111. Compare this vol., ii, 19).—In order to ascertain whether the abnormal depressions of the freezing point of cyclohexane are due to the formation of solid solutions, the authors have made further experiments on the behaviour of piperidine in this solvent.

It is found that the cryoscopic behaviour of piperidine in cyclohexane containing a small amount of p -dibromobenzene is similar to that exhibited in the pure solvent. Determinations were made of amounts of piperidine and p -dibromobenzene in the crystals separating from such solutions, the results indicating that solid solutions are formed between the cyclohexane and piperidine; the results were, however, not sufficiently accurate to admit of conclusions being drawn concerning the concentrations of these solid solutions or the coefficients of distribution of the piperidine between the solid and liquid phases.

The freezing-point curve of the system piperidine-cyclohexane consists of two branches meeting at a eutectic point at about -33° , at which the mixture contains 62.5% of piperidine.

The m. p. of piperidine is found to be -13° , the value usually given in text-books being -17° .
T. H. P.

Latent Heat of Fusion and Specific Heat of Propionic Acid. GUSTAVE MASSOL and A. FAUCON (*Compt. rend.*, 1909, 149, 345—348).—The acid which was used in the determination of the latent heat of fusion melted at -19.8° , and was kept for three hours at -20° before the experiment. The mean value obtained was 23.35 Cal., whereas the numbers calculated from the formulæ of van't Hoff and de Forcrand are respectively 26.7 and 30.36 Cal. The latent heat is supposed to vary with the time which has elapsed since solidification took place.

The specific heat of solid propionic acid between -46° and -19.8° was found to be 0.728, which is very much greater than that of the liquid (0.535).
H. M. D.

Modification of the Beckmann Apparatus by which Constant Readings are Obtained in Determining the Boiling Points of Aqueous Solutions. EDMUND KNECHT and J. P. BATEY (*Mem. Manchester Phil. Soc.*, 1909, 53, xix, 1—6).—Both Bigelow (*Abstr.*, 1900, ii, 9) and Beckmann (*Abstr.*, 1908, ii, 633, 1014) have stated that electric heating is not suitable for the ebullioscopic method for determining molecular weights in aqueous solution owing to the electrolysis which takes place. These investigators used a heating coil of 5 ohms resistance, the drop in potential across the coil being from $7\frac{1}{2}$ to 10 volts.

The authors find that the electrical method of heating is quite satisfactory, even with aqueous solutions, when a heating coil of low resistance is used. In their apparatus the resistance of the coil at 100° is 0.47 ohms, and the drop in potential across the coil in order to obtain a heating current of 6.5 amperes is only 3 volts. Experiments which were made on solutions of potassium chloride and iodide showed that the amount of electrolysis was negligible.

Measurements of the molecular elevations of the boiling point of several electrolytes and non-electrolytes gave results which agreed with those obtained by other observers by the usual method.

T. S. P.

Vapour Pressure of Ice. MAX THIESEN (*Ann. Physik*, 1909, [iv], 29, 1057—1062).—The data obtained by Scheel and Heuse (this vol., ii, 643) for the vapour pressure of ice can be satisfactorily represented by the formula: $\log p/p_0 = 9.632(1 - 0.00035t)t/T$, or by $\log p/p_0 = 8.891.t/252 + t$. In these equations, t and T represent temperatures measured respectively from 0° and absolute zero, and p_0 and p the vapour pressures of ice at 0° and t° .
H. M. D.

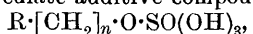
Isotherms of Monatomic Gases and their Binary Mixtures. III. Data Concerning Neon and Helium. H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 175—178).—By cooling with liquid hydrogen, neon was condensed in a tube connected with a manometer. The liquid hydrogen was then

removed, and the temperature of the experimental tube gradually allowed to rise, the pressure at which the meniscus disappeared being noted. In this way it was found that the triple-point pressure was 35 cm., and the critical pressure 29 atmospheres.

In a somewhat similar manner the critical pressure of helium was found to be 2.75 atmospheres. During these experiments the vapour pressure of the liquid helium was lowered to 2.2 mm., and a temperature reached which was estimated to lie below 2.5° abs.; this is the lowest temperature which has hitherto been attained. Even at this low pressure and temperature the helium remains a light mobile liquid. T. S. P.

Condition of Substances in Solution in Absolute Sulphuric Acid. III. and IV. GIUSEPPE ODDO and E. SCANDOLO (*Gazzetta*, 1909, 39, ii, 1—21, 44—47. Compare this vol., ii, 377).—The authors have investigated the cryoscopic behaviour of solutions of alcohols of various types dissolved in absolute sulphuric acid, special care being taken to avoid the presence of traces of sulphur trioxide in the acid employed.

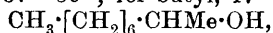
The normal primary alcohols, methyl, ethyl, propyl, butyl, heptyl, and octyl, exhibit uniform behaviour, the molecular weights in absolute sulphuric acid being 36—38% of the theoretical values. These results, and also those obtained from a qualitative study of the solutions, show that, when these alcohols dissolve in sulphuric acid, the reaction taking place is expressed solely by the equation: $\text{SO}_2(\text{OH})_2 + \text{R} \cdot [\text{CH}_2]_n \cdot \text{OH} = \text{OH} \cdot \text{SO}_2 \cdot \text{O} \cdot [\text{CH}_2]_n \cdot \text{R} + \text{H}_2\text{O}$, according to which the molecular weight of the alcohol in the solution should be 37% of the calculated value. Whether the above reaction takes place directly or by way of the intermediate additive compound,



cannot be determined from the cryoscopic data.

Primary alcohols with a side-chain behave dissimilarly. The molecular weight of *isobutyl* alcohol in absolute sulphuric acid is 42—44%, that of *active amyl* alcohol, 44—46%, and that of *isoamyl* alcohol 36—38% of the theoretical values. The influence of the side-chain hence depends on its complexity and on its position in the molecule. If it starts from the γ -carbon atom and is not complicated, the behaviour of the alcohol differs but little, if at all, from that of the normal primary alcohols. If, however, the branching takes place at the β -carbon atom, elimination of unsaturated hydrocarbon according to the equation $\text{SO}_3\text{H} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CHRR}' = \text{H}_2\text{SO}_4 + \text{CH}_2 \cdot \text{CRR}'$ soon commences, such elimination increasing in rapidity with the complexity of R and R'. Should these hydrocarbons remain in solution and not be ionised, they would not cause the molecular weight to change from 37% of the theoretical value; it is therefore supposed that they separate in small, transparent drops, possibly in a colloidal condition, the molecular weight increasing with the abundance of such separation.

The molecular weights of secondary alcohols in absolute sulphuric acid are for *isopropyl*, 37—39%; for *butyl*, 47—49%; for *octyl*,



42—44%, and for *menthol*, 35—37% of the theoretical values. Other

factors besides the secondary nature and the branching are here at work.

Of the three tertiary alcohols examined, trimethylcarbinol and dimethylethylcarbinol give molecular weights equal to 48—50% of the theoretical values in freezing absolute sulphuric acid. These high values are related to the prompt elimination of the unsaturated hydrocarbon, as is indicated by qualitative study of the solutions. Triphenylcarbinol, however, gives a molecular weight 25—27% of the calculated value. Like all alcohols, triphenylcarbinol in absolute sulphuric acid immediately gives rise to the corresponding ester, which, in this case, acts as a true salt, not of the oxonium, but of the triphenylcarbon type. The theoretical molecular weight under such conditions should be 27·27% of the calculated value.

In the fourth part of this paper, the authors give the results of a study of the nature of the oil separating from a solution of *isobutyl* alcohol in absolute sulphuric acid. Except for a small inseparable fraction, the oil is non-oxygenated, and consists entirely of hydrocarbons of the paraffin series, being very similar in its properties to American petroleum. The mechanism of the formation of these hydrocarbons is as follows. By elimination of water, the alcohol gives rise to the corresponding unsaturated hydrocarbon, which then forms various polymerides. In contact with sulphuric acid, the latter are partly oxidised and partly reduced to the saturated hydrocarbon, which separates, whilst the sulphuric acid is reduced to sulphurous acid and ultimately to sulphur.

Hantzsch's work (Abstr., 1908, ii, 14, 462; this vol., ii, 18) is criticised.
T. H. P.

Simplified Method and Apparatus for Determining the Calorific Power of Combustible Gases. PAUL LEMOULT (*Compt. rend.*, 1909, 149, 454—456).—The combustion of equal volumes of hydrogen and carbon monoxide, according to the equations: $\text{H}_2 + \text{O} = \text{H}_2\text{O} + 69 \text{ Cal.}$, $\text{CO} + \text{O} = \text{CO}_2 + 68\cdot2 \text{ Cal.}$, if carried out in presence of alkali, gives rise to the same contraction and requires the same volume of oxygen. As the heats of combustion of these two gases are practically equal to 68·6 Cal., for calorimetric purposes hydrogen and carbon monoxide may be considered together. If only hydrogen and carbon monoxide are present, taking a as the contraction on combustion and b as the volume of oxygen required relative to the original volume of gas, the calorific value per litre will be given by $P = 2\cdot049a$ or $P = 6\cdot147b$, subject to correction for temperature and pressure. If besides hydrogen and carbon monoxide other combustible gases are present, a will not be equal to $3b$. In the usual case where methane is present in quantity, taking its heat of combustion as 213·2 Cal., it easily follows that $P = (0\cdot914a + 3\cdot405b)$. When no methane is present, a is equal to $3b$, and this equation reduces to the one given above.

The author shows that the presence of ethylene, benzene, acetylene, etc., in the usual small proportions, introduces an error which cannot exceed 2%, that is, of the same order as the experimental error in most calorimeters. The estimation of calorific power by the author's method,

which requires as data only the volume of oxygen used and the contraction in volume on combustion in presence of alkali, can be carried out in a simple portable apparatus. By this means the calorific value of the town gas at Lille was found to be 497·8 and 500·7 Cal. per litre, whereas the Berthelot bomb calorimeter gave 503·2 Cal.

R. J. C.

Thermochemistry of Nitrous Acid. W. SVENTOSLAVSKY [in part, with S. TSCHEGOLEFF, SKRJISCHEVSKY, W. OSSMULSKY, and S. GERICH] (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 587—641).—The author has studied, by the methods previously employed (this vol., ii, 23, 213, 547), the heats of solution, neutralisation, and decomposition of nitrous acid and the action of nitrous acid on phenols, tertiary aromatic amines, secondary amines, primary aromatic amines, carbamide, and hydroxylamine. The results confirm many of the conclusions previously drawn (*loc. cit.*), such as the general law of the increase of the heat of formation of an atomic linking as the molecular weight of the compound increases. The following points are also brought out by the numbers obtained.

The thermochemical characters of the linkings of hydroxylamine and nitrous acid, and thermal investigation of the reaction of the former with quinones and of the latter with phenols, show that the heat of transformation of nitrosophenol into quinoneoxime is nil.

The complete analogy found to exist between nitrosophenols and tertiary aromatic nitrosoamines indicates that the nitroso-group functions in both classes of compounds, and weighs against the quinonoid formula for them.

T. H. P.

Heat of Formation of Cuprous and Cupric Sulphides. H. VON WARTENBERG (*Zeitsch. physikal. Chem.*, 1909, 67, 446—453).—According to Thomsen, cuprous sulphide combines with sulphur to form cupric sulphide without absorption or development of heat, but as this statement is in conflict with other observations, the heats of formation of the two sulphides have been determined by bringing about the combination of the dry elements in a modified form of calorimeter. The results are as follows: $2\text{Cu} + \text{S}_a = \text{Cu}_2\text{S}_{\text{cryst.}} + 19\cdot0 \text{ Cal.}$; $2\text{Cu} + 2\text{S}_a = 2\text{CuS}_{\text{cryst.}} + 23\cdot2 \text{ Cal.}$ (S_a = rhombic sulphur). Hence a little heat is given out when cupric sulphide is formed from cuprous sulphide and sulphur. Cupric sulphide can be formed by direct combination only within narrow limits of temperature; at lower temperatures the rate of formation is too small, and at higher temperatures its dissociation pressure exceeds one atmosphere.

G. S.

Density of Mixtures of Water and Ethyl Alcohol. F. SCHWERS (*Rec. trav. chim.*, 1909, 28, 261—266).—The densities of mixtures of water and ethyl alcohol at temperatures between 0° and 30° have been determined by Mendeléeff (*Ann. Phys. Chem.*, 1869, [ii], 138). The author has determined the densities of mixtures containing from 4·99% to 93·55% of alcohol at temperatures varying from 14·6° to 74·2° by the method previously employed for mixtures of glycol and glycerol with water (this vol., i, 80). The composition of the various

mixtures studied was determined by reference to Mendeléeff's results, after determining their density at a low temperature. The results are given in tabular form, and the variation of the contraction (on mixing) with the temperature is plotted in a series of curves. The observation of Kopp, that this contraction diminishes as the temperature increases for all mixtures containing more than 16.5% of alcohol, and increases with the temperature for mixtures containing less than 16.5%, whilst for the mixture containing 16.5% it is constant, is confirmed. In addition, the author observes that between 55° and 65° the contraction of all the mixtures, except that containing 16.5% of alcohol, ceases to vary for a certain small alteration in temperature, this phenomenon being exhibited by a slight flattening of the curves at this point. This point of inflexion is less marked than in mixtures of glycol and water, and still less than in the glycerol-water mixtures.

E. H.

Is there Contraction when Sucrose is Dissolved in Water?

R. OLIZY (*Bull. Assoc. chim. Sucr. Dist.*, 1909, 27, 60—69).—Sucrose and water are placed separately in a closed vessel, and the pressure of the air in the vessel carefully determined. When solution takes place, the pressure remains unaltered, showing that there is no change of volume when sucrose dissolves in water. The density of dissolved sucrose, calculated from the density of solutions, is 1.612 at 15°, in exact agreement with the value for solid sucrose given by Kopp. The relation between the density, d , and concentration of sugar solutions is accurately represented by the formula $100(d_4^{15} - 1) = 0.37965s$, where s is the number of grams of sucrose per 100 c.c. of the solution at 15°.

G. S.

Change of Density of Liquid Systems during Chemical Reactions. ALFRED BENRATH (*Zeitsch. physikal. Chem.*, 1909, 67, 501—511).—It is shown by experiments on the hydrolysis of sucrose and on the formation and decomposition of esters that the rate of some reactions can be followed by measuring the change of density, the latter being proportional to the change of concentration of the reacting substances. A reaction proceeds with expansion or contraction according as the number of dissolved molecules diminishes or increases. Increase of the external pressure, and the addition of indifferent substances which increase the internal pressure, accelerate reactions accompanied by contraction, and retard those attended by expansion.

G. S.

Adsorption of Gold by Charcoal from Aqueous Solutions of its Salts. S. BRUSSOW (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 137—138).—The different kinds of charcoal used were: (1) bone charcoal, either dried at 110° or undried; (2) wood charcoal, in the form of powder; (3) coke of the ordinary commercial variety; (4) retort carbon. The adsorption of the gold was observed either by shaking the charcoal with the solution of the gold salt, or by filtering the gold solution through the charcoal, or else by simply immersing the charcoal in the solution. The gold solutions varied in strength from 0.000045 to 0.002 gram AuCl_3 per 1 c.c. of solution.

In all cases the gold was completely withdrawn from the solution, the chlorine being left behind. Salts, such as sodium chloride, magnesium sulphate, magnesium chloride, calcium sulphate, and potassium hydrogen carbonate, did not affect the adsorption.

Solutions of the bromide and iodide of gold and of potassium aurous cyanide behaved similarly to the solution of gold chloride. T. S. P.

Some Colour Demonstrations of the Dissociating Action of Water. ROBERT L. TAYLOR (*Mem. Manchester Phil. Soc.*, 1909, 53, [xviii], 1—3).—A recapitulation of some of the applications of the dissociation theory to the explanation of the colour of various salts, for example, copper sulphate, ferric thiocyanate, and potassium permanganate, in aqueous solution. T. S. P.

Intervention of Osmotic Pressure in Dyeing. DANIEL A. ROSENSTIEHL (*Compt. rend.*, 1909, 149, 396—399).—The author advances reasons which lead him to suppose that the action of dyes is due to physical cohesion between the fabric and the colouring matter, and that intimate contact between the two is brought about through the intervention of osmotic pressure. W. O. W.

Osmotic Pressure of Complex Solutions. ALEXANDER A. JAKOWKIN (*Zeitsch. physikal. Chem.*, 1909, 67, 309—320. Compare Abstr., 1901, ii, 87).—As complex solution the comparatively simple case of one solute in a mixture of two solvents is considered. It is shown theoretically that the complex solvent is in osmotic equilibrium with the complex solution when the ratio of the "molecular roots" of the vapour pressures of the components of the solvent ($\sqrt[m]{p}$, where m is the molecular weight) is the same for the two phases.

To test the theory, the partial pressures of the two components in a mixture of the ether of ethyleneglycol and water (the complex solvent) and in solutions of glycerol (a non-volatile solute) in the complex solvent have been determined at 50° (compare Makovetski, Abstr., 1908, i, 753). A mixture containing 36.8% of glycerol and the water and the ether in varying proportions was used. The osmotic pressure, calculated from the observations according to the formulæ deduced, is about 1.5 times the gas pressure in water alone, and in mixtures containing up to 20% by weight of the ether, but diminishes to about one-sixth of the gas pressure when the solution contains 60 mol.% of the ether. G. S.

Piezoechemical Studies. II. Influence of Pressure on Solubility. ERNST COHEN and L. R. SINNIGE (*Zeitsch. physikal. Chem.*, 1909, 67, 432—445. Compare this vol., ii, 291, 641).—An arrangement by which solubilities under high pressures may be accurately determined is figured and described in detail. The apparatus is provided with an electro-magnetic stirrer, and the temperature is measured with a platinum resistance thermometer. The solubility of $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$, expressed as the number of grams of anhydrous salt in 100 grams of water at 25° under different pressures, is as follows :

76.80 at 1 atmosphere, 78.00 at 500 atmospheres, 78.72 at 1000 atmospheres. For $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ at 25° , 57.95 grams anhydrous salt at 1 atmosphere, 57.91 grams at 500 atmospheres, 57.55 grams at 1000 atmospheres. G. S.

Formation of Solid Surfaces on Liquids. G. NAGEL (*Ann. Physik*, 1909, [iv], 29, 1029—1056).—It is shown that the formation of solid layers at the surface of solutions is a phenomenon of frequent occurrence. For different types of solutions, such as solutions of dyes, metallic salts, and colloidal metals, it has been found that this is due to the separation of insoluble substances at the surface, and that these are either present in the form of very fine suspensions in the liquid or are the result of chemical changes at the surface of the liquid.

In the special case of an aqueous solution of magenta, which was examined in detail, the experiments show that the formation of the surface layer is not influenced by the surrounding air, and that the substance in the solid layer is insoluble in water.

From observations on the thinnest surface layers formed in solutions of cobalt chloride, 6μ is deduced as the upper limiting value for the radius of the sphere of molecular action. H. M. D.

Reciprocal Action of Substances in Solution. EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 569—586).—In considering the actions which substances in solution exert one on the other, the author makes the two following assumptions: (1) That pairs of liquids exist which are soluble in one another in all proportions, and retain, in the solutions so formed, their original properties absolutely unchanged. To the property of forming such solutions he gives the name *isofluidism*. (2) That all possible solutions represent in their properties a series continuous from the most simple, formed by isofluidic substances, to the most complex, which exhibit distinct chemical action between the components.

Isofluidic substances should form solutions without either expansion or contraction, the specific volume being a linear function and the density a hyperbolic function of the proportion of one of the two constituents.

The author has measured the deviations from these simple relations exhibited by solutions in varying proportions of ethyl iodide and ethyl acetate; benzene and ethyl chloride; chlorobenzene and bromobenzene; benzene and chlorobenzene; benzene and bromobenzene; benzene and toluene; toluene and chlorobenzene; toluene and bromobenzene; benzene and carbon tetrachloride; chloroform and carbon tetrachloride; ethylene dichloride and ethylene dibromide; carbon tetrachloride and chlorobenzene; carbon tetrachloride and bromobenzene; ethyl acetate and ethyl formate; ethyl acetate and methyl acetate, and methyl acetate and ethyl formate. Tables are given showing in each case (1) the difference, δ , between the observed, D_H , and calculated contractions, D_B , and (2) the contraction constant, K , defined by the equation: $D_B = K \cdot m_1 m_2$, where m_1 and m_2 are the molecular percentages of the two constituents in the solution.

For the volume of 1 mol. of the solution, the author deduces an expression of the form: $A + Bx + Cx^2$, where x is the content of one of the components in the solution, and A , B , and C constants for the given pair of substances. This expression shows that the contraction is a maximum for the solution containing the two components in equal molecular proportions, the amount of the contraction diminishing symmetrically to zero for each of the pure constituents.

The author is of opinion that the contraction is not the result of chemical action between the component liquids, but rather of a physico-mechanical action. For not only is it difficult to imagine compounds such as benzene and toluene uniting to form a chemical compound, but it is improbable that, with liquids of such varying chemical functions as those examined by the author, such compounds should always be formed from the two components in equimolecular proportions.

T. H. P.

Crystallisation from Aqueous Solutions. II. ROBERT MARC (*Zeitsch. physikal. Chem.*, 1909, **67**, 470—500. Compare Abstr., 1908, ii, 160).—The experiments were made by the method already described, except that the rate of crystallisation was determined by measuring the variation in the conductivity of the supersaturated solution; a special apparatus for this purpose is described. Measurements have been made with potassium sulphate and dichromate, potassium and ammonium alum and silver acetate, and in all cases the rate of crystallisation is proportional to the square of the supersaturation. The temperature-coefficient between 0° and 10° is 1.5—1.6 in all the cases investigated. The velocity with which different substances crystallise in equivalent circumstances is not the same. The velocity of dissolution is, under equivalent conditions, always greater than the velocity of crystallisation, a result which appears to be incompatible with Nernst's view that a crystal is surrounded by a layer of saturated solution. When crystals are added to a supersaturated solution, the concentration of the solution diminishes very rapidly within the first half-minute, apparently owing to adsorption, and a correction has therefore to be applied to the constants calculated for a reaction of the second order. This rapid change during the first interval is approximately proportional to the concentration of the solution.

G. S.

Relation between the Density and Crystallographic Constants in Certain Groups of Substances. LUIGI COLOMBA (*Atti. R. Accad. Sci. Torino*, 1909, **44**, 684—698. Compare this vol., ii, 560).—The author applies the principles previously expounded to certain groups of substances, for which certain modifications are necessitated.

The first substances considered are those which contain constituents unknown in the free state. For example, magnetite, ilmenite, and bixbyite contain ferrous oxide. The value for this oxide of the hypothetical molecular volume necessary for determining the value of v'' in $\Sigma v''$ is arrived at by applying to magnetite the equation corresponding with the spinel group (*loc. cit.*). The number, 11.42 (D 6.29), thus

found for the molecular volume of ferrous oxide agrees fairly well with the value, 11.76 (D 6.13), similarly obtained from ilmenite (ferrous titanate). Taking the mean of these two values, the calculated densities for magnetite, ilmenite, and bixbyite (FeMnO_3) are 5.13, 4.73, and 5.19, the experimental numbers being 5.15, 4.72 and 4.95 respectively; the indifferent agreement in the case of bixbyite is due to the presence of SiO_2 , MgO and Al_2O_3 , which lower the density. Similar differences caused by impurities are found for hercynite and chromite, whilst for the various members of the granite group, differences are found owing to the replacement of certain of the oxides present by others in varying amounts.

The following cases are also discussed: (1) the rhombohedral carbonates, with which it is necessary to ascertain a hypothetical value for the molecular volume of carbon dioxide in the crystalline state; (2) the mercury compounds, cinnabar, metacinnabarite, and tiemannite; (3) substances which may be regarded as additive products, characterised by the fact that the components and the additive product are all of the same crystallographic type, such as pentlandite and chalcopyrite; (4) pyrites, hauerite, and laurite, for which concordant results are obtained by taking the value 15.61 (D 2.06) for the atomic volume of sulphur instead of 16.41, and (5) sperrylite (PtAs_3) and skutterudite (CoAs_3), in which no such modification of the atomic volume of arsenic is necessary; (6) cobaltite, gersdorffite, and ulmannite, for which the index of deformation is 1.36, 1.34, and 1.34 respectively; regarding these compounds as additive products of a disulphide with a diarsenide or a diantimonide, their index of deformation should be 1.343, the mean of the values 1.612 and 1.0746 (*loc. cit.*).
T. H. P.

Influence of Impurities on the Lower Limits of Crystallisation. MAURICE PADOA and L. MERVINI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 58—63).—The author has measured the crystallisation velocities and lower limits of crystallisation for (1) triphenylmethane mixed with benzophenone, aniline, apiole, or α -naphthylamine; (2) diacetylcotin mixed with benzophenone, bromonitrobenzene, apiole, or amyl alcohol; (3) salipyrine mixed with benzophenone or bromonitrobenzene (compare Bogojawlensky, *Abstr.*, 1899, ii, 206).

The results obtained show that the addition of one substance to another always produces a lowering of the inferior temperature limit of crystallisation. In most cases, this inferior limit remains constant while the concentration of the added substance varies within wide limits, although in some instances it is continually lowered by fresh addition.
T. H. P.

Experiments and Models in Illustration of Liquid Crystals. OTTO LEHMANN (*Physikal. Zeitsch.*, 1909, 10, 553—560).—The author describes thirty-two experiments which are designed to illustrate the nature and properties of liquid crystals, and to show the relationships between solid and liquid crystals.

If the orientating forces in the molecules are magnetic forces, the molecules of liquid crystals must represent astatic magnetic systems.

Models of such astatic systems built up from horse-shoe magnets are described and illustrated.
H. M. D.

Vapour Pressure of the Granules of Solid Substances. P. N. PAWLOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 679—684).—The author has investigated the relation between the vapour pressure and size of solid granules by placing small granules of various substances in closed chambers, and observing from time to time the changes in their magnitudes, the temperature of the surrounding air being 13—15°. The compounds examined were diphenylmethane, triphenylmethane, iodoform, dibenzyl, menthol, salol, guaiacol, and azoxyphenetole.

In the case of diphenylmethane, for example, the granules employed were, at the least, 2μ in diameter. In two days' time, these small granules diminished in number, and many as large as 30μ appeared. After six days, very few granules less than 7μ in size were found, and after a month, granules less than 14μ in diameter were rare. In part, the crystals were collected in heaps along the edges of the chamber, and all the crystals exhibited rounded angles.

Assuming that the pressure of saturated vapours follows the laws of ideal gases, the Clausius-Clapeyron equation for the evaporation of solids leads to the expression $d(\log p)/dT = Q/2T^2$, where p is the pressure of the saturated vapour, Q the molecular heat of evaporation, and T the absolute temperature. From this expression, the author deduces the equation $p_2\pi_1/\pi_2p_1 < 1$, where p_1 and p_2 are the vapour pressures of the finest granules, and π_1 and π_2 the vapour pressures of the coarse granules at two neighbouring temperatures, T_1 and T_2 ($T_2 > T_1$). This inequality determines the course of the vapour pressure curves for the granules considered, and renders it evident that, in the general case, these curves will intersect. From the author's previous deductions (this vol., ii, 295), it follows that, if the free surface energy is independent of the radius of the granule, the vapour-pressure curves will meet at an infinite temperature. If, however, the free surface energy is a function of the granule-radius, the curves will meet at some finite temperature. The relations between the vapour-pressure curves for the liquid and for the small and large solid granules in these two cases are discussed.
T. H. P.

Relations between the Surface Modifications of Solid Crystalline Substances. Nature of Liquid Crystals. P. N. PAWLOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 685—688).—The variations in the physico-chemical properties of solid granules of different magnitudes being explained by the unequal quantities of surface energy per unit mass of the granules, the author terms such granules surface modifications of solid consistency.

Corresponding with the two types of vapour-pressure curves (see preceding abstract), two classes of surface modifications may be distinguished. With substances of the first class, the point of intersection of the vapour-pressure curves lies above the m. p., so that the transformation of one surface modification into the other cannot be observed. Such substances the author terms monotropic with respect

to the transformation of their surface modifications. All substances will be monotropic which exhibit direct change of the solid crystals into the isotropic liquid.

With substances of the second class, the vapour-pressure curves for the large and small granules meet at a temperature below that at which the substance is converted into isotropic liquid (m. p.), so that the surface modifications can, in this case, be converted one into the other at a temperature lower than the m. p.; such substances are termed enantiotropic. Below this transformation temperature, the coarse-grained modification will be stable, whilst above it, the stable modification will consist of the smallest crystalline individuals capable of existence. This aggregate of small crystals will form a liquid phase, exhibiting surface tension and the other properties characteristic of liquids. To this class of enantiotropic substances must be referred that group of compounds which, on melting, are transformed into anisotropic liquids, that is, the so-called liquid crystals. The latter are hence not crystals, but consist of crystalline dust condensed to a liquid, in which, in some circumstances, the separate individuals may be regularly orientated.

T. H. P.

Composition of the Gases in Very Hot Flames. FRITZ HABER and H. J. HODSMAN (*Zeitsch. physikal. Chem.*, 1909, **67**, 343—383).—In a previous paper, the equilibria in the flame of carbon monoxide burning in oxygen have been investigated by a special method (Haber and Le Rossignol, this vol., ii, 384), and from the results and the heat of combustion of the mixture, the temperature of the flame has been calculated (calorimetric method). The temperature of the flame has also been estimated from the above results, the known equilibria at lower temperatures, and the specific heats of the gases (thermodynamic method), but the results of the two methods are only in moderate agreement. In order to obtain further data, the above experiments have been repeated and extended. The results depend on the degree of moisture present in the flame. With moist carbon monoxide, results in good agreement with those already described were obtained, but when the oxygen is in excess and is still further increased, the value of $K = [\text{CO}_2]/[\text{CO}][\text{O}_2]^{\frac{1}{2}}$ increases continuously, and the difference between the calorimetric and thermodynamic values of the temperature becomes regularly greater. To account for these results, it is suggested that an endothermic product is formed from the oxygen in the flame; this may be ozone, oxygen atoms, or products of the electrolytic dissociation of oxygen. Ozone has been detected qualitatively in the flame. The equilibrium relations of ozone as a function of the temperature are discussed in detail.

Experiments have also been made with acetylene burning in oxygen; the method used in obtaining a suitable flame is described at length. The temperature of the flame is higher than that of carbon monoxide (over 3000° when the gases are in the theoretical ratio), and with excess of oxygen there is greater dissociation of carbon dioxide than in the carbon monoxide flame under corresponding conditions. The equilibrium, $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$, in the acetylene flame has also been in-

vestigated, and the results are in fair agreement with those of Nernst and Wartenberg.

The hydrogen-oxygen flame has been examined under the same conditions, but the method does not suffice to prevent recombination of the products during removal from the flame. Ozone and nitrous fumes can readily be detected in the hydrogen-oxygen flame a little above the inner cone, but attempts to detect hydrogen peroxide under these conditions have not led to very satisfactory results. The acetylene flame contained the largest proportion of nitrous fumes: under certain conditions as much as 4 volumes to 100 volumes of carbon dioxide.

It is considered that in gases above 2500° , electric dissociation plays a great part in the changes taking place. G. S.

Demonstration of the Phase Rule. BOULOUCH (*Compt. rend.*, 1909, 149, 449—450. Compare Muller, *Abstr.*, 1908, ii, 466).—The attempt made by Muller to deduce the phase rule without the aid of thermodynamics depends on the assumption that, when two phases are in equilibrium, equal quantities of an independent constituent are transferred in both directions across the surface of separation in a given period of time, these quantities being a function of the pressure, temperature, and composition of the phases. There is no evidence that the equilibrium between phases is of this mobile character, or, if it is, that pressure and temperature play any part. In the simple equilibrium between liquid and vapour, the reversible transference of matter from one phase to the other depends on volume alone. R. J. C.

The P - T - X Space Figure for a System of two Components which are Miscible in all Proportions in the Solid or Liquid Crystalline Phase. ANDREAS SMITS (*Zeitsch. physikal. Chem.*, 1909, 67, 464—469).—A theoretical paper in which a projected pressure-temperature composition space model for the system in question is constructed and certain deductions drawn. G. S.

Phenomena Occurring when the Plait-point Curve Meets the Three-phase Line of a Dissociating Binary Compound. ANDREAS SMITS (*Zeitsch. physikal. Chem.*, 1909, 67, 454—463).—A theoretical paper. Only cases are dealt with in which the compound is miscible with its components in all proportions in the liquid form. The results throw light on the phenomena occurring when compounds under high pressure are raised to such temperatures that critical phenomena occur in the case of saturated solutions. G. S.

Dynamic Allotropy of Sulphur. The System Sulphur-Benzoinic Acid. HUGO R. KRUYT (*Zeitsch. physikal. Chem.*, 1909, 67, 321—342. Compare this vol., ii, 228).—The first part of the paper consists of a theoretical investigation of the isothermals of a pseudo-ternary system in which there is the possibility of the formation of three phases, the case in which equilibrium is attained, as well as that in which equilibrium is not attained, being considered. The

theory is applied to explain the behaviour of the system sulphurbenzoic acid, the two components, besides the acid, being S_{μ} and S_{λ} . The fusing-point and miscibility curves of the system have been investigated in the usual way. Benzoic acid melts at 121.7° ; at 118.5° the acid is in equilibrium with two liquid layers, and at 170° there is a three-phase equilibrium between three liquid layers, the phases containing 2.2%, 2.8%, and 82.6% of benzoic acid respectively.

G. S.

Saponification in Stages of the Esters of Dibasic Acids. II.

JULIUS MEYER (*Zeitsch. physikal. Chem.*, 1909, 67, 257—308).—In a previous paper (this vol., ii, 391) the results of an investigation of the hydrolysis of the esters of dibasic acids in the presence of dilute hydrochloric acid were given; in the present paper the saponification by dilute alkali of the methyl and ethyl esters of malonic and succinic acids, of the methyl esters of camphoric acid, and of the acetic esters of glycol and glycerol is discussed. For the first group, the reactions proceed in the two stages: (1) di-ester + alkali \rightarrow alkali salt of mono-ester + alcohol; (2) alkali salt of mono-ester + alkali \rightarrow alkali salt of dibasic acid + alcohol, and in the first part of the paper formulæ are deduced which admit of the calculation of the constant of the first reaction when the experimental data for the latter and the constant for the second reaction are known.

The saponification of the two acetates of glycol by alkali is in both cases bimolecular, and the value of the velocity constant for the first reaction is double that of the second. Similarly, the data for the saponification of the three glycerol acetates are also well represented by the equation for a bimolecular reaction; the velocity constants for the successive stages are in the ratio 3 : 2 : 1.

On the other hand, the reaction between the di-esters of dibasic acids and alkali is not bimolecular, and there is no simple relationship between the constants for the two stages of the reaction. At 25° , the first ester group of malonic acid is split off about 100 times, and for succinic acid about ten times, more rapidly than the second group. In both cases the methyl esters are saponified rather more rapidly than the ethyl esters.

Besides the above symmetrical esters, the *V* and *E* esters and the di-ester of camphoric acid have been saponified in a mixture of methyl alcohol and water at 35° and 45° . In this case there are four velocity constants, those of the *V* and *E* mono-esters, and the constants representing the velocity with which one group is split off from the di-ester, giving rise to the salts of the *V* and *E* mono-esters respectively. The reaction in the case of the mono-esters is bimolecular, and the ratio *E* : *V* is 38 : 1 at 35° and 53.4 : 1 at 45° . The saponification of the di-ester is very complicated.

The temperature-coefficients of the various reactions have been measured; in almost all cases the quotient for 10° lies between 2 and 3.

The results are interpreted according to the kinetic theory already discussed when dealing with hydrolysis in the presence of acids. The reason why there is no simple relationship between the constants for the two stages of the saponification of a symmetrical ester, such as

malonic ester, is that the product formed in the first stage is a salt, for example, potassium ethyl malonate, which is highly ionised, and the anion $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}'$ is not readily acted on by the OH' group, owing to the mutual repulsion of the negative charges. G. S.

Inorganic Chemistry.

Electrolytic Preparation of Hypochlorites. W. N. OGLOBLIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 670—679).—After reviewing previous work on the electrolysis of sodium chloride solutions, the author describes his own experiments on this subject, the results of which are briefly as follows.

Other conditions being constant, the greatest amount of active chlorine is obtained at the ordinary temperature from the most concentrated solution of sodium chloride. As the hypochlorite solutions formed are decomposed by the action of air and light, the greatest yield of active chlorine is obtained when the interruption of the current during electrolysis is least. The proportion of active chlorine increases with the period of electrolysis. The more the temperature rises in the electrolytic cell, the less is the yield of active chlorine. The greater the current employed, the greater will be the active chlorine obtained and the less the amounts of salt and current used. The loss of chlorine increases with the time of exposure of the solution to sunlight and air.

T. H. P.

Caro's Acid. HERMANN AHRLE (*Zeitsch. angew. Chem.*, 1909, 22, 1713—1715).—An improved form of apparatus (compare this vol., ii, 395) is described, by means of which anhydrous sulphur trioxide and hydrogen peroxide may be quantitatively mixed in any desired proportion and the resulting mixture analysed. If hydrogen peroxide is slowly added drop by drop to sulphur trioxide, Caro's acid is first formed and then transformed by the excess of sulphur trioxide into persulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$. On the other hand, if the sulphur trioxide is added to the hydrogen peroxide, persulphuric acid can seldom be detected. In experiments to determine the composition of Caro's acid, known weights of sulphur trioxide and hydrogen peroxide, the latter in excess, were mixed, and the resulting mixture analysed. The amounts of hydrogen peroxide and of Caro's acid were determined by means of permanganate and ferrous sulphate, and the amount of free sulphuric acid by means of a solution of acid barium phosphate. The results are in accordance with the formula H_2SO_5 for Caro's acid, and are not in agreement with the formula $\text{H}_2\text{S}_2\text{O}_9$. Towards phenolphthalein, Caro's acid behaves as a monobasic acid, only the H-atom of the OH-group in the SO_2OH -residue being dissociated in aqueous solution (compare Price, *Trans.*, 1906, 89, 53).

T. S. P.

Mixed Crystals of Sulphur and Tellurium. GIOVANNI PELLINI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 19—24).—Sulphur and tellurium do not appear to unite to form a compound, but form a series of mixed crystals, which may be obtained both by fusion and from solution. Certain of these crystals are isomorphous with trimetric sulphur, those containing 0.557% of tellurium, obtained by the author, having the axial ratios $a:b:c=0.81316:1:1.86929$, whilst for artificial sulphur crystals, the ratios are $a:b:c=0.8108:1:1.9005$. A solid amorphous solution of tellurium and sulphur was obtained, which is insoluble in carbon disulphide. The red sulphur of Japan is probably an isomorphous mixture of sulphur, selenium, and tellurium. The position of tellurium in the sixth group of the periodic system is supported by the isomorphism of sulphur, selenium, and tellurium.

T. H. P.

Molecular Weight of Selenium in Solution. F. OLIVARI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 94—100. Compare this vol., ii, 568).—Study of the solubility equilibrium between the components of mixtures of mercuric chloride with sulphur or selenium shows that the solubility of the components is not mutual, fused mercuric chloride dissolving sulphur and selenium, but not being appreciably dissolved by them. With tellurium and fused mercuric chloride, chemical action occurs to some extent, mercurous chloride being formed: $2\text{HgCl}_2 + \text{Te} = \text{Hg}_2\text{Cl}_2 + \text{TeCl}_2$.

Cryoscopic measurements of solutions of sulphur in fused mercuric chloride give normal results, corresponding with the formula S_8 . With selenium, dilute solutions yield depressions of the freezing point, indicating that the selenium molecule varies between Se_3 and Se_4 , the complexity of the molecule increasing with the concentration until it approaches Se_8 . This complex molecule undergoes dissociation on dilution of the solution, and is less stable than the sulphur molecule S_8 .

T. H. P.

Fusibility of Mixtures of Sulphur, Selenium, and Tellurium with Metals. HENRI PÉLABON (*Ann. Chim. Phys.*, 1909, [viii], 17, 526—566).—The author gives a connected account of his researches on the melting-point curves of mixtures of antimony, tin, silver, lead, thallium, arsenic, bismuth, and gold with sulphur, selenium, and tellurium, and the action of hydrogen on certain of the mixtures, from the point of view of the formation of compounds and eutectic mixtures (compare this vol., ii, 584).

The cryoscopic constant of tellurium lies between 510 and 535.

R. J. C.

Silicone. OTTO HÖNIGSCHMID (*Monatsh.*, 1909, 30, 509—525).—Silicone is the name given by Wöhler to the substance produced by the action of concentrated hydrochloric acid on calcium silicide, CaSi_2 ; the present investigation was undertaken with the object of establishing which of the two alternative formulæ suggested for this substance by Wöhler was correct. Analyses depending on the measurement of the hydrogen evolved by heating the substance in a vacuum

agree with the formula $\text{Si}_3\text{H}_3\text{O}_2$; from the readiness with which hydrogen is evolved in these circumstances, it is concluded that this element is attached to silicon and not to the oxygen; the black residue which remains after the hydrogen has been driven off is probably a new suboxide of the formula Si_3O_2 , analogous to carbon suboxide; it reacts at 400° with chlorine or hydrogen chloride to give silicon chloride, a little iron chloride, and pure white silicic acid.

The colourless substance, leucone, which is produced by exposing silicone to light and air, represents an intermediate step in the oxidation of silicone to silicon dioxide.

When heated in a vacuum, leucone evolves hydrogen, leaving a brown residue, which is probably a new oxide of the formula Si_3O_4 .
P. H.

Inactive Gases and the Equation of State. HANS HAPPEL (*Ann. Physik*, 1909, [iv], 30, 175-181).—In reply to the criticisms of Rudorf (compare this vol., ii, 571), the author shows that his equation represents the behaviour of the inactive gases better than the ordinary form of the equation of state does, and maintains the correctness of his earlier views.
G. S.

The Electrolytic Separation of the Alkali Metals from Fused Alkali Hydroxides and the Solubility of the Metals in the Electrolyte. GEORG VON HEVESY (*Zeitsch. Elektrochem.*, 1909, 15, 529-536).—The solubility of sodium in fused sodium hydroxide is determined by heating a mixture of the two substances for from one to eighty hours in a thin brass (or at temperatures above 500° , nickel) tube, which is closed by a ground-in stopper and enclosed in a strong iron tube, also closed by a ground-in plug, which is held in position by a screw. After heating, the tube is immersed in cold water, which causes the sodium hydroxide to solidify without diminution of the quantity of sodium dissolved in it. The quantity of sodium taken up by the sodium hydroxide is independent of the excess of metal used; also a rich solution formed at a low temperature loses sodium at a higher temperature. The saturation values found (expressed in grams of sodium per 100 grams of sodium hydroxide) are: 480° , 25.3; 600° , 10.1; 610° , 9.9; 670° , 9.5; 760° , 7.9; 800° , 6.9. Below 480° , saturation is not attained in fifty hours.

The solubility of sodium alloyed with thallium, cadmium, and gold was also determined at 480° . The added metal is insoluble in fused sodium hydroxide, and it is found that the addition diminishes the solubility in proportion to the amount added. Further, taking the molecular weight of the metals dissolved in sodium as being proportional to the depression of the freezing point of the sodium, the lowering of the solubility of sodium is proportional to the number of dissolved molecules and independent of the nature of the metal. In accordance with this, it is found that zinc, which does not depress the freezing point of sodium, has no effect on its solubility in fused sodium hydroxide.

The solubility of potassium in fused potassium hydroxide is much

smaller; the results obtained are: 480° , 7.8—8.9; 600° , 3—4; 650° , 2—2.7; 700° , 0.5—1.3.

Some experiments on the yields of sodium and potassium obtained in the electrolysis of the fused hydroxides (using an iron cathode surrounded by an inverted magnesia crucible which acts as a diaphragm) showed that in similar circumstances the yield of sodium is much less than that of potassium, and that it diminishes much more quickly as the temperature rises. It is shown that the sodium is not only more soluble, but that it diffuses through the fused hydroxide much more rapidly than potassium.

The addition of sodium chloride, bromide, or iodide to fused sodium hydroxide has no measurable effect on the solubility of sodium in it. T. E.

Action of Hydrogen on Sodium. ALFRED HOLT, jun. (*Mem. Manchester Phil. Soc.*, 1909, 53, xvii, 1—5).—When sodium is heated in an atmosphere of hydrogen at 270° for some days, the absorption of gas is small, and is accounted for by the formation of a film of the hydride. When heated in a current of hydrogen at about 400° , the sodium remains bright, but the hydride sublimes on to the cool portion of the tube. On allowing the sodium to cool, it becomes covered with a layer of hydride; on reheating, the film of hydride disappears at about 370° , only to reappear on the cooler parts of the tube.

When the pure sodium hydride is heated in a current of hydrogen, it decomposes at a temperature below that at which it begins to sublime, that is, decomposition of the hydride takes place at a lower temperature when heated alone than when it is present as a film on the surface of molten sodium.

At temperatures of 400 — 450° , the absorption of hydrogen by sodium is very small.

Moissan (*Abstr.*, 1902, ii, 206) has shown that when sodium is heated to temperatures between 340° and 430° some hydride is formed, and remains dissolved in the molten metal, whereas Troost and Hautefeuille (this Journ., 1874, 767) found that at 380° sodium absorbed a volume of hydrogen, consistent with the formation of the compound Na_2H .

In the light of his own experiments, the author co-ordinates the results of Moissan and Troost and Hautefeuille as follows: When sodium is heated in a current of hydrogen at atmospheric pressure, combination begins at 270° , the hydride NaH being formed. This hydride dissolves in the excess of sodium; its vapour tension is thereby reduced, and hence none of it sublimes. With rise in temperature more hydride is formed, the ratio of sodium to hydride decreasing; hence the vapour tension of the hydride becomes greater, until at length it begins to sublime, this taking place at a temperature of about 380° . At this temperature the composition of the solution of the hydride in sodium corresponds with Troost's and Hautefeuille's compound, Na_2H or $\text{NaH}\cdot\text{H}$. Thus the formation of this easily dissociating compound is quite consistent with the sublimation of the compound NaH . T. S. F.

The Atomic Weight of Silver. GUSTAV D. HINRICHS (*Mon. Sci.*, 1909, [iv], 23, i, 383—388).—Richards' statements (this vol., ii, 231) in regard to the superiority of his determinations of the atomic weights of silver, chlorine, and nitrogen over those of Stas are discussed adversely by the author, who takes exception to the trustworthiness assumed.

F. M. G. M.

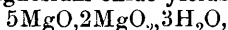
Silicides of the Metals of the Alkaline Earths. OTTO HÖNIGSCHMID (*Monatsh.*, 1909, 30, 497—508).—The analysis of various samples of commercial silicides reveals the following facts. The product obtained by heating calcium with an excess of silicon consists of calcium silicide of the composition CaSi_2 , mixed with a small quantity of iron silicide and excess of silicon; when treated with concentrated hydrochloric acid it yields yellow silicone (compare this vol., ii, 805); with dilute hydrochloric acid it yields hydrogen silicide together with partly decomposed yellow silicone. Another sample prepared by heating together calcium with silicon in the proportions required by the formula Ca_3Si_2 consists almost entirely of this substance together with traces of calcium carbide and iron silicide; with concentrated hydrochloric acid it yields a white silicon oxide and a quantity of spontaneously inflammable hydrogen silicide.

The samples of barium silicide examined were very impure, and contained in addition to the compound BaSi_2 , 40% of iron silicide and 20% of silicon; when treated with dilute or concentrated hydrochloric acid, it yields hydrogen silicide together with a white silicon oxide, which is being further investigated.

Commercial magnesium silicide contains the compound Mg_2Si together with some free silicon and a little iron silicide.

P. H.

Magnesium Peroxides. ORESTE CARRASCO (*Gazzetta*, 1909, 39, ii, 47—55).—The action of an ethereal solution of nearly anhydrous hydrogen peroxide on magnesium oxide yields the compound,



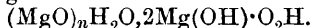
which, by treatment with a further quantity of ethereal peroxide solution, is converted into the compound, $3\text{MgO}, 2\text{MgO}_2, 3\text{H}_2\text{O}$. Further treatment of the latter with ethereal peroxide solution results in the formation of the compound, $2\text{MgO}, 2\text{MgO}_2, 3\text{H}_2\text{O}$, which is stable at 30° and when gradually heated from 50° to 70° yields successively



and the compound, $4\text{MgO}, 2\text{MgO}_2, 3\text{H}_2\text{O}$.

These magnesium peroxides are obtained in the form of light, white powders, which decompose violently when heated, and are also decomposed by water.

The main cause of the difficulty of obtaining higher peroxides than Mg_2O_3 is the great tendency of the normal peroxide to form double compounds with magnesium oxide of the form



The action of an ethereal solution of hydrogen peroxide on a mixture of magnesium oxide and potassium chloride gives the compound, $\text{KCl}, \text{MgO}(\text{OH})_2$, which is a moderately stable compound and evolves oxygen slowly when treated with water. The similar com-

pound, $\text{MgCl}_2 \cdot 2\text{MgO}$, Aq, is extremely stable and hygroscopic. Compounds with potassium bromide and sodium chloride could not be obtained.
T. H. P.

Magnesium Oxychlorides. O. KALLAUNER (*Chem. Zeit.*, 1909, 33, 871).—When Sorel's cement (a mixture of magnesia and magnesium chloride) is extracted with cold water, the whole of the magnesium chloride may be removed; a residue of constant composition is not obtained. Absolute alcohol extracts the whole of the chloride from mixtures with more than 40% of water and less than 24% of magnesium chloride. The weight does not become constant in a month's exposure over sulphuric acid, and at 130° hydrochloric acid begins to be evolved. The free magnesia present cannot be converted quantitatively into carbonate by carbon dioxide. The author thinks that the cement contains no definite oxychloride, but consists of a solid solution of magnesium hydroxide in magnesium chloride.
T. E.

Solutions of Colloidal Metals obtained by the Action of Boiling Distilled Water. II. MARGHERITA TRAUBE-MENGARINI and ALBERTO SCALA (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 111—116. Compare this vol., ii, 731).—The authors have made measurements of the amounts of platinum and silver dissolved in the colloidal state by distilled water under certain conditions.

When a bright strip of lead is immersed in distilled water, solution of the metal takes place almost immediately, the liquid becoming turbid and ultimately depositing a white, crystalline substance, the amount of which gradually increases. On the other hand, if the lead is immersed in a drinking water containing carbonates of the alkaline earths, no solution of the metal occurs for some time; the acid carbonates seem to form an insoluble compound with the lead, probably a double carbonate, which is deposited on the metal and protects it from further attack. When the immersion is prolonged, the metal dissolves.

Lead was also immersed in Mangiatorella water, which gives 0.694 gram of dry residue per litre (at 180°), consisting mainly of silica, calcium sulphate, calcium, sodium and potassium chlorides, calcium, magnesium and sodium hydrogen carbonates, dissolved carbon dioxide, oxygen, and nitrogen. No solution of the lead occurred, even when the supposed protecting layer was repeatedly removed by means of glass paper.
T. H. P.

Decomposition of Copper Sulphate in a Current of Dry Air in Relation to the Temperature. W. VANJUKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 688—717).—The author has examined the behaviour of crystallised copper sulphate when heated at different temperatures in a glazed porcelain tube placed in a Heraeus furnace, the temperature being measured by means of a thermocouple connected with a galvanometer. The principal results obtained are as follows.

The decomposition of copper sulphate with evolution of the elements of sulphuric acid commences under the above conditions at 341°

(Bradford, *Trans. Amer. Inst. Mining Eng.*, 1902, 59, gave 653°). Within the temperature limits 341—653°, the movement of the galvanometer needle is arrested three times, at 380°, 503°, and 621°, which correspond with the formation of one and the same basic salt, $8\text{CuO}\cdot 3\text{SO}_3$, to the extents of 1.09, 2.38, and 5.87%. Between the limits 653—670°, an orange-yellow basic salt, $2\text{CuO}\cdot \text{SO}_3$, is formed. Decomposition of this salt, with formation of cupric oxide, begins at 704° and is complete at 751°. But even at 850° copper sulphate is not completely decomposed, the residue always containing traces of sulphur.

When pentahydrated copper sulphate is heated in dry air, the hydrate, $\text{CuSO}_4\cdot \text{H}_2\text{O}$, is formed at 93—99°, and the formation of anhydrous salt begins at 155° and is complete at 233°. At 180°, $4\frac{1}{2}\text{H}_2\text{O}$ is removed.

T. H. P.

Double Fluorides of Quadrivalent Cerium. EBERHARD RIMBACH and HERMAN F. C. KILIAN (*Annalen*, 1909, 368, 101—109).—Only one double fluoride of cerium has been described hitherto, namely, the potassium cerium fluoride, $2\text{CeF}_4\cdot 3\text{KF}\cdot 2\text{H}_2\text{O}$ (compare Brauner, *Abstr.*, 1882, 8). All attempts to prepare this salt, likewise the analogous lithium, sodium, rubidium, caesium, and ammonium compounds, were, however, unsuccessful; in no case was a simple substance obtained, although the mean composition of the various samples of the potassium ceric fluoride which were prepared corresponded approximately with the above formula.

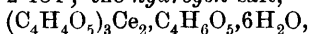
On the other hand, double salts of ceric fluoride with the fluorides of cadmium, copper, cobalt, nickel, and zinc having the general formula: $\text{MF}_2\cdot 2\text{CeF}_4\cdot 7\text{H}_2\text{O}$ are readily obtained in a pure state by treating a solution of ceric hydroxide in hydrofluoric acid with a solution of the metallic hydroxide in an excess of hydrofluoric acid. Manganese does not form a double fluoride under these conditions. The double fluorides are crystalline substances, and are decomposed more or less readily by water. The *zinc* and *cadmium* salts are white; the *copper* salt is pale blue; the *nickel* salt is apple-green; the *cobalt* salt is pale pink.

W. H. G.

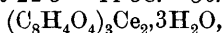
Cerous Salts of Organic Acids. (EBERHARD RIMBACH and HERMAN F. C. KILIAN (*Annalen*, 1909, 368, 110—125. Compare Wolff, *Abstr.*, 1905, ii, 457).—An account of the preparation and properties of cerous salts of certain organic acids. The normal salts are obtained by decomposing a solution of cerous nitrate with the neutral salt of the organic acid; the hydrogen salts are prepared by treating cerous carbonate with a solution of the acid. The solubility of the majority of the salts has been determined; the values recorded refer to the number of grams of the anhydrous salt present in one litre of the saturated solution at the stated temperature. It is shown that the composition of a mixture of fumaric and maleic acids may be determined with a fair degree of accuracy by making use of the different solubilities of the cerous salts.

Cerous malonate, $(\text{C}_3\text{H}_2\text{O}_4)_3\text{Ce}_2\cdot 6\text{H}_2\text{O}$, forms white crystals; sol. at 22.5° = 0.1606; the *hydrogen* salt, $(\text{C}_3\text{H}_2\text{O}_4)_3\text{Ce}_2\cdot \text{C}_3\text{H}_4\text{O}_4\cdot 6\text{H}_2\text{O}$,

crystallises in small, slender needles; sol. at $22.5^\circ = 2.017$. *Cerous glycollate*, $(C_2H_3O_3)_3Ce$, is a white, crystalline powder; sol. at $20^\circ = 3.563$. *Cerous malate*, $(C_4H_4O_5)_3Ce_2 \cdot 8H_2O$, is an amorphous, white powder; sol. at $21^\circ = 2.484$; the *hydrogen salt*,



is a white powder; sol. at $22.5^\circ = 11.58$. *Cerous phthalate*,



is obtained by acting on a neutral cerous salt solution with potassium phthalate; it forms a white, microcrystalline powder. An analogous salt with $10H_2O$ is obtained by adding cerous carbonate to a solution of phthalic acid until it no longer dissolves, and then evaporating the solution; it forms stellate aggregates of needles; sol. at $23^\circ = 2.945$. The *hydrogen phthalate*, $(C_8H_4O_4)_3Ce_2 \cdot C_8H_6O_4 \cdot 4H_2O$, crystallises in stellate groups of needles; sol. at $22.5^\circ = 2.988$. *Cerous maleate*, $(C_4H_2O_4)_3Ce_2 \cdot 7H_2O$, forms white crystals; sol. at $18.5^\circ = 2.238$; the *hydrogen salt*, $(C_4H_2O_4)_3Ce_2 \cdot 3C_4H_4O_4$, with $15H_2O$, forms small, white crystals, and with $16H_2O$ crystallises in large, faintly yellow plates, m. p. 83° ; both of these salts dissolve readily in water. *Cerous fumarate* ($10H_2O$) is a white powder; sol. at $20^\circ = 0.117$; the *hydrogen fumarate* ($2H_2O$) is a lemon-yellow, crystalline powder; sol. at $18.5^\circ = 0.243$. *Cerous crotonate*, $(C_4H_5O_2)_3Ce \cdot (C_4H_5O_2)_2Ce \cdot OH \cdot 11H_2O$, crystallises in tufts of soft, silky needles; sol. at $21^\circ = 6.816$.

W. H. G.

Solubility of Iron Oxide. PAUL ROHLAND (*Zeitsch. anal. Chem.*, 1909, 48, 629).—A solution of calcium hydrogen carbonate slowly dissolves ferric oxide, and the velocity of the reaction may be much increased by addition of alkali sulphates or calcium sulphate.

It is not improbable that a temporary reduction of the ferric oxide takes place. The phenomenon may be explained by assuming that the HCO_3' , HSO_4' , and SO_4'' ions have a more powerful action when occurring simultaneously than when they occur alone; the action of the HSO_4' and SO_4'' ions is probably of a catalytic nature. L. DE K.

Anhydrous Tungstates. NICOLA PARRAVANO (*Gazzetta*, 1909, 39, ii, 55—60).—The author has investigated the freezing-point diagram of the system $Na_2WO_4-WO_3$. Sodium tungstate melts at 698° , and at 588° and 564° undergoes two transformations, that at 564° being accompanied by the development of a considerable amount of heat, so that the temperature remains constant at this point for a considerable time. By addition of tungsten trioxide, the m. p. of sodium tungstate at first falls to the eutectic point, 626° , and then rises to the maximum, 731° , corresponding with $Na_2W_2O_7$. From 626° to 588° the mixtures between Na_2WO_4 and $Na_2W_2O_7$ are composed of α - Na_2WO_4 and $Na_2W_2O_7$; from 588° to 564° of β - Na_2WO_4 and $Na_2W_2O_7$, and below 564° , of γ - Na_2WO_4 and $Na_2W_2O_7$. The further course of the curve renders possible the existence of $Na_2W_5O_{16}$, but seems to exclude the tritungstate, $Na_2W_3O_{10}$. T. H. P.

Uranous Oxide. WILHELM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1909, 744—746).—Magnesium or aluminium in powder

reduces uranyl chloride in aqueous solution, forming black uranous oxide. Mercury has no action on the chloride. The chloride may also be reduced by lime or barium hydroxide in the absence of air, but cupric oxide placed in a solution of uranyl chloride is converted into cupric chloride with a trace of copper uranate. T. A. H.

A Mode of Formation of Uranyl Nitrate. WILHELM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1909, 743—744).—On adding excess of silver nitrate to a solution of uranyl chloride and evaporating the filtrate to dryness, a mixture of uranyl nitrate, a red basic nitrate, and a double nitrate of uranyl and silver is obtained.

T. A. H.

Hydrolytic Decomposition of Bismuth Iodide. RENÉ DUBRISAY (*Compt. rend.*, 1909, 149, 451—453. Compare this vol., ii, 742).—The addition of water to solutions of bismuth iodide gives a black precipitate, which turns brick-red when the concentration of bismuth in the liquid phase falls below 0.002 gram-atoms per litre. The curve representing the variation of bismuth with iodine in the liquid phase exhibits a discontinuity, whence it follows that the solid phase undergoes a transformation at this point, that is, that the red and black precipitates are two distinct *oxyiodides*. As the temperature is raised, the dissociation of bismuth iodide increases, but so long as only the black precipitate is present, the curves obtained are unbroken.

The brick-red oxyiodide, well washed with water but not dried, contains bismuth and iodine in the proportions to indicate the formula BiOI. The black oxyiodide, which could not be washed, was dried on a porous plate until it contained only 3% of mother liquor, and then gave analytical results indicating the formula $\text{Bi}_2\text{O}_3 \cdot 5\text{HI}$ or $2\text{BiOI} \cdot 3\text{HI} \cdot \text{H}_2\text{O}$. R. J. C.

Mineralogical Chemistry.

Danburite from Madagascar. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1908, 31, 315—318).—Some rough, corroded crystals from Maharitra in the neighbourhood of Mt. Bity, with quite the appearance of yellow topaz, proved on examination to be danburite. Attached to them are fragments of lepidolite and rubellite, indicating that they had been derived from the pegmatite-veins. Analysis by F. Pisani gave :

SiO ₂ .	B ₂ O ₃	Al ₂ O ₃ , Fe ₂ O ₃ .	CaO.	Total.	Sp. gr.
48·50	27·50	0·50	24·25	100·75	3·10

A gem-stone cut from this material also closely resembles topaz in appearance, from which it may be distinguished by its inferior hardness (H = 7) and D, but not by the refractive indices.

L. J. S.

Egyptian Minerals. J. COUYAT (*Bull. Soc. franç. Min.*, 1908, 31, 341—349).—Various minerals are described, and analyses given of the following. Thenardite, as crystals reaching 4 cm. in length, occurring with halite and trona at the Natron lakes, gave on analysis :

SO ₃ .	Na ₂ O.	MgO.	Ca.	Cl.	Loss on ignition.	Total.
56.78	41.72	0.79	trace.	trace.	1.03	100.32

Peridot, occurring as crystals of gem quality in drusy cavities in an altered dunite (serpentine) on St. John's Island in the Red Sea. The cavities also contain nepouite. Peridot is the only fresh mineral present, and it is presumably of later formation. Analysis gave :

SiO ₂ .	MgO.	FeO.	MnO + NiO.	Al ₂ O ₃ .	Loss on ignition.	Total
41.3	48.9	9.0	0.8	nil	0.15	100.15

L. J. S.

Radioactive Minerals from Madagascar. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1908, 31, 312—314).—Hatchettolite and autunite have already been described (this vol., ii, 58), and the following species are now recorded. Euxenite (?), as a single, indistinct crystal found in a specimen of pegmatite from Mt. Bandahély in the north of the island ; the material is blackish-brown, optically isotropic, and contains uranium. Fergusonite, a massive fragment, probably from pegmatite, found between Tamatave and Béforona ; it is optically isotropic, D 5.58. Analysis by F. Pisani gave :

Ch ₂ O ₅ .	SnO ₂ .	ThO ₂ .	UO ₂	(Y,Er) ₂ O ₃ .	(Ce,La,Di) ₂ O ₃ .	CaO.
50.10	0.20	2.07	6.15	31.20	6.15	1.40
		MgO.	FeO.	H ₂ O.	Total.	
		0.37	0.59	1.94	100.17	

L. J. S.

Oncosine from Variney (Valle d'Aosta). GIUSEPPE PIOLTI (*Atti R. Accad. Sci. Torino*, 1909, 44, 743—746).—This sample of oncosine has the hardness 2.5 and D¹⁶ 2.819, and on analysis gives the following results :

SiO ₂ .	Al ₂ O ₃ .	FeO.	MgO.	K ₂ O.	Li ₂ O.	H ₂ O.	Total.
50.98	25.63	0.35	6.31	12.32	trace	4.14	99.73

Oncosine can be distinguished by its green colour and density, and by the fact that it swells when fused, from cossaite (a variety of paragonite), which is bluish-green, does not swell when melted, and has D 2.95.

T. H. P.

Synthesis of Chlorite by the Action of Alkaline Solutions on Pyroxene. GEORGES FRIEDEL and GRANDJEAN (*Bull. Soc. franç. Min.*, 1909, 32, 139—150).—Augite, when heated with a solution of sodium aluminate in a platinum tube for thirty-six hours at 550—560°, gave rise to long needles of natrolite, octahedra of spinel (?), and scales of chlorite (?). Diopside heated with a solution of sodium hydroxide under the same conditions gave rise to reddish-brown scales, 1/10 mm.

across, of chlorite, which are optically biaxial and positive, and strongly pleochroic. Analysis of this product, which is near to penninite, gave:

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO.	MgO.	H ₂ O.	Total.	Sp. gr.
28·4	15·2	4·4	2·3	36·2	11·5	98·0	2·67—2·70

L. J. S.

Druse Minerals in the Granite of Waldstein, Fichtelgebirge. V. DÜRRFELD (*Zeitsch. Kryst. Min.*, 1909, 46, 563—598).—A detailed description is given of twenty-one mineral species found in the drusy cavities of the granite of Waldstein (at Epprechtstein and Grosse Waldstein); these include quartz, orthoclase, albite, zinnwaldite, topaz, tourmaline, cassiterite, etc., and the rarer species, herderite and euclase. Analyses are given of the following. Orthoclase: I, a white Baveno-twin from Epprechtstein; II, a pea-green Baveno-twin from Grosse Waldstein. Zinnwaldite, III. Muscovite, IV. Albite, V, from Epprechtstein, and VI from Grosse Waldstein. Gilbertite, as yellowish-green to white, granular-scaly aggregates, D 2·65—2·72, VII:

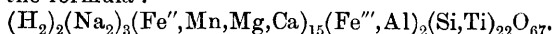
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	F.	Loss on ignition.	Total (less O for F).	Sp. gr.
I.	64·60	20·48	trace	—	0·36	0·48	10·98	3·95	—	0·33	101·18	2·493
II.	65·60	19·45	trace	—	2·16	trace	7·68	4·68	—	0·24	99·81	2·505
III.	46·90	24·68	—	2·92	1·25	0·97	9·87	1·51	6·60	2·98	99·13*	—
IV.	46·54	30·39	4·42	2·98	0·35	0·94	5·57	1·44	0·58	5·31	98·52	2·72
V.	66·26	20·74	trace	—	0·53	trace	0·58	11·22	—	0·41	99·76	—
VI.	67·11	21·41	trace	—	0·12	trace	trace	10·52	—	0·42	99·58	—
VII.	47·19	30·69	2·20	2·83	trace	0·80	6·74	3·73	0·53	5·11	99·82†	—

* Including Li₂O, 4·22; MnO, trace.

† Also trace Li₂O.

L. J. S.

Cossyrite from Pantelleria. J. SOELLNER (*Zeitsch. Kryst. Min.*, 1909, 46, 518—562).—A detailed description is given of the small, prismatic crystals of cossyrite which are found weathered out of the pantellerite of the island of Pantelleria. The crystallographic constants are: $a:b:c = 0·66856:1:0·35173$; $\alpha = 90^\circ 4\frac{3}{4}'$; $\beta = 102^\circ 30'$; $\gamma = 90^\circ 18\frac{1}{2}'$. The angle between the good prismatic cleavages $m\{110\}$ and $\mu\{1\bar{1}0\}$ is $66^\circ 16'$; D 3·802. The following analysis by M. Ditt-rich gives the formula:



SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO.	MnO.	MgO.
40·83	8·22	0·20	5·31	34·71	1·39	0·57
CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.		
0·77	6·61	trace	1·29	99·90		

Cossyrite, ænigmatite, and rhönite (Abstr., 1907, ii, 972) are considered to form a group of isomorphous minerals intermediate between the pyroxenes and amphiboles, the two former representing the alkali members of the series, and the last, a member rich in sesquioxides.

L. J. S.

Analysis of Neptunite from San Benito Co., California. W. M. BRADLEY (*Amer. J. Sci.*, 1909, [iv], 28, 15—16; *Zeitsch. Kryst. Min.*, 1909, 46, 516—517).—The supposed new mineral, carlosite, found with benitoite in San Benito Co., California (Abstr., 1907, ii, 705), has already been proved to be identical with the neptunite from Greenland. The following results (mean of two analyses) lead to the same formula, $R'_2R''_2TiSi_4O_{12}$, and differ from the analyses of the Greenland mineral only in showing rather less manganese with correspondingly more calcium and magnesium.

SiO ₂ .	TiO ₂ .	MnO.	CaO.	MgO.	FeO.	K ₂ O.	Na ₂ O.	Total.
52.87	17.82	0.85	1.56	1.44	11.69	5.08	9.56	100.88

L. J. S.

Principal Uranium and Thorium Minerals. BÉLA SZILARD (*Le Radium*, 1909, 6, 233—240).—The paper consists of a table of 111 minerals, setting forth their main constituents, crystalline character, percentage of uranium or thorium or both, and the localities where they occur. From the accompanying map of the world with these localities marked, no conclusion can be drawn, since the large tracts where no uranium or thorium is found have probably not been thoroughly searched.

R. J. C.

Physiological Chemistry.

Dissociation Curve of Blood. JOSEPH BARCROFT and MARIO CAMIS. **Dissociation Curve of Hæmoglobin.** J. BARCROFT and FF. ROBERTS (*J. Physiol.*, 1909, 39, 118—142, 143—148).—Curves of the dissociation of hæmoglobin in water and in saline solutions are given, and confirmation obtained of Bohr's curves of hæmoglobin in water, and of the effect of carbon dioxide in dissociating oxygen from blood. The differences between the curves obtained from dog's and human blood are due to differences in the saline constituents of the red corpuscles. There is no reason for departing from the view that the oxygen is united chemically with hæmoglobin, and that this union is fundamentally a mass action of the type: $\text{Hb} + \text{O}_2 \rightleftharpoons \text{HbO}_2$. The hyperbolic form of Hüfner's curve is confirmed. W. D. H.

Bio-chemistry of Hæmolysis. BENJAMIN MOORE, FREDERICK P. WILSON, and LANCELOT HUTCHINSON (*Bio-Chem. J.*, 1909, 4, 346—368).—The hæmolytic agent and the substance attacked have a powerful mutual effect on one another's solubilities. As a result, phosphatides are dissolved out of the corpuscle, so setting free hæmoglobin. The class of unsaturated soaps of fatty acids, saponin, mowrin, digitalin, and bile salts possess common properties, and are all unsaturated substances capable of bromination. Their effect on the heart also is

probably due to combination with the cardiac lipoids. Although no line can be drawn between physical and chemical action, the first step appears to be "physical," namely, one of lowering of surface tension with an accompanying tendency to solution. The balancing action of hæmolysers is discussed, but in the case of closely similar hæmolysers, an additive action is obtained. In the case of balancing, the interaction of two hæmolysers leaves nothing free to touch the corpuscles. Thus a mere trace of oleate breaks down corpuscles in saline suspension, but in serum much more must be added, for complement or the serum proteins alone act as protectors. The oleates ought not, however, to be described as anti-complements, as probably there is no specific action between them and the complement. Sodium oleate can also be balanced by lecithin. In alkaline solution, oxidising agents favour, and reducing agents restrain, hæmolysis, but an oxidising agent alone cannot replace complement in an active hæmolytic serum, and it is not probable that complement has the nature of a peroxide.

W. D. H.

Hæmolytic Action of Certain Bile Derivatives. HUGH MACLEAN and LANCELOT HUTCHINSON (*Bio-Chem. J.*, 1909, 4, 369—384).—The sodium salts of cholic, choleic, and glycocholic acids are hæmolysers. The minimum dose giving the maximum effect in the shortest time is termed the "minimal-optimum hæmolytic dose." For instance, it was found that in the case of sodium cholate, 0.1 c.c. of 0.1M-solution is the minimal-optimum dose; mixed with 1 c.c. of 5% sheep's red corpuscles (the total volume being made up to 5 c.c.), hæmolysis was complete within five minutes. Stronger solutions gave a much less marked effect, a solution eight times as strong requiring 155 minutes, and a dose eighty times as large requiring thirteen minutes to produce the same effect. In all cases, cholesterol produced a marked anti-hæmolytic effect. The addition of fresh sheep's serum is also anti-hæmolytic, but in some cases an apparent augmentation is evident. This was due to the amount of serum used being unable to completely neutralise the laking action of the bile salts; hence a relative smaller amount of active hæmolysers being present, a more powerful effect is produced, as the amount of hæmolytic agent then approaches the minimal-optimum dose. The inhibitory action of serum does not depend on the presence of complement; an inactivated serum acts equally well.

W. D. H.

Influence of Cholesterol on Hæmolysis by Soaps. HENRI ISCOVESCO (*Arch. exp. Path. Pharm.*, 1909, 61, 94).—Note on a paper by Meyerstein (this vol., ii, 681); the author had already shown that if cholesterol is to inhibit the hæmolytic action of sera and of soaps, it must first be incubated with them.

G. B.

The Amount of Peptolytic Ferments in Rabbits' and Dogs' Plasma, [and in the Red Blood Corpuscles of these Animals] under Various Conditions. EMIL ABDERHALDEN and LUDWIG PINCUSOHN (*Zeitsch. physiol. Chem.*, 1909, 61, 200—204).—Differences occur in different species of animals in the peptolytic properties of the blood-plasma. Thus the plasma (or serum) of the rabbit rapidly

decomposes glycyl-*l*-tyrosine into its components, whilst that of the dog has little or no action. If the animals are previously treated with injections of horse-serum or egg-white, the peptolytic power of the blood is increased.

W. D. H.

Production of Immune Substances. The Differences in Agglutinin-content in Plasma and Serum. GEORGES DREYER and E. W. ANILEY WALKER (*J. Path. Bact.*, 1909, 14, 28—38, 39—48).—Evidence is adduced that complement and specific immune substances are produced as secretions by the leucocytes. The plasma is richer in agglutinin than the serum; this is due to adsorption by the clot and corpuscles; a subsequent rise in agglutinin-content is due to secretion from the leucocytes.

W. D. H.

An Anti-serum to Globin. CARL H. BROWNING and G. HASWELL WILSON (*J. Path. Bact.*, 1909, 14, 137—138).—The injection of globin in animals produces an anti-globin. The action is specific; thus the protein constituents of the hæmoglobin of different species differ in their bio-chemical characters.

W. D. H.

Digestion in the Animal Body. XXXIII. The Rôle of the Intestinal Epithelium in the Digestion and Absorption of Proteins. E. S. LONDON (*Zeitsch. physiol. Chem.*, 1909, 61, 69—71. Compare this vol., ii, 593).—The intestinal epithelium of eight dogs in inanition was compared with that of the same number of animals two hours after an abundant meal of gliadin. The latter yielded on hydrolysis about twice as much glutamic acid as the former. The interpretation of this result is not attempted.

W. D. H.

The Time Relations in the Course of Protein Decomposition with Different Diets. TH. BOETTCHER and HANS VOGT (*Arch. exp. Path. Pharm.*, 1909, 61, 7—17).—When dogs are fed on meat, the excretion of nitrogen in the urine is delayed, if after feeding, relatively small quantities of dextrose are administered intravenously or subcutaneously.

G. B.

Origin of Uric Acid. R. H. ADERS PLIMMER (*J. Physiol.*, 1909, 39, 98—117).—Details of a metabolism experiment on a healthy man are given on a meat diet, a purine-free diet, and a purine-rich diet. Administration of guanine and xanthine did not increase the uric acid output; administration of large amounts of purines in herring-roë increased the output, but the excess of uric acid only corresponded with about a tenth of the total purines ingested. Liebig's extract caused a great increase, more than half the purines in it being converted into uric acid. In fact, scarcely any relation between purines and uric acid was found, and the prevalent opinion that the purines of the food and tissues are the sole source of uric acid needs revision, so also do prevailing views on uricolysis.

W. D. H.

The Value of Protein Cleavage Products in Metabolism. X. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1909, 61, 194—199. Compare this vol., ii, 327).—Dogs were fed (a) on the cleavage products of casein; (b) on the same from which *l*-tryptophan had been removed,

and (c) on the same to which *l*-tryptophan had been added. *a* and *c* maintained equilibrium, whilst *b* did not. Sickness and diarrhoea were observed, as in former experiments, but the cause of these symptoms is not clear.

W. D. H.

Nuclein Metabolism in a Dog with an Eck's Fistula. EMIL ABDERHALDEN, E. S. LONDON, and ALFRED SCHITTENHELM (*Zeitsch. physiol. Chem.*, 1909, 61, 413—418).—When the liver is thrown out of gear by the performance of an Eck's fistula, the cleavage of nucleic acid and the deamidising and oxidation of purine bases are not affected, but the conversion of uric acid into allantoin is lessened; it therefore appears that other organs besides the liver are concerned in nuclein metabolism.

W. D. H.

Action of Pancreatic Juice on Glycogen, Starch, and its Compounds. MME. Z. GRUZEWSKA and BERRY (*Compt. rend.*, 1909, 149 359—361).—Normal pancreatic juice acts less readily on glycogen and amylopectin than on starch. In each case the rapidity of the action is increased by neutralising the alkalinity of the pancreatic juice.

N. H. J. M.

Absorption of Protein. OTTO COHNHEIM and F. MAKITA (*Zeitsch. physiol. Chem.*, 1909, 61, 189—193. Compare this vol., ii, 414).—Surviving fish intestine was filled with peptone solution and suspended in Ringer's fluid. After some hours, nitrogen was found in the outer fluid, and a considerable quantity of it was in the form of ammonia. Ammonia was similarly detected during the absorption of aspartic acid and of lysine. If glycine or tyrosine was employed, no ammonia could be detected; in the case of glycine, a relatively small amount of a volatile base was found, but no glyoxylic acid. In the case of tyrosine, the outer fluid also contained a volatile base, and gave the diazo-reaction. If the intestine of a dog or cat filled with a solution of tyrosine or glycine was employed, the outer fluid contained ammonia.

W. D. H.

Lecithin and other Components of Egg-yolks. E. TORNANI (*Boll. Chim. Farm.*, 1909, 48, 520—521).—The proportion of lecithin occurring in egg-yolk varies considerably. The yolks of eggs, which have apparently kept well, exhibit, after some time, substantial alterations in their composition, especially in respect to the quantities of lecithin and cholesterol they contain. In this regard, too, marked differences are found between fertilised and unfertilised eggs.

T. H. P.

Degradation of Glycogen and Formation of Sugar in the Liver of Normal Dogs, and of those Deprived of their Pancreas. HANS HINSELMANN (*Zeitsch. physiol. Chem.*, 1909, 61, 265—275).—The first rise in the sugar of the blood after extirpation of the pancreas is attributed to an increased formation of sugar in the liver, and an increased breakdown of glycogen in the liver. A number of experiments bearing this out are quoted, and a definite action of the pancreas is upheld, in spite of Pflüger's opinions.

W. D. H.

Effects of Temperature on the Osmotic Properties of Muscle. D. H. DE SOUZA (*Quart. J. exp. Physiol.*, 1909, 2, 219—228).—A solution of sodium chloride isotonic for an injured muscle at one temperature is isotonic for muscle at other temperatures provided coagulation does not occur. Both the gain and loss of weight in a muscle in hypotonic or hypertonic solutions are increased in rapidity by rise in temperature. W. D. H.

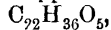
Action of Guanidine on Muscles. MARIO CAMIS (*J. Physiol.*, 1909, 39, 73—97).—Guanidine acts on frog's muscles by producing spontaneous twitching and by affecting their contractility; the former effect is inconstant, and can also be obtained on denervated muscles. The effect on contractility is the same on normal muscles, and in those in which the nerve-endings are degenerated. The hypothesis adopted is that guanidine acts by combining with two different substances in the muscle, one of which is responsible for the twitches and the other for changes in contractility. W. D. H.

Organ-extracts of Selachian Fishes. II. A. SUWA (*Pflüger's Archiv*, 1909, 129, 231—239. Compare this vol., ii, 685).—This paper gives further details of trimethylamine oxide found in extract of selachian muscle, and never before found either in the animal or vegetable organism. Its identity was further proved by the preparation of trimethylamine from it by distillation with concentrated potassium hydroxide and zinc, and by the analysis of certain of its salts (chloride, picrate, platinichloride). Trimethylamine is formed from it by putrefaction. Intravenous injection of the hydrochloride causes a slight and somewhat prolonged rise of arterial pressure. Feeding rabbits with the base, or injecting it subcutaneously, is followed by its partial destruction in the body, and an appearance of part in the urine as trimethylamine and dimethylamine. W. D. H.

Chemical Composition of Ox-bile. N. ALBERTO BARBIERI (*Compt. rend.*, 1909, 149, 150—152).—A description of a method for separating the constituents of bile by means of selective solvents. Besides neurine, cholesterol, tristearin, biliverdin, proteins, and the usual biliary salts, the author has isolated from ox-bile a bitter resin containing C 61.67, H 9.36, N 2.1, S 1.35, P 0.35, ash 3%, and a yellow powder, soluble in water, for which the name "crude biline" is suggested. This substance is a mixture rich in mineral matter, but free from sulphates; it forms a copper derivative, from which a yellow, crystalline colouring matter has been obtained. W. O. W.

The Bile of Polar Animals. III. The Bile of the Walrus. OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1909, 61, 454—494. Compare Abstr., 1901, ii, 520; 1903, ii, 86; 1904, ii, 831).—Walrus bile contains no glycocholic acid, but another acid of doubtful composition; it may be either choleic, deoxycholic, or β -phocæocholic acid. Taurocholeic acid is found in addition to taurocholic acid, but the chief constituent is a new acid, sparingly soluble in water, and readily crystallisable therefrom, which is named *α -phocæataurocholic*

acid, but is probably tauro-oxycholic acid. Its sodium salt has $\alpha_D + 41^\circ$; the cholic acid obtained from it appears to have the formula



and its sodium salt has $\alpha_D + 35-36^\circ$, and m. p. $152-154^\circ$; it does not give a blue iodine compound. Another acid of the same group present is β -phocaetaurocholic, which yields a cholic acid with formula $\text{C}_{24}\text{H}_{40}\text{O}_5$ (isocholic acid); this crystallises from acetone, melts at $220-222^\circ$, and resembles a choleic acid in yielding a sparingly soluble barium salt, and showing no colour reaction with hydrochloric acid. It also does not give a blue iodine compound. W. D. H.

Existence of Carbophosphates in Milk. Their Precipitation by Pasteurisation. A. BARILLÉ (*Compt. rend.*, 1909, 149, 356-358).—Pasteurised milk was found to contain more insoluble and soluble phosphoric acid than the original milk, whilst phosphoric acid in the form of calcium and magnesium carbophosphates was almost entirely precipitated. N. H. J. M.

Excretion of Iodine from the Dog's Organism, when given in the Form of 3:5-Di-iodo-*l*-tyrosine, 3:5-Di-iodoglycyl-*l*-tyrosine, 3:5-Di-iodo-*d*-iodopropionyl-*l*-tyrosine, and 3:5-Di-iodopalmityl-*l*-tyrosine. EMIL ABDERHALDEN and SLAVU (*Zeitsch. physiol. Chem.*, 1909, 61, 405-412).—If 3:5-di-iodo-*l*-tyrosine is given, it is easily decomposed in the dog's organism, and liberates iodine, whereas in the case of 3:5-di-iodoglycyl-*l*-tyrosine, the iodine largely appears in the urine in organic combination. 3:5-Di-iodo-*d*-iodopropionyl-*l*-tyrosine also readily gives up a part of its iodine. After the subcutaneous administration of these compounds of iodine, relatively large quantities are excreted into the intestine and are found in the faeces. W. D. H.

The Limits of Hippuric Acid Formation in Man and the Technique of Hippuric Acid Estimation. JOH. LEWINSKI (*Arch. exp. Path. Pharm.*, 1909, 61, 88-93).—Reply to Brugsch's criticism (*Zeitsch. exp. Path. Ther.*, 5, pt. 3) of the author's method of hippuric acid estimation (*Abstr.*, 1908, ii, 518). The author adheres to his statement that the amount of hippuric acid in the urine after the administration of benzoic acid is much greater than that found by other observers. G. B.

Protein Metabolism in Cystinuria. HORATIO B. WILLIAMS and CHARLES G. L. WOLF (*J. Biol. Chem.*, 1909, 6, 337-348).—The following points were investigated in a case of cystinuria; increase of protein in the diet led to an increase in the output of "neutral sulphur," probably due to an increase in cystine excretion. If cystine was given by the mouth, the increase of neutral sulphur in the urine was small, the greater amount of the cystine given being oxidised and appearing as inorganic sulphates, as in health. If tyrosine was given, none appeared in the urine; if the tyrosine was absorbed, the patient was able to deamidate the 2 grams given. No diamines or amino-acids were found in the urine. W. D. H.

Unestimated Substances in Diabetic Urine. HENRI LABBÉ and G. VITRI (*Compt. rend.*, 1909, 149, 415—418).—In addition to the normal organic substances, indeterminable by direct analysis, the urine of diabetic patients contains considerable quantities of unexplored materials quite distinct from the ordinary pathological carbohydrates. The amount of these unknown products has been determined in a number of cases by subtracting from the total organic extract the number obtained by multiplying the total nitrogen by 1.21, this being the factor for indeterminable material in normal urine. The results, which are given in tabular form, show that the amount of abnormal diabetic material may exceed the weight of sugar present. The extreme values encountered were 2.8 grams and 146.9 grams for the urine of twenty-four hours.

W. O. W.

Diabetic Lævulosuria and the Detection of Lævulose in Urine. WILHELM VOIT (*Zeitsch. physiol. Chem.*, 1909, 61, 92—94. Compare this vol., ii, 688).—Polemical. Borchardt's test for lævulose is regarded as untrustworthy.

W. D. H.

The Ferments of Nuclein Metabolism in Gout. J. R. MILLER and WALTER JONES (*Zeitsch. physiol. Chem.*, 1909, 61, 395—404).—The uricolytic enzyme is absent from the human liver in gout, but this cannot be the cause of that disease, for Wiechowski's statement that the same is true for normal human organs is confirmed.

Just as guanase is absent from the organs of the pig, so is adenase absent from those of man. The principal seat of uric acid formation (from guanine) is the liver, and that organ in man is rich in guanase and xantho-oxydase. Guanase is also present to some extent in the lung and kidney, but it is absent from the spleen.

W. D. H.

Cholesterol in Cerebro-spinal Fluid. GIACOMO PIGHINI (*Zeitsch. physiol. Chem.*, 1909, 61, 508—516).—In a number of organic nervous diseases (progressive paralysis, dementia præcox, etc.), cholesterol is often found in the cerebro-spinal fluid. The fluid from normal cases, or cases of functional disease, is free from cholesterol. In the majority of cases of epilepsy it is also absent. It is believed that, like choline, it originates from the breakdown of nervous tissues, and it probably plays a part in the Wassermann reaction.

W. D. H.

Contents of a Pancreatic Cyst. G. DORNER (*Zeitsch. physiol. Chem.*, 1909, 61, 244—255).—The contents of the cyst differed considerably from pancreatic juice obtained in cases of fistula. The amount of protein was increased, but no trypsin or protrypsin was present. The diastatic and lipolytic enzymes were present.

W. D. H.

The Presence of a Dye Resembling Urorosein in Certain Pathological Urines. VINCENZ ARNOLD (*Zeitsch. physiol. Chem.*, 1909, 61, 240—243).—In convalescents from scarlet-fever, urorosein often occurs in their urine. Simultaneously another pigment also occurs which differs from urorosein in some of its properties, including the absorption-spectrum. The name *nephrorosein* is suggested.

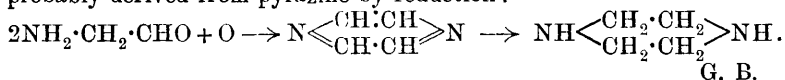
W. D. H.

Action of Ultraviolet Rays on the Tetanus Toxine. P. CERNOVODEANU and VICTOR HENRI (*Compt. rend.*, 1909, 149, 365—368).—The action of ultra-violet rays on the tetanus toxine was found to increase when the solution is diluted. This increased action is due to the dilution of the broth which absorbs the active rays. The action of the rays is the same in absence of air as when air is present.

Small amounts of iodine and of hydrogen peroxide increase the activity of the tetanus toxine; larger amounts destroy it.

N. H. J. M.

Behaviour of Aminoacetaldehyde in the Animal Organism. T. KIKKOJI and CARL NEUBERG (*Biochem. Zeitsch.*, 1909, 20, 463—467. Compare this vol., i, 702).—Aminoacetaldehyde, given to rabbits by the mouth, is excreted in the urine as pyrazine; the same oxidation can readily be brought about *in vitro*. Spermine (= piperazine?) is probably derived from pyrazine by reduction:



G. B.

Tetraethylarsonium Iodide and its Pharmacological Action. SOSSJA GORNAJA (*Arch. exp. Path. Pharm.*, 1909, 61, 76—87).—An improved method of preparation of the substance (from arsenic and ethyl iodide) is described. Its central paralytic action is four times as great as that of the tetramethyl derivative; it possesses neither a curare nor a specific arsenic action.

G. B.

Chemistry of Vegetable Physiology and Agriculture.

Bacteria which Decompose Cyanamide. HUBERT KAPPEN (*Centr. Bakt. Par.*, 1909, ii, 24, 382—404).—Successive cultivations in solutions of calcium cyanamide and cyanamide yielded bacteria which decompose cyanamide under certain conditions. No decomposing action due to carbon dioxide was observed, and organic acids, such as acetic, butyric, or lactic acids, are also without action on cyanamide when employed in amounts such as might be produced from the dextrose. The favourable action of dextrose in promoting the decomposition of cyanamide cannot, therefore, be due to fermentation products; it is probably due to a physiological action on the bacteria.

Certain fungi, having strong reducing power, seem to play an important part in the decomposition of cyanamide. N. H. J. M.

Alcoholic Fermentation in Presence of Sulphurous Acid. P. MARTINAND (*Compt. rend.*, 1909, 149, 465—467).—The feeble fermentation which occurs when brewer's yeast is introduced into grape juice containing free sulphurous acid is caused, not by the yeast

cells, but by micro-organisms resembling *Torula*. These bring about the formation of aldehydes, with which the sulphurous acid enters into combination; a part of the acid also undergoes oxidation to sulphuric acid. Normal yeast fermentation does not occur until the sulphurous acid has disappeared.

W. O. W.

Life of Yeast after Fermentation. E. KAYSER and A. DEMOLON (*Compt. rend.*, 1909, 149, 152—155. Compare Abstr., 1907, ii, 714; 1908, i, 317; this vol., ii, 170; Trillat, Abstr., 1908, ii, 615).—White wine was exposed in shallow vessels, at different temperatures, to the action of yeast for six months, and the amount of alcohol and volatile acids and the total acidity determined at the commencement and at the end of this period. Similar experiments were carried out on red wine kept in long-necked flasks, completely filled to prevent access of air. In each case the aldehydes, esters, and higher alcohols were determined in the corresponding "eau de vie."

The results are given in tabular form. A disappearance of alcohol was observed in each case; the extent to which this occurred was dependent on the history of the yeast and on the nutriment provided (ammonium sulphate or leucine). The disappearance was most marked in the shallow vessels exposed to air, due allowance having been made for loss by evaporation.

The amount of aldehydes was considerably increased, whilst the total acidity was diminished. The proportion of furfural was increased in presence of leucine, whilst the amount of esters and of higher alcohols remained fairly constant. As in the cases studied previously, the addition of mercuric chloride has a protecting influence on the alcohol. It would appear, therefore, that, after fermentation is complete, the yeast cells behave as physiologically normal cells, the intramolecular respiration being succeeded by normal respiration, during which the yeast, even at low temperatures, utilises the organic acids as nutritive material.

W. O. W.

Addition of Ammonium Salts in the Fermentation of Fruit and Grape Wines. A Correction. BIERBERG (*Centr. Bakt. Par.*, 1909, ii, 24, 404—405. Compare this vol., ii, 423).—Addition of ammonium salts in the fermentation of wines is unnecessary when there is no excess of sugar present, and may even retard fermentation.

N. H. J. M.

Influence of Anæsthesia and of Cold on the Fission of Certain Glucosides in Plants. LÉON GUIGNARD (*Compt. rend.*, 1909, 149, 91—93. Compare Mirande, following abstract).—Exposure of living plants to the action of anæsthetics brings about interaction between the glucoside and the corresponding ferment. Thus mustard oil is formed in abundance when the leaves of certain *Cruciferae* are submitted to the action of chloroform.

The same phenomenon is brought about by exposure to cold, produced by the evaporation of methyl chloride. Under the same conditions, *Gaultheria procumbens* liberates methyl salicylate, whilst cyanogenetic plants evolve hydrogen cyanide.

W. O. W.

Influence of Certain Vapours on Vegetal Cyanogenesis. Rapid Method for Detecting Plants containing Hydrogen Cyanide. MARCEL MIRANDE (*Compt. rend.*, 1909, 149, 140—142. Compare Guignard, preceding abstract).—Cyanogenetic plants liberate hydrogen cyanide when exposed to the action of substances which inhibit their chlorophyllic functions, such as mercury vapour, carbon disulphide, or anæsthetics, such as chloroform. The phenomenon is readily observed by placing under a clock glass a laurel leaf, together with some chloroform and a piece of Guignard's sodium picrate paper (*Bull. Sci. Pharm.*, 1906, 13). In a few minutes the latter turns from yellow to red under the action of the hydrogen cyanide. The phenomenon is independent of the action of light.

This reaction is recommended as affording a convenient method for recognising cyanogenetic plants. W. O. W.

Rennet of Belladonna. C. GERBER (*Compt. rend.*, 1909, 149, 137—139. Compare Abstr., 1907, i, 1100; this vol., ii, 512).—A description of the properties of the rennet of *Belladonna* and of its distribution in the plant. The distribution of the diastase corresponds approximately with that of the alkaloids, the leaves containing more than the root and the root more than the stem. Rennet is found in all the components of the stalk and root, even in the wood fibre. The rennet is extremely resistant to the action of heat; it has an optimum temperature of 90°, and readily brings about coagulation of boiling milk. It is only feebly activated by calcium salts, whilst salts of the alkali metals have a retarding influence. The behaviour of the diastase in presence of alkalis resembles that of the vegetable rennets previously studied, in presence of sodium fluoride (*Compt. rend. Soc. Biol.*, 62, 1223). The latter substance exerts an accelerating influence only in the presence of sodium chloride. W. O. W.

Phosphoric Acid in Plant Leaves. JOSEF. SESSL (*Zeitsch. landw. Vers.-Wesen Osterr.*, 1909, 12, 157—167).—An investigation on the occurrence of phosphorus in the leaves of plants during different seasons of the year. The total phosphorus was estimated, also the proportions of this element organically combined and soluble in organic solvents. The analytical results obtained from different plants are tabulated, and indicate that, as a rule, the phosphorus content of the leaves reaches its maximum in June or July (the period of greatest growth), a steady decrease being noted from that time until October. In the case of a maple (*Acer pseudoplatanus*), however, the total phosphorus reached its maximum in August. It was also found that red leaves contained less phosphorus than the green ones obtained from the same plant. F. M. G. M.

Carbohydrates contained in Plant Seeds. ERNST SCHULZE and CH. GODET (*Zeitsch. physiol. Chem.*, 1909, 61, 279—351).—The object of this investigation was to determine the nature of the carbohydrates present in the seeds of plants.

None of the kernels of the seeds investigated was found to contain either pentoses or hexoses.

Twenty-seven varieties were examined for sucrose, and in only two cases with a negative result, possibly because the quantities present were so small as to render its isolation impossible. Other soluble carbohydrates are always present; these, as a rule, yield mucic acid when oxidised, from which fact the conclusion may be drawn that they would yield galactose on hydrolysis. Only in three cases has this carbohydrate been isolated; raffinose is found in wheat, whilst lupeose has been isolated from the yellow lupine (*Lupinus luteus*) and the blue lupine (*Lupinus angustifolius*).

Pentosans are present in very small quantities (less than 1%) in some seeds, whilst they are totally absent in others.

The fact that the soluble carbohydrates present in seeds are derived from dextrose, lævulose, and galactose, shows that these sugars are particularly suitable for the nutrition of the young plant, since there can be little doubt that these carbohydrates serve as reserve materials and are broken down into the simpler sugars during germination.

Insoluble carbohydrates, namely, starches, celluloses, and hemicelluloses, are also present in the seed-kernels. The hemicelluloses on hydrolysis yield a mixture of hexoses; many yield galactose, others mannose; several also yield a pentose, probably arabinose.

The seed husks and shells contain only very small quantities of soluble carbohydrates. They are composed mainly of nitrogen-free substances insoluble in ether, water, and malt extract, of which the hemicelluloses are present in considerable quantities. The latter on hydrolysis yield arabinose, xylose, and galactose in varying quantities. The rest of the husk is composed of cellulose, wood-gum, lignin, and various indefinite, brown substances.

The portion of the cell-walls insoluble in hot dilute mineral acid contains cellulose, which, on hydrolysis, yields dextrose and sometimes mannose.

W. H. G.

Chemistry and Pharmacology of Insect Powder. J. FUJITANI (*Arch. exp. Path. Pharm.*, 1909, **61**, 47—75).—The powder (from flowers of *Chrysanthemum cinerariaefolium*) owes its activity to a neutral non-nitrogenous syrup, for which the name *pyrethrone* is suggested; it is an ester, and readily yields on hydrolysis the alcohol, *pyrethrol*, and various ill-defined acids. Pyrethrol, $C_{21}H_{34}O$, is physiologically inert; it has m. p. 199° , b. p. 290° ; $[\alpha]_D^{20}$ in chloroform solution $+72.75$ — 73.75° ; it yields a crystalline *acetyl* derivative, m. p. 222° .

Pyrethrone is a nerve poison, but not a protoplasmic poison. Fishes and insects are very susceptible to it, but protozoa are not affected. In warm-blooded animals the poison stimulates the various centres of the medulla, giving rise to epileptiform convulsions, etc.

G. B.

Analytical Chemistry.

A New Filtering Crucible. O. BRUNCK (*Chem. Zeit.*, 1909, 33, 649—650).—An ordinary Gooch crucible made of porcelain. The asbestos filter has, however, been replaced by a layer of spongy platinum firmly adhering to the porcelain. After weighing, the bulk of the precipitate is removed by gently tapping the crucible, and the last traces are removed with a suitable solvent. L. DE K.

A New Apparatus for Fractional Distillation. PHILIPPE MALVEZIN (*Bull. Soc. chim.*, 1909, [iv], 5, 835—838).—The author modifies the Lebel-Henninger column by removing the side-tubes and separating the bulbs by flat glass plates, pierced by thin, bent glass tubes which compel the ascending vapour to bubble through the condensed liquid after the manner of the Coffey still. Experiments described show an appreciable increase in efficiency. E. H.

Modification of Scheibler's Extractor for Use with Large Quantities of a Solid. C. LORING JACKSON and LATHAM CLARKE (*Amer. Chem. J.*, 1909, 42, 287—291).—An account is given of a form of Scheibler's apparatus (*Ber.*, 1880, 13, 338) for the extraction of solids on the continuous infusion principle. It is constructed of metal instead of glass, and is suitable for use when large quantities of material are to be extracted. For particulars of the various parts and their dimensions, the description and diagram in the original must be consulted. E. G.

Simplified Form of Constant Volume Ureometer. ANDRÉ JOB and CLARENS (*J. Pharm. Chim.*, 1909, [vi], 30, 97—100).—A description and sketch of a simple form of ureometer specially suitable for students' use, which is stated to give accurate results. The apparatus consists of a flask closed by a three-hole rubber stopper, and connected with a simple U-shaped manometer fitted with a sliding scale. The stopper is fitted with a 2 c.c. pipette, the upper end of which may be connected by rubber tubing to a piece of quill tubing inserted in the remaining hole. Twenty c.c. of hypobromite solution are placed in the flask, and 2 c.c. of urine drawn into the pipette and retained by a clip. The stopper is inserted, and the flask placed in a water-bath at the laboratory temperature. The tubing from the pipette is then connected with the quill tube, and when the manometer has become steady, the clip is removed, allowing the urine to fall into the flask. The pressure is then read on the manometer. It is necessary to calibrate the apparatus by determining the increase of pressure produced by a known weight of pure carbamide. W. O. W.

Estimation of Acids in Hydrogen Peroxide by Titration. OTTO LÜNING (*Zeitsch. angew. Chem.*, 1909, 22, 1549—1550).—If a definite quantity of hydrochloric or sulphuric acid is added to a pure 3%

solution of hydrogen peroxide, either direct or indirect titration in the cold with $N/10$ -sodium hydroxide and phenolphthalein as indicator gives the exact amount of acid added. If, however, a definite quantity of sodium hydroxide is added to a solution of hydrogen peroxide and the latter heated until oxygen ceases to be evolved, titration with acid only gives half the amount of sodium hydroxide added (compare Endemann, this vol., ii, 432). On the other hand, if a known excess of acid is added to the alkaline solution after the evolution of oxygen has ceased, and the liquid again heated for a short time, titration with alkali gives the correct amount of sodium hydroxide previously added.

These results are explained by assuming that a sodium peroxide hydrate is formed which is relatively stable towards acids in the cold, but which is destroyed by warming with acids. They furthermore show that Endemann's method (*loc. cit.*) for determining the acidity of hydrogen peroxide solutions is incorrect; excess of sodium hydroxide should be added to the cold solution and titrated back with acid without previous heating.

Hydrogen peroxide and dilute sulphuric acid do not form persulphuric acid.
T. S. P.

A Proposed Test for Halogens. G. B. NEAVE (*Analyst*, 1909, 34, 345—346).—Richmond (*Abstr.*, 1908, ii, 530) noticed that when a substance containing a halogen is dissolved in alcohol and then shaken with mercury and sulphuric acid, a mercurous halide is formed. The author having made a number of experiments, arrives at the conclusion that the test answers fairly well qualitatively, but is unsuitable for quantitative purposes.
L. DE K.

Estimation of Total Sulphur in Urine. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1909, 6, 363—371).—The method proposed consists in carrying out the oxidation with a mixture of copper nitrate and sodium or potassium chlorate. It is claimed that the method is rapid, and gives practically the same results as Folin's sodium peroxide method.
W. D. H.

Estimation of Total Sulphur in Urine. STANLEY RITSON (*Bio-Chem. J.*, 1909, 4, 337—342, 343—345).—From the comparison of a number of urines, it is found that Schulz's method (oxidation with fuming nitric acid) gives the lowest results, whilst the Asbóth-Modrakowski method (oxidation with sodium peroxide) gives the highest figures, and must therefore be considered the most trustworthy of the methods at present in use. The Pringsheim (oxidation with sodium peroxide brought about by the introduction of a red-hot iron nail into the mixture), Kanschegg (oxidation by fuming nitric acid and potassium nitrate), and Folin's modification of the Asbóth-Modrakowski method all give immediate figures.

The Asbóth-Modrakowski method possesses the disadvantage of being too lengthy for experiments, such as those on metabolism, where a large number of analyses have to be made, and a new method is recommended which gives still higher figures, and can be rapidly performed. The new method is a modification of the Pringsheim

method, and consists in carrying out the oxidation with a mixture of barium peroxide and sodium peroxide in the proportion 1:7. A higher temperature is reached by fusion with this mixture; a red-hot iron nail is introduced, the reaction is over in a few seconds, and the barium sulphate formed in the reaction is collected and weighed.

W. D. H.

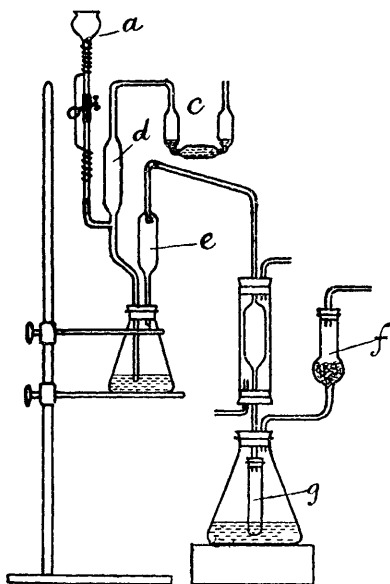
Estimation of Combined Sulphur in Caoutchouc. TH. BUDDE (*Gummi Zeit.*, 1909, 23, 1143—1144).—About one gram of the caoutchouc is soaked during twenty-four hours in carbon tetrachloride (30—40 c.c.), and then treated with 250 c.c. of a brominating mixture (1000 c.c. of carbon tetrachloride, 6 c.c. of bromine, 1 gram of iodine). After a further six hours, 125 c.c. of alcohol are added, and the mixture filtered after twelve hours. The residue is treated with 10—15 c.c. of bromine, and, after twenty-four hours, diluted with water and heated on a sand-bath; the insoluble residue is boiled twice with water and washed successively with alcohol and ether. The sulphur is estimated in the filtrates by the known methods of Henricque, or Frank and Marekwald.

F. M. G. M.

Estimation of Sulphuric Acid as Barium Sulphate in Solutions containing Chlorides. JULIUS F. SACHER (*Chem. Zeit.*, 1909, 33, 941—942. Compare Ruppin, this vol., ii, 343).—In order to obtain accurate results, the solution should contain about 0.1 gram of the sulphate (reckoned as potassium sulphate) per 100 c.c. After

heating to boiling and adding 1 c.c. of *N*/5-hydrochloric acid, a boiling 3% solution of barium chloride is added in about three times the theoretical quantity required. After fourteen hours, the precipitate is collected and washed with cold water until free from chlorides; hot water should not be used, as this dissolves barium sulphate to a slight extent.

L. DE K.



Modified Apparatus for Estimation of Nitrogen by the Kjeldahl Process. FRANK E. WESTON and HENRY R. ELLIS (*Chem. News*, 1909, 100, 50).—The accompanying diagram represents the apparatus for distilling off the ammonia in a Kjeldahl estimation. After diluting the sulphuric acid with water and cooling, sodium hydroxide solution is introduced

through the funnel *a*. Bulbs *c*, which are altogether of about 15 c.c. capacity, contain concentrated sulphuric acid, and are to prevent any ammonia entering the apparatus when air is drawn through. The bulb *d* is to prevent any sodium hydroxide solution from coming in contact with the acid in bulbs *c*. The trap *e* is to prevent any solid matter being carried over during distillation. Tube *f* contains broken glass, and is connected to the pump, and *g* is a small test-tube having a small hole at the bottom. During the distillation a steady current of air is drawn through the apparatus, enabling the operation to proceed with absolutely no bumping, and requiring very little attention.

J. V. E.

Estimation of Nitrates in Waters containing Chlorine. RENÉ MARCILLE (*Ann. Chim. anal.*, 1909, 14, 303—304).—Perrier and Farcy (this vol., ii, 344) having stated that nitrates cannot be determined directly by Grandval and Lajoux's process in the case of waters containing chlorine, the author recalls the fact that he has recommended the use of ammoniacal silver sulphate for removal of the chlorine (*Abstr.*, 1902, ii, 173).

L. DE K.

Colorimetric Estimation of Phosphorus with Uranium Acetate and Potassium Ferrocyanide. ROBERT B. GIBSON and CLARENCE ESTES (*J. Biol. Chem.*, 1909, 6, 349—358).—The principle of the method is to add excess of uranium acetate solution to an aliquot part of the diluted fusion or digestion, and then, after filtering off the precipitated uranium phosphate, to determine colorimetrically the uncombined uranium with potassium ferrocyanide. The results are stated to be trustworthy.

W. D. H.

Estimation of Phosphoric Acid in Mineral Phosphates. GUNNER JÖRGENSEN (*Analyst*, 1909, 34, 392—393).—Minute details of the author's process—now the official one in Denmark. The essential points are that the phosphate is dissolved in boiling nitric acid, and the solution made up with water to a definite volume. In an aliquot part, the phosphoric acid is precipitated at 50° with an excess of molybdate solution, and the yellow precipitate is washed repeatedly with acid solution of ammonium nitrate. After dissolving the same in 2½% ammonia, the liquid is heated to boiling and then precipitated with magnesia mixture. After four hours, the precipitate is collected in a platinum crucible filter, packed with spongy platinum, washed with 2½% ammonia solution, then once with alcohol, dried, ignited, and weighed.

L. DE K.

Estimation of Phosphoric Acid in Metabolism Experiments. H. SCHAUMANN (*Zeitsch. anal. Chem.*, 1909, 48, 612—617).—The author prefers the process recommended by Neumann (*Abstr.*, 1899, ii, 54). This consists essentially in destroying the organic matters by heating with concentrated sulphuric and nitric acids. When destruction is complete, the residue is heated further to expel the excess of nitric acid, and, after diluting with water and filtering, the phosphoric acid is estimated by the molybdate process; the resulting yellow pre-

precipitate is dissolved in $N/2$ -sodium hydroxide, boiled to expel the ammonia, and the solution is titrated with $N/2$ -hydrochloric acid, using phenolphthalein as indicator.

Convenient quantities to work on are 0.5—1 gram of seeds, flesh, animal or human organs. Of blood, 5 c.c. should be taken, and other liquids should be concentrated to about 5 c.c. A rather complicated but convenient suction apparatus is described for collecting and washing the yellow precipitate.

L. DE K.

Detection and Approximate Estimation of Small Quantities of Arsenic. R. BENSEMANN (*Zeitsch. angew. Chem.*, 1909, 22, 1804—1806).—A slight modification of the well known Otto apparatus. The reduction tube is heated in three places, thus ensuring at least two mirrors.

The author passes the gases over dry cotton wool and then through a U-tube containing a few sticks of sodium hydroxide before entering the reduction tube. The objections to the apparatus on account of danger of explosion, and to the use of sodium hydroxide as a drying agent, appear unfounded.

The mirrors obtained are compared with standard mirrors. The amount of arsenic present should, however, not exceed 0.2 mg., otherwise the mirrors become difficult of comparison. The method is specially recommended for ascertaining the purity of dyes. One gram of the sample is mixed with 5 grams of a mixture of nitre and sodium carbonate (1—2), and gradually transferred into a red-hot platinum crucible. The mass is then dissolved in water and mixed with 50 c.c. of 25% sulphuric acid. The whole is evaporated until sulphuric fumes cease, and then dissolved in water and diluted to 100 c.c. A suitable portion is then used for the test.

L. DE K.

Non-reducibility of Arsenic Acid in Alkaline Solution. Method of Detecting Arsenites in Arsenates. ERCOLE COVELLI (*Boll. Chim. Farm.*, 1909, 48, 623—625).—Arsenic acid in alkaline solution resists all reducing agents, including nascent hydrogen, by which, however, arsenious acid is reduced to hydrogen arsenide. The following method admits of the detection of an arsenite in presence of an arsenate. To 5 c.c. of the liquid to be examined are added two potassium hydroxide pastilles, a piece of granulated zinc, and a piece of iron wire, the two metals being in contact in the liquid. In presence of arsenates alone, evolution of gas is slow, the surfaces of the metals remain bright, and a paper, moistened with ammoniacal silver nitrate solution and placed in the mouth of the test-tube, remains white. If, however, even a very small amount of arsenious acid is present, the development of hydrogen is more rapid, the zinc and iron blacken, and hydrogen arsenide is evolved.

T. H. P.

Estimation of Small Quantities of Carbon Dioxide. OTTO WARBURG (*Zeitsch. physiol. Chem.*, 1909, 61, 261—264).—The method described is a modification of that of Pettenkofer, based on the observation that a hot solution of barium hydroxide absorbs carbon dioxide far more rapidly than a cold solution. By this method, small quantities

of carbon dioxide (0.001 gram) may be estimated with an accuracy of 4–5%. A figure of the apparatus is given in the original. W. H. G.

Detection of Free Carbonic Acid in Water. LUDWIG BITTER (*Hyg. Rundsch.*, 1909, 19, 633).—The method consists in titrating the water with a solution containing 0.9091 gram of pure sodium hydroxide per litre, using phenolphthalein as indicator. F. M. G. M.

Micro-chemical Analysis. VII. The Last Group [Magnesium, Lithium, Potassium, and Sodium]. NICOLAAS SCHOORL (*Zeitsch. anal. Chem.*, 1909, 48, 593–611. Compare this vol., ii, 762).—The residue freed from ammonium salts is dissolved in water and a little hydrochloric acid and the magnesium is precipitated with barium hydroxide, and, after being converted into magnesium ammonium phosphate, it is examined under the microscope. The filtrate is freed from barium hydroxide by means of carbon dioxide, and the solution is evaporated to dryness. Lithium chloride is then extracted with absolute alcohol, and, after expelling the alcohol, the residue is treated with a solution of sodium hydrogen carbonate; the lithium carbonate formed is then recognised under the microscope.

The residue insoluble in alcohol may contain potassium and sodium. Traces of potassium are best precipitated with cobaltic sodium nitrite, and then finally converted into the platinum double compound after igniting the cobalt compound. Either of the precipitates may be recognised microscopically. When much potassium is present, it is best removed by evaporation with ammonium perchlorate. The residue is then extracted with alcohol, and, after evaporating and igniting the residue, the sodium is converted into the double uranyl acetate compound and examined microscopically.

Advantage may be taken also of the insolubility of potassium hydrogen tartrate in alcohol. Ammonium may be set free with calcium oxide and then converted into the chloride. L. DE K.

Volumetric Estimation of Calcium Oxide in Presence of Dissolved Silica. KARL BALTHASAR (*Chem. Zeit.*, 1909, 33, 646–647).—0.7 Gram of the cement is treated in a porcelain dish with concentrated hydrochloric acid until decomposed, warming if necessary. The liquid is then transferred to a 350 c.c. flask, and the basin is rinsed with water, using altogether about 100 c.c. After boiling for a few minutes to expel any carbon dioxide, 50 c.c. of an ammoniacal mixture are added, the boiling being continued. This ammonia solution is prepared by placing in a litre flask 25 grams of ammonium chloride and 100 c.c. of concentrated acetic acid, and diluting with ammonia to the mark. While the liquid is still boiling, 50 c.c. of *N*/2-oxalic acid are added, the mixture is cooled, and diluted with water to the mark. The liquid is filtered, and in 50 c.c. of the clear filtrate the excess of oxalic acid is estimated by means of *N*/10-permanganate, after addition of 5 c.c. of sulphuric acid and a few c.c. of manganous sulphate solution. The amount of calcium oxide is then easily calculated. L DE K

Estimation of Free Calcium Oxide in Cements. ROBERT BRANDENBURG (*Chem. Zeit.*, 1909, 33, 880).—It is proposed to estimate the amount of free calcium oxide by distillation with ammonium bromide dissolved in absolute alcohol. The ammonia liberated corresponds with the calcium oxide present. L. DE K.

Estimation of the Hardness of Water by Clark's Method. GALEAZZO PICCININI (*Atti. R. Accad. Sci. Torino*, 1909, 44, 842—857).—The author's experiments deal with the estimation of the hardness of waters containing known amounts of calcium, barium, and magnesium salts by means of Clark's method, various soaps being employed. The results obtained lead to the following conclusions.

With waters containing calcium and magnesium salts, the rapidity with which the estimation is effected has a considerable influence on the results when the soap used contains a preponderating proportion of alkali oleates. When calcium salts predominate over those of magnesium, results not greatly inferior to the true ones are obtained, even when working rapidly, provided that potash soap, prepared in the ordinary way from lead soap and potassium carbonate, is employed. Pure sodium or potassium oleate should not be used, since it yields erroneous values, which are low or high according as the calcium or magnesium salts predominate. The disturbing influence of marked quantities of magnesium salts is exercised in the direction of giving high rather than low values for the hardness of a water. Alcoholic solutions of sodium stearate, prepared so that they correspond with Faist and Knauss's tables, contain a definite, stable salt, and give exact results quite independently of the rapidity with which the estimation is executed. T. H. P.

Estimation of Zinc, Copper, and Cobalt by means of Ammonium Hydroxide. WILHELM VAUBEL (*Zeitsch. angew. Chem.*, 1909, 22, 1716—1717).—The hydroxides of zinc, copper, and cobalt, which are obtained by precipitation with sodium hydroxide, do not filter readily and are difficult to wash. The author proposes the use of ammonium hydroxide in place of sodium hydroxide, the method of procedure being as follows: The solution of the salt is first made neutral to litmus by means of alkali hydroxide or sodium carbonate. Phenolphthalein is then added, and ammonium hydroxide until a red colour is obtained. In the case of copper, the ammonium hydroxide is added until the deep blue colour of an ammoniacal copper solution is formed; in the case of zinc, the solution is then heated to boiling until the red colour disappears, or until all the metal has been precipitated in the case of copper and cobalt. A slight excess of ammonium hydroxide is of no consequence, but a large excess should not be used, owing to the solvent action of ammonium salts on the precipitates in question. The preliminary neutralisation of the acid with sodium hydroxide is to prevent the accumulation of ammonium salts in solution. The results are quantitative.

T. S. P.

Quantitative Separation of Lead and Bismuth. J. C. GALLETTY and GEORGE G. HENDERSON (*Analyst*, 1909, 34, 389—391).—The authors recommend Clark's process (separation of the bismuth by means of steel wire, *Abstr.*, 1900, ii, 371), but think the method may be improved by finally precipitating the bismuth from its hot solution, containing 2½% of free nitric acid, with sodium hydrogen phosphate, instead of ammonium carbonate. The precipitate, after being washed with acid water containing a trace of ammonium nitrate, is ignited and weighed as bismuth phosphate.

Attempts to separate lead from bismuth by taking advantage of the solubility of lead phosphate in nitric acid of 1—2.5% strength were unsuccessful.
L. DE K.

Gravimetric Estimation of Copper Sulphate. P. B. DALLIMORE (*Pharm. J.*, 1909, [iv], 29, 271).—Three grams of the coarsely-powdered sample are heated in a porcelain dish on a water-bath with an excess of hypophosphorous acid, diluted with an equal volume of water, until the copper has completely precipitated as metal. This is washed with water until free from acidity, and then with alcohol and ether. Finally, it is burnt to oxide in a porcelain crucible and weighed as such.
L. DE K.

Estimation of Mercury and Antimony Sulphides in Vulcanised Caoutchouc. FRANK and FELIX JACOBSON (*Gummi Zeit.*, 1909, 23, 1046).—The caoutchouc is cut into small fragments, evaporated down twice with nitric acid, and the operation repeated several times with the addition of potassium chlorate, and finally with hydrochloric acid. The residue is treated with the latter acid, the solution filtered hot, and diluted with water. As the viscous mass produced at this stage frequently hinders filtration, a more prolonged boiling with concentrated nitric acid may be necessary. The mercury and antimony are precipitated from the hot filtrate with hydrogen sulphide, the mixed sulphides collected, and weighed in a tared Gooch crucible after washing successively with alcohol, ether, carbon disulphide, and ether. The antimony sulphide is dissolved with yellow ammonium polysulphide, and the residual mercuric sulphide weighed. As a further control, the antimony is converted into tetroxide by treatment with nitric acid in a tared basin. Any other metals present are estimated in the filtrate from the mixed sulphides.
F. M. G. M.

Rapid Estimation of Iron in Iron Ores. JAMES S. MACLAURIN and WILLIE DONOVAN (*J. Soc. Chem. Ind.*, 1909, 28, 827—828).—The finely-powdered ore is introduced into a hard glass bulb-tube and, if necessary, ignited in a current of air to expel volatile matters. It is then heated in a current of coal gas for about thirty minutes, but when dealing with iron ores other than limonites, hydrogen should be employed. The contents of the bulb are then transferred to a flask, the metallic iron formed is dissolved in dilute sulphuric acid in a current of carbon dioxide, and the solution is then at once titrated with standard permanganate.
L. DE K.

Use of Ammonium Nitrate in Analysis of Metals. L. LOVITON (*Ann. Chim. anal.*, 1909, 14, 325).—Iron or steel coated with copper, brass, or nickel may be freed from those metals by simply immersing a few grams of the sample in ammonium nitrate in a state of fusion for a few moments. The copper, etc., will be found to be oxidised, and may be removed by washing; the iron, which is scarcely attacked, can then be weighed.

Tin and antimony also resist the action of ammonium nitrate.

L. DE K.

Quantitative Precipitation of Aluminium, Chromium, and Iron. ERIK SCHIRM (*Chem. Zeit.*, 1909, 33, 877—878).—The solution containing 0.1—0.2 gram of either of the metals is carefully neutralised with ammonia, taking care not to form a permanent precipitate, and diluted to about 250 c.c. After adding 20 c.c. of a 6% solution of ammonium nitrite, the whole is boiled in a beaker, covered with a watch-glass, until no more nitrous fumes are evolved. The precipitate formed is then washed by decantation, and collected on a filter as usual, which operation is much facilitated by the physical character of the precipitate. If the liquid should have become acid during the boiling, this should be neutralised with a few drops of ammonia. The washed precipitate is then ignited and weighed.

L. DE K.

The Estimation of Tungsten in Tungsten-Steel. HUGO BARTONEC (*Österr. Chem. Zeit.*, 1909, [ii], 12, 114—115).—The methods usually employed for the estimation of tungsten take about two days for completion, and are considered by the author to give low results. The following processes, which were practically tested on known mixtures of tungsten, silica, and iron, can be finished in six to seven hours.

The steel (1.5—2 grams) is heated on a sand-bath with about 40 c.c. of concentrated hydrochloric acid and 10 c.c. of nitric acid. The evaporation must not be completed, as otherwise the iron is not easily eliminated. The liquid (10—15 c.c.) is diluted with four or five times its volume of water, cooled, and filtered. The residual tungstic acid and silica are dealt with by either of the following methods: (1) The precipitate is washed with hot dilute hydrochloric acid until free from iron, the tungstic acid then dissolved with warm dilute ammonium carbonate, the solution evaporated in a tared platinum crucible, and the tungsten weighed as WO_3 ; (2) the residue is washed with hot dilute hydrochloric acid, and then freed from the latter with 5% sodium nitrate solution to prevent the formation of colloidal tungstic acid. The precipitate is then extracted with a measured quantity of $N/10$ -sodium hydroxide (about 30 c.c.), and the excess of alkali titrated with $N/10$ -sulphuric acid, using phenolphthalein as indicator.

F. M. G. M.

Detection of Methyl Alcohol in Ethyl Alcohol. ANTON VORISEK (*J. Soc. Chem. Ind.*, 1909, 28, 823—825).—0.5—1.0 c.c. of the alcohol or alcoholic distillate is mixed with 1 c.c. of 0.8% chromic acid solution, and diluted with water to 4—5 c.c. in a test-tube. After adding two or three small pieces of pumice, the tube is connected

with an air condenser, and the contents are boiled over a small flame until 3 or 4 c.c. have been collected in a test-tube serving as receiver. The condensing tube is then rinsed with 2 c.c. of water, which are added to the contents of the receiver. To the distillate are added 1 drop of 0.4% ferric chloride solution and 2 drops of albumin solution (white of one egg beaten up with 50 c.c. of water and 2 drops of chloroform for preserving purposes), and, after mixing 4—5 c.c. of sulphuric acid free from nitric compounds, are carefully and slowly poured down the side of the tube, and the zone of contact is then observed. If methyl alcohol is present in the sample, formaldehyde will have been formed, and a violet coloration is obtained either at once or in a few minutes (Hehner's test).

L. DE K.

The Sabatier-Senderens Test for Distinguishing between Primary, Secondary, and Tertiary Alcohols. G. B. NEAVE (*Analyst*, 1909, 34, 346—348).—The process (Abstr., 1905, i, 254) consists in passing the vapour of the alcohol over finely divided copper at 300°. Primary alcohols yield hydrogen and aldehydes, secondary alcohols, hydrogen and ketones, and tertiary alcohols, water and unsaturated hydrocarbons.

The author having experimented with 30 different alcohols, has fully confirmed the value of the test.

L. DE K.

Is Formaldehyde Produced by Boiling Solutions of Sucrose? CHARLES H. LA WALL (*Amer. J. Pharm.*, 1909, 81, 394—396).—A. A. Ramsay's statement (Abstr., 1908, ii, 994) that boiling solutions of sucrose give off appreciable quantities of formaldehyde is incorrect. Ramsay relied entirely on Hehner's milk-sulphuric acid test, and thus mistook for formaldehyde the furfuraldehyde which is produced when sucrose solutions are boiled. In testing for formaldehyde, the Rimini test with phenylhydrazine hydrochloride and sodium nitroprusside should be used; furfuraldehyde was detected with aniline acetate.

G. B.

Copper Reagents and Estimation of Sugars; Copper Lactate Reagent. C. CARREZ (*Ann. Chim. anal.*, 1909, 14, 332—338).—After trying unsuccessfully to replace the tartaric acid in the Fehling solution by some other organic acids and some of the higher alcohols, the author has succeeded by using lactic acid. The new solution is prepared as follows: 180 grams of lactic acid (D 1.21) are diluted with 200 c.c. of water, and 200 c.c. of aqueous sodium hydroxide (D 1.332) are added. After boiling for a few minutes, the solution is carefully neutralised by either more alkali or lactic acid and allowed to cool, when a cold solution of 34.63 grams of copper sulphate in 250 c.c. of water is added, and the whole is then made up to 1 litre. When required for use, 10 c.c. are mixed with 15 c.c. of aqueous sodium hydroxide (80 grams per litre), 5 c.c. of 5% potassium ferrocyanide solution, and not more than 30 c.c. of water, if any (Bonnans's titration process).

As the degree of alkalinity is of great influence, it is advisable that the reducing power of the liquid should be specially ascertained;

a solution of pure dextrose (3 grams per litre) is recommended. The time of boiling also greatly influences the result, but when working under strictly equal conditions, the method gives good results in practice. L. DE K.

Estimation of Lactose in Milk by Michaelis and Rona's 'Iron Method.' KARL OPPENHEIM (*Chem. Zeit.*, 1909, 33, 927—928).—Ten c.c. of the sample are diluted with 13 c.c. of water, and 7 c.c. of colloidal ferric hydroxide are added. The liquid is passed through a dry filter, and the lactose is then estimated polarimetrically. L. DE K.

Detection of Raffinose in Plants; its Presence in Two Leguminous Seeds. ÉMILE BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1909, 149, 361—364; *J. Pharm. Chim.*, 1909, [vi], 30, 162—167).—The solution is hydrolysed successively with invertin and melibiase; a reduction in the rotatory power indicates the presence of raffinose. The action of the melibiase will, however, be more or less marked if the raffinose is accompanied by a lævo-glucoside which is hydrolysed by invertin.

Raffinose was found to be present in seeds of *Erythrina fusca* and *Entada scandens*. N. H. J. M.

Estimation of Dry Wine Extracts. G. PATUREL (*Ann. Chim. anal.*, 1909, 14, 329—332).—Twenty c.c. of the sample are placed in a glass evaporating dish, 55 mm. in diameter and 22 mm. in height, and evaporated on a water-bath at a temperature not exceeding 55°. After about two hours and a-half, when the residue occupies about 0.3—0.5 c.c., the dish is inclined in several directions in order to spread the mass equally over the bottom, and the rest of the moisture is then removed by drying in a desiccator over sulphuric acid. After twenty-four hours, the residue is weighed. L. DE K.

Colour Reaction of Cholic Acid and Dilute Hydrochloric Acid. OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1909, 61, 495—498).—If powdered cholic acid is shaken with 25% hydrochloric acid at room temperature, and kept, the fluid becomes yellow or yellowish-green; after four to eight hours, it is more or less bluish-violet, and after twenty-four hours, a deep bluish-violet. On further standing after filtering, it deposits a flocculent, yellowish-white precipitate, which can be collected, and twenty-four hours later another precipitate forms, and this can be repeated, the fluid ultimately becoming bluish-green with a reddish tint by transmitted light and, finally, yellow. This bluish-violet solution gives a strong absorption band near the D-line. The various changes are accelerated by warming. The reaction is delicate, but is not a general test for bile acids, or even for all cholic acids.

W. D. H.

Quantitative Estimation of Glycuronic Acid in Urine by the Furfuraldehyde-Hydrochloric Acid Distillation Method. CARL TOLLENS (*Zeitsch. physiol. Chem.*, 1909, 61, 95—111).—The method is based on that of B. Tollens (*Abstr.*, 1908, ii, 74). The

glycuronic acid, in 250 c.c. of urine, is precipitated by ammoniacal lead acetate; the precipitate is collected on a hardened filter, washed, and transferred to a flask with 100 c.c. of hydrochloric acid (D 1.06). This is rapidly distilled, fresh hydrochloric acid being added from time to time. When furfuraldehyde no longer distils over (the aniline acetate reaction generally becomes negative when 400—500 c.c. have been collected), an excess of phloroglucinol in hydrochloric acid is added to the distillate; the precipitated phloroglucide is dried and weighed, and represents one-third of the weight of the glycuronic lactone present in the urine.

The qualitative reaction with naphtharesorcinol (Abstr., 1908, ii, 740) may also be used colorimetrically as a rough estimation of glycuronic acid. G. B.

Preparation of Hypobromite from a Bromide for the Estimation of Urea. ANDRÉ JOB and CLARENS (*J. Pharm. Chim.*, 1909, [vi], 30, 100—101).—A solution of hypobromite for the estimation of urea in urine is conveniently prepared by mixing "eau de Javel" (aqueous potassium hypochlorite) with an aqueous solution of potassium bromide in the proportion of 1 gram of potassium bromide to 20 c.c. of "eau de Javel." W. O. W.

Preparation of Hypobromite from Potassium Bromide and "Eau de Javel." G. MEILLÈRE (*J. Pharm. Chim.*, 1909, [vi], 30, 211).—The method described by Job and Clarens (preceding abstract) for the preparation of a solution of alkali hypobromite has already been suggested by the author (*Compt. Rend. Soc. Biol.*, 1900). W. O. W.

Detection of Trimethylamine in Urine. TAKEDA (*Pflüger's Archiv*, 1909, 129, 82—88).—In any method for the detection of free trimethylamine in urine, any possible liberation of that substance from compounds must be avoided. The best tests for the purpose are those of Krüger-Reich and of Shaffer. In human urine, preformed trimethylamine is perhaps sometimes present. In the urine of horses and dogs (even when fed on material rich in choline) it is absent. During the ammoniacal fermentation of urine it is liberated. W. D. H.

Formaldehyde-Titration of Amino-acids in Urine. HANS MALFATTI (*Zeitsch. physiol. Chem.*, 1909, 61, 499—507).—The formaldehyde-titration for the estimation of ammonia (Abstr., 1908, ii, 531) gives too high results if the urine contains such amino-acids as glycine. The principle of the method for the estimation of amino-acids (which is described with full details) consists in performing an ammonia estimation by other means, then titrating another sample of the same urine with formaldehyde, and calculating the amino-acids by difference; or the ammonia may be first removed by mercuric chloride in a neutral or weakly alkaline solution, and then, after removal of the excess of mercury, the amino-acids may be estimated by titration with formaldehyde. The method is stated to yield good results. W. D. H.

Distinctive Reactions for Nevralteine, Pyramidone, and Antipyrine. A. MONFERRINO (*Boll. Chim. Farm.*, 1909, 48, 515—520).—When present together in aqueous solution, these three compounds may be detected as follows: the antipyrine gives a green coloration, changing to bluish-green with potassium nitrite and concentrated sulphuric acid, with which, also, pyramidone gives a transient, amethyst-violet coloration if it is present in greater quantity than the antipyrine. With potassium nitrite and acetic acid, pyramidone yields a less transient amethyst-violet colour, whilst a little of the violet liquid obtained by addition of ferric chloride, when added to concentrated sulphuric acid, gives a green coloration, due to the nevralteine.

Nevralteine (sodium *p*-phenetidinomethanesulphonate,
 $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$)

should give the following tests: (1) perfectly soluble in 10 parts of water; (2) the addition of excess of sulphuric acid to the violet solution yielded by ferric chloride should change it to sky-blue and then to green, but the acid which falls to the bottom of the tube should not be coloured yellow, neither should a flocculent precipitate be formed, even slowly; (3) addition of concentrated sulphuric acid to the aqueous solution should give a precipitate of shining scales, which, on addition of nitrite solution, dissolve, giving a red liquid; there should be no flocculent precipitate which is not changed by the addition of nitrite; (4) the aqueous solution should not, even after several hours, give a precipitate with acetic acid. T. H. P.

Reaction to Distinguish between α - and β -Eucaines. G. CANDUSSIO (*Boll. Chim. Farm.*, 1909, 48, 630. Compare this vol., ii, 450).—In reply to Saporetti (this vol., ii, 771), the author points out that the addition of 2 drops of a solution containing 1 gram of potassium iodide, 0.5 gram of iodine, and 10 grams of water to 2 c.c. of 1% β -eucaine solution yields a reddish-brown, rust-like precipitate, which, after one to two hours, becomes reduced in volume to such an extent that it forms an intense, brownish-red coloration adhering to the bottom of the tube. With α -eucaine, under similar conditions, a yellowish-brown precipitate is formed, which, after one to two hours, becomes orange-yellow without change of volume. T. H. P.

Estimation of Morphine in Opium. C. E. CARLSON (*Pharm. Zentr.-h.*, 1909, 50, 721—725).—A slight modification of the process given in the Swedish Pharmacopœia, 1908 (shaking the aqueous extract of the sample with ethyl acetate in presence of ammonia, and collecting and finally titrating the morphine separated).

The use of a separating funnel as a precipitation vessel is recommended, it being then easier to separate the aqueous layer containing the morphine crystals from the supernatant ethyl acetate. The filter containing the morphine is dried at 60—70°, and the morphine is then dissolved on the filter by means of standard hydrochloric acid, delivered in small portions from the funnel. Both funnel and filter are then washed with small quantities of water until every trace of acidity has been removed. L. DE K.

Free Nicotine in Tobacco Smoke. JULIUS TÓTH (*Chem. Zeit.*, 1909, 33, 866—867).—The smoke derived from 300 ordinary cigars yielded 8.786 grams of free organic bases, calculated as nicotine, and 0.661 gram of nicotine in combination with organic acids; therefore, 93% of the total organic bases found existed in the free state.

The total nicotine was estimated by means of the author's ether-benzene method after liberating the alkaloid with sodium hydroxide. The free nicotine was estimated in the same manner, no alkali being employed.

L. DE K.

Methods of Rendering Adrenaline and Catechol Reactions more Delicate. GUSTAV BAYER (*Biochem. Zeitsch.*, 1909, 20, 178—188).—The green coloration of catechol solution produced by ferric chloride is changed to a reddish-brown colour in the presence of aromatic amino-sulphonic acids, and becomes more intense. Thus in the presence of sulphanilic acid the reaction for adrenaline is ten times as sensitive as with ferric chloride alone. The reactions for adrenaline with iodic acid (Fränkel and Allers, this vol., ii, 628) and with sodium dichromate are also rendered more delicate, but at the same time less specific.

The formation of adrenaline when putrid meat is added to minced adrenal gland, which Abelous, Soulié, and Toujan (*Compt. rend. Soc. Biol.*, 1905, 57, 301, 589) regarded as taking place, is in reality simulated by an increase in the delicacy of the iodine reaction for adrenaline employed by these authors, which increase is due to certain protein fission products present in the putrid meat (compare Barger and Walpole, this vol., ii, 416).

G. B.

Quantitative Estimation of Cantharidin. L. E. WALBUM (*Pharm. Zentr.-h.*, 1909, 50, 661—664).—A modification of the Baudin method (*J. Pharm. Chim.*, 1888, 18, 391), the results agreeing fairly well with those obtained by the new process of Self and Greenish. The 15 c.c. of carbon disulphide used by Baudin are utterly insufficient to remove the fat from the cantharidin crystals. The author now uses a mixture of 70 c.c. of light petroleum of low b. p. and 50 c.c. of absolute alcohol. A correction of +0.025 gram of cantharidin should be made. The washing of the cantharidin with the solvent is much facilitated by using a centrifuge-glass instead of the double filter.

L. DE K.

Brominated Indigotins. ARTHUR BINZ and TH. MARX (*Zeitsch. angew. Chem.*, 1909, 22, 1757—1759).—The authors' object is the separation of the constituents of synthetic indigos into which halogenated indigotins have been introduced intentionally or otherwise. Three samples of synthetic indigo, containing 30—40% of bromine, have been examined. Oxidation is of little use, since inseparable mixtures of brominated isatins are produced; from these, *p*-bromo-aniline is obtained by distillation with potassium hydroxide. 5-Bromo-anthranilic acid is obtained by oxidation with manganese dioxide and aqueous alcoholic potassium hydroxide at 150°, two of the samples, however, yielding this acid mixed with undetermined by-products.

A successful separation is effected by extracting the sample with chloroform in a Soxhlet apparatus, whereby tribromoindigotin is dissolved. The residue is shaken with a cold mixture of glacial acetic acid (80 vols.) and concentrated sulphuric acid (20 vols.), which dissolves indigotin and bromoindigotin, but leaves dibromoindigotin almost unaffected. The presence of indigotin is detected by heating the sample with the preceding mixture of acids on the water-bath and precipitating the solution with ether; the product is hydrolysed, the precipitate weighed, and the sulphuric acid in the filtrate estimated. The method is not trustworthy, however, because the bromo- and dibromo-indigotins, which are reprecipitated unchanged, but in a colloidal state, obstinately retain sulphuric acid, which cannot be washed out completely, so that the percentage of indigotin is always too high.

C. S.

Rapid Method for the Estimation of Albumin in Urine. K. BRAUNGARD (*Chem. Zeit.*, 1907, 33, 942).—An improved Esbach tube, the bottom part of which is drawn out and provided with a scale, enabling the amount of albumin to be read off to 0.1 part per 1000.

After introducing the urine and the usual solution of citric and picric acids, the whole is centrifugalised for about two minutes and the volume of the deposit is read off.

L. DE K.

Detection of Proteins in Urine. BLANC and RAMEAU (*Ann. Chim. anal.*, 1909, 14, 204—205).—A table giving a systematic course for the detection in urine of acetic-soluble albumin, serin, globulin, ψ -albumin, propeptones, peptones, ψ -mucin, mucin, nucleo-albumins, and alkali-albumins.

L. DE K.

Detection of Peptolytic Enzymes. EMIL ABDERHALDEN and ALFRED SCHITTENHELM (*Zeitsch. physiol. Chem.*, 1909, 61, 421—425).—The change which peptolytic enzymes produce in polarisation when polypeptides are decomposed into their amino-acids is unsuitable as a general test for such enzymes; the detection of free tryptophan from a polypeptide containing it is also not free from objections. The substance best adapted for the purpose is glycyl-*l*-tyrosine, prepared from silk and known commercially as Peptone Roche. Its solution is rendered alkaline, and the extract or fluid suspected to contain an enzyme of the erepsin type is added; if such an enzyme is present, tyrosine is deposited on cooling, and its amount is a measure of the amount of enzyme. Normal gastric juice contains no such enzyme, but in some abnormal cases it is found.

W. D. H./

General and Physical Chemistry.

Optical Perceptibility and Electrical Migration of Dissolved Molecules. ALFRED COEHN (*Zeitsch. Elektrochem.*, 1909, 15, 652—654).—Water was purified by Spring's method (Abstr., 1899, ii, 537) until it was optically pure. A 0.5*N*-solution of sucrose, treated in the same way and examined in sunlight with the ultra-microscope, showed a visible cone of light. Dust particles appear as single points of light in the ultra-microscope, whilst the cone observed was quite homogeneous, and is therefore probably due to the sugar molecules.

Sucrose, when dissolved in dilute hydrochloric acid, has no effect on its conductivity, which shows that the ions are not added on to the sucrose molecules. In such solutions the sucrose always moves with an electric current towards the cathode. The author regards this as indicating that the sucrose molecules carry an electrical double layer in the same way as solid particles suspended in a liquid. T. E.

Crystallo-optical Investigations. HEINRICH BAUMHAUER (*Zeitsch. Kryst. Min.*, 1909, 47, 1—21).—Determinations of the refractive indices for light of different wave-lengths are given for tin dioxide (artificial cassiterite), zircon, anatase, wulfenite, phosgenite, sulphur, potassium lithium platino-cyanide, and rubidium lithium platino-cyanide. These results, together with those previously obtained for some other substances, are plotted as curves to illustrate the difference in dispersion for the extraordinary and ordinary rays. L. J. S.

Relation between the Refractive Index and the Density of Some Crystallised Silicates and their Glasses. ESPER S. LARSEN (*Amer. J. Sci.*, 1909, [iv], 28, 263—274).—The refractive indices and densities of certain silicate glasses and artificial minerals have been determined. The data for the glasses indicate that neither the refractive index nor the specific volume is strictly additive in character.

The specific refractivities, calculated either from the formula of Gladstone and Dale or that of Lorentz and Lorenz, are, however, sensibly additive both for the glasses and for the isomorphous series of soda-lime feldspars. If the crystallised silicates are compared with glasses of the same composition, the values of the specific refractivity are found to differ considerably, the deviation amounting to as much as 11%. H. M. D.

Application of the Formulæ of Pulfrich and Hess to Mixtures of Ethyl Alcohol and Water. ANTONY G. DOROSCHEWSKY and S. V. DVORSCHANTSCHIK (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 849—855.* Compare Abstr., 1908, ii, 241, 785).—Hess (this vol., ii, 1) gives the following generalised form to Pulfrich's equation (*Zeitsch. physikal. Chem.*, 1889, 4, 561) representing the relation

* and *Zeitsch. physikal. Chem.*, 1909, 68, 43—48.

between the refraction of a mixture of liquids and its contraction : $(R - R_v)/R = qc$, where R_v is the calculated refraction of the mixture, R the actual refraction, c the amount of contraction $[(D - D_v)/D]$, and q is a constant for any one binary mixture and is indicated by α , β , or γ , according as the refraction is expressed in the form $n - 1$, $(n^2 - 1)/(n^2 + 2)$, or $n^2 - 1$. Hess's statement that the values of α , β , and γ are practically independent of the temperature is contradicted by his own numbers for these constants at different temperatures (thallium light) :

	15°.	20°.	25°.	30°.
α	0.977	0.900	0.881	0.854
β	0.885	0.821	0.798	0.774
γ	1.117	1.032	0.992	0.975

The authors show that these numbers, when employed to calculate the compositions of alcohol-water mixtures at different temperatures, yield results exhibiting considerable divergence among themselves. Determinations of the values of β and γ for the D -line, and for mixtures containing from 10 to 90% of alcohol, at 15°, 20°, and 25° give the following mean and limiting numbers : β , 0.882 (0.871—0.897) ; γ , 1.112 (1.100—1.133).

Calculations made with these mean values and with the mean value previously obtained for α (Abstr., 1908, ii, 785) give results in close approximation to the truth. Gladstone's refraction formula is to be preferred to the other two, owing to its greater simplicity and to the somewhat greater accuracy of the results to which it leads.

T. H. P.

Molecular Refractions of Esters of Imino-acids and their Nitroso-derivatives. GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 909—920).—The feebly basic character of the imino-acids, which is explainable by the proximity of two carboxyl groups to the imino-group, also finds expression in the molecular refractions of the esters of these acids. The experimental values for these refractions are considerably less than the values calculated from the atomic refractions, the value taken for nitrogen being that found by Brühl (Abstr., 1895, ii, 194) for secondary aliphatic amines ; the influence of the carboxyl groups in this direction diminishes as the distance of these groups from the imino-group increases. These results are in complete harmony with that of Brühl (Trans., 1907, 93, 115), who found that union of amino-nitrogen with electronegative radicles conditions a depression in the molecular refraction. For aliphatic imino-acids, this depression is constant, the mean value being 0.64, but for esters of aromatic iminodiacetic acids the depression is considerably less than 0.64, so that the experimental and calculated molecular refractions differ only slightly ; it may be that this diminution of the depression is due to the increase of molecular weight, as was observed by Nasini and Carrara (Abstr., 1894, ii, 302) for pyrrole, furan, thiophen, and their homologues.

The author's measurements of the refractions of esters of imino-acids and of the nitroso-derivatives of these esters show that the atomic refraction of nitrogen does not remain constant even for one

and the same class of organic compounds, but varies between fairly wide limits.

The numerical results obtained are as follows; the depression of the molecular refraction below the calculated value is indicated by Δ .

Dimethyl iminodiacetate, $\text{NH}(\text{CH}_2\cdot\text{CO}_2\text{Me})_2$, D_4^{13} 1.1732, n_D^{13} 1.4415, $\Delta = 0.66$. Diethyl ester, D_4^{20} 1.0805, $n_D^{18.5}$ 1.4365, $\Delta = 0.60$; its nitroso-derivative, $\text{NO}\cdot\text{N}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, b. p. 164—165°/15 mm., D_4^{20} 1.1684, n_D^{20} 1.4527, $\Delta = 0.28$. Dibutyl ester, D_4^{18} 1.0086, n_D^{18} 1.4405, $\Delta = 0.63$.

Dimethyl *C*-methyliminodiacetate, $D_4^{12.5}$ 1.1160—1.1245, $n_D^{19.5}$ 1.4369, $\Delta = 0.72$; its nitroso-derivative, b. p. 180—181°/28 mm., D_4^{15} 1.2293, D_4^{25} 1.2383, n_D^{19} 1.4598, $\Delta = 0.50$. Diethyl ester, D_4^{20} 1.0467, D_4^{23} 1.0527, n_D^{21} 1.4320, $\Delta = 0.58$; its nitroso-derivative, D_4^{20} 1.1409, D_4^{14} 1.1462, n_D^{21} 1.4513, $\Delta = 0.46$.

Diethyl *C*-ethyliminodiacetate is a colourless liquid, b. p. 132°/14 mm., D_4^{20} 1.0353, n_D^{20} 1.4360, $\Delta = 0.71$; its nitroso-derivative, a viscous, yellow liquid, b. p. 173°/16 mm., D_4^{22} 1.1169, n_D^{22} 1.4516, $\Delta = 0.49$.

Diethyl *C*-isobutyliminodiacetate, D_4^{20} 0.9997, n_D^{20} 1.4362, $\Delta = 0.61$; its nitroso-derivative, D_4^{19} 1.0807, $n_D^{19.5}$ 1.4520, $\Delta = 0.67$.

Diethyl α -propio- β -iminobutyrate, D_4^{19} 1.0072, D_4^{27} 1.0002, n_D^{18} 1.4326, $\Delta = 0.61$; its nitroso-derivative, D_4^{19} 1.1135, D_4^{25} 1.1082, n_D^{21} 1.4563, $\Delta = 0.86$.

Diethyl *sym.*-*CC*-dimethyliminodipropionate, D_4^{18} 1.0028, D_4^{27} 0.9950, n_D^{20} 1.4380, $\Delta = 0.43$.

Dimethyl *C*-phenyliminodiacetate, b. p. 220—221°/17 mm. (Stadnikoff, this vol., i, 106, gave 188—189°/17 mm.), D_4^{16} 1.1705, D_4^{25} 1.1622, n_D^{18} 1.5111, $\Delta = 0.38$. Diethyl ester, D_4^{20} 1.1059, n_D^{20} 1.4976, $\Delta = 0.15$.

Diethyl *sym.*-*C*-phenyl-*C*-methyliminodiacetate, D_4^{16} 1.0811, D_4^{24} 1.0730, n_D^{19} 1.4899, molecular refraction 74.89 (found), 74.99 (calc.).

Trimethyl iminotriacetate, $\text{N}(\text{CH}_2\cdot\text{CO}_2\text{Me})_3$, is a colourless, viscous liquid, b. p. 167°/13 mm., $D_4^{16.5}$ 1.2130, $D_4^{27.5}$ 1.2018, n_D^{20} 1.4500, $\Delta = 1.43$. Triethyl ester, b. p. 184°/17 mm. [Heintz, *Annalen*, 1866, 140, 264, gave 280—290° (decomp.)], $D_4^{16.5}$ 1.1118, $D_4^{9.5}$ 1.1182, $n_D^{19.5}$ 1.4440, $\Delta = 1.14$.
T. H. P.

Influence of the Medium on the Lines of Spark Spectra.
HEINRICH FINGER (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1909, 7, 369—392).—The experiments given in a previous paper (compare this vol., ii, 774) are discussed in full detail. Comparison of the spectra of the spark discharges in water and air between electrodes made of different metals shows that the air spectrum, which is always formed with spark discharges in air, is missing when water is the medium. In its place there is a more or less extended continuous spectrum, in which the position of the maximum varies with different elements. In many cases, but not in all, the water vapour spectrum occurs together with the continuous spectrum, but the lines are reversed. The lines of the ordinary spark spectra are affected in different ways. Some are missing, some are reversed, others self-reversed, while still others are broadened symmetrically or on one

side only ; in many cases there is a combination of these effects. In some cases, for example, tantalum, the spark spectrum under water is exactly the same as in air. These changes do not depend on the form and position of the electrodes, the same spectrum being always obtained when electrodes of pure metal are used. In the case of alloys, other reversal phenomena occur.

In none of the spectra do the lines of hydrogen or oxygen, which gases are always formed during the discharge, or of the salt dissolved in the water, occur. The water used was that of the ordinary town supply. In a 1% solution of sodium chloride, however, with iron electrodes the sodium lines could be seen with the naked eye, although very weak. With stronger solutions the increased conductivity of the water diminished the intensity of the spark discharge, and hence of the spectrum ; nevertheless, the characteristic changes in the spectral lines seem to be independent of the nature of the medium, which may be either distilled water, ordinary water, a solution of sodium chloride, or a solution of barium chloride.

A consideration of all the observed phenomena shows that the question of spark discharges under water is extremely complicated, so that at present no adequate explanation can be given. The phenomena are different in character from those obtained in spark discharges through gases at high pressures.

T. S. P.

Behaviour of Ice in the Ultra-Red Spectrum. GÜNTHER BODE (*Ann. Physik*, 1909, [iv], 30, 326—336).—The great difference between the values of the dielectric constants of ice and water indicates a corresponding difference in the refractive indices for infinitely long waves, and this has led the author to examine the behaviour of ice towards ultra-red radiation. Measurements were made of the radiation absorbed by thin plates, and also of that reflected from the surface of a block of ice cooled down to about -10° . For wavelengths between 1 and 6μ , the same absorption maxima are found as in the case of water, and anomalous reflexion is exhibited in the same region.

H. M. D.

Constitution of Amino-acids. HEINRICH LEY and M. ULRICH (*Ber.*, 1909, 42, 3440—3449).—The fact that the limits of absorption in the aniline bases are shifted by salt formation away from the less refrangible part of the spectrum owing to the diminution in the unsaturation of the amino-group by salt formation (Hartley, Baly, and Collie, *Trans.*, 1905, 87, 1332, 1822) is illustrated also when the amine is converted into a quaternary ammonium salt. The ultra-violet absorption spectrum of phenyltrimethylammonium chloride is the same as that of aniline hydrochloride in the regions of continuous absorption and differs, where selective absorption is observed, only in giving one broad band instead of many small bands.

The transparency of an aromatic amino-compound is also increased by internal salt formation. From a comparison of the absorption spectra of methyl dimethylantranilate, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$, and σ -benzobetaine, $\text{C}_6\text{H}_4 \text{--} \begin{array}{c} \text{NMe}_3 \\ \text{--CO--} \end{array} \text{O}$, the conclusion is drawn that if an

acid and its ester give the same spectrum, the former has an "open" structure, whilst if the acid is more transparent than the ester it exists as an internal salt of betaine-like character. Instances of the first kind are anilinoacetic acid and its ethyl ester, and methyl-anthranilic acid and its methyl ester. Examples of the second kind are dimethylanthranilic acid and its methyl ester, and piperidinoacetic acid and its ethyl ester.

C. S.

Ultra-violet Absorption, Fluorescence, and Magnetic Rotation of Sodium Vapour. ROBERT W. WOOD (*Phil. Mag.*, 1909, [vi], 18, 530—535. Compare this vol., ii, 106).—By making use of a larger quartz spectrograph, the Balmer series of double lines has been increased from thirty to forty-eight, the wave-lengths of which are tabulated. The higher members of the series make their appearance as the density of the sodium vapour is increased, and simultaneously the lower members are obliterated by channelled spectra which accompany them. These channelled spectra are analogous to that which accompanies the *D*-lines, but the constitution of the former is somewhat different, in that they are spread out in both directions above and below the lines which they accompany.

There appears to be no connexion between the mechanisms which produce the *D*-lines and the visible channelled spectra, on the one hand, and the ultra-violet double lines, on the other. The evidence seems to show that the different lines of the Balmer series and their accompanying channelled spectra are produced by different entities, and it is suggested that these are atoms which have lost one, two, three, four, etc., electrons.

A determination of the magnetic rotation at the first two ultra-violet members of the Balmer series shows that this is in the same direction as at the *D*-lines.

H. M. D.

Phosphorescence of Organic Substances at Low Temperatures. J. DZIERZBICKI and JOSEPH DE KOWALSKI (*Bull. Acad. sci. Cracow*, 1909, 724—731; *Arch. sci. phys. nat.*, 1907, [iv], 28, 227—236).—In the experiments described, the presence of a very small percentage of impurity affects the results, consequently only dilute alcoholic solutions are used. The solutions are cooled by liquid air, exposed for fifteen seconds to the light of a mercury-vapour lamp, and the intensity and persistence of the phosphorescence examined by an untired eye. Aromatic hydrocarbons and their di-substituted derivatives containing halogen atoms and hydroxyl, methoxy-, amino-, nitro-, and carboxyl groups have been examined. In all cases the para-isomeride exhibits the greatest intensity and persistence, the meta- and the ortho-derivatives following, usually in this order.

Experiments on solutions of benzene, toluene, and the xylenes show that the introduction of a methyl group into the benzene nucleus increases the intensity of the phosphorescence, and that the entrance of a second methyl group causes a further increase only when the group enters the para-position; mesitylene and ψ -cumene are more phosphorescent than *p*-xylene. Similar remarks are true of benzene, aniline, and the toluidines.

The entrance of chlorine into the aniline molecule diminishes the intensity, and most when it enters the para-position.

Comparing benzene, toluene, aniline, and phenol, it appears that the amino-group is most effective in increasing the intensity of the phosphorescence, being followed in order by the hydroxyl and the methyl groups; as regards persistence, the toluene solution has the longest persistence, followed by those of benzene, aniline, and phenol.

C. S.

Optical Activity and the Product of Asymmetry. J. WALLACE WALKER (*J. Physical. Chem.*, 1909, 13, 574—584).—Bose and Willers (this vol., ii, 361) have recently stated that, using the Crum-Brown formula for the asymmetry product,

$$M[\alpha] = (C_1 - C_2)(C_1 - C_3)(C_1 - C_4)(C_2 - C_3)(C_2 - C_4)/(C_3 - C_4),$$

it is possible to find values for the activity constants C_1 , C_2 , C_3 , and C_4 of the groups which admit of the calculation of the molecular rotation with a moderate degree of accuracy. Some years ago the author made an unsuccessful attempt to prove the validity of Crum-Brown's formula by choosing various values for the constants, and now shows by a mathematical method that it is not possible to assign rotation equivalents to all radicles, from which the molecular rotations of the substances containing them may be calculated by Crum-Brown's equation.

If eight optically active substances all possess one common radicle, and the other radicles are chosen from a group of six, a certain relationship must hold between the numerical values of the respective molecular rotations provided that rotation equivalents can be assigned to each. Substances fulfilling these requirements are the methyl and ethyl esters of lactic, mandelic, chloropropionic, and chlorophenylacetic acids. They have been carefully prepared, and the molecular rotation measured at a series of temperatures between 10° and 70°. By using these numbers it is shown that the mathematical relationship referred to above does not hold, and therefore that no single rotation equivalent can be assigned to each radicle.

The values of the molecular rotation are as follows: Methyl lactate, -796 at 20°, -966 at 70°; ethyl lactate, -1216 at 20°, -1434 at 70°; methyl mandelate, -27590 at 20°, -23820 at 70°; ethyl mandelate, -22570 at 20°, -19710 at 70°; methyl chloropropionate, +2888 at 20°, +2524 at 70°; ethyl chloropropionate, +2576 at 20°, +2207 at 70°; methyl chlorophenylacetate, +7002 at 20°, +5978 at 70°; ethyl chlorophenylacetate, +6622 at 20°, +5571 at 70°. Many of the results are not in satisfactory agreement with those of Walden (*Abstr.*, 1895, i, 450; 1896, i, 139).

G. S.

Photochemical Equilibrium of Hydrogen Chloride. ALFRED COEHN and ALEXANDRA WASSILJEWA (*Ber.*, 1909, 42, 3183—3186).—The equilibrium point of hydrogen chloride in the dark lies practically at the point of complete formation of this compound from its elements. This equilibrium can be brought about in the absence of light by submitting the mixture of hydrogen and chlorine to the catalytic action of charcoal. Hitherto the question has not been investigated as to

whether hydrogen chloride is decomposed into its elements to any extent under the action of light.

The authors find that if pure hydrogen chloride is submitted to the action of ultraviolet light from a mercury-quartz lamp, it is split up to such an extent that, on collecting the gases over a solution of potassium iodide, about 2 c.c. of hydrogen are produced in a quarter of an hour. The hydrogen chloride was passed through a quartz tube, which was at a distance of about 2 cm. from the lamp, and the tubing through which the gases were led away from the quartz tube was protected from all light. If the quartz tube was replaced by one made of ordinary glass or of Uviol glass, no decomposition of the hydrogen chloride took place.

The constant for the photochemical equilibrium is

$$k = ([H_2][Cl_2])/[HCl]^2 = 6.25 \times 10^{-6}.$$

Details are reserved for a further communication.

T. S. P.

Electrochemistry of Light. VIII. WILDER D. BANCROFT (*J. Physical Chem.*, 1909, 13, 538—573. Compare this vol., ii, 454, 632).—The paper deals mainly with photographic reversals, when both a positive and a negative image occur on the plate. The work of Waterhouse, Guébhart, Kogelmann, Homolka, Carey Lea, and others is discussed at length, and in many cases their observations are explained on the author's theory of reversal.

Waterhouse has shown that the addition of thiocarbamide to the developer produces reversal, and the author shows that both the positive image as well as the negative image consists of silver, and not of silver sulphide as might perhaps be expected. For this and other reasons it is suggested that the thiocarbamide renders the unexposed silver bromide relatively more sensitive than the exposed bromide, the positive image being therefore the more dense. This view is supported by the fact that the process can be divided into two stages. If an exposed plate is dipped into a solution of thiocarbamide alone, the emulsion is ripened, and when the plate is washed and then immersed in an ordinary developer, a positive is obtained. The Guébhart reversal can be accounted for on similar lines, the sensitising agent in this case being sodium sulphite. Some special cases of retarded development are discussed in detail.

Carey Lea's apparent reversals with dilute, but not with concentrated, sodium hypophosphite are due to the fact that the hypophosphite acts both as a reducing agent and as a solvent for silver bromide. If the immersion is comparatively short, the reducing action is the more important, and the treated portion develops dark. G. S.

Reduction of Ferric Chloride by the Light of the Mercury Vapour Lamp. ALFRED BENRATH (*J. pr. Chem.*, 1909, [ii], 80, 283—287).—It has been shown previously (Abstr., 1905, i, 730) that methyl alcoholic ferric chloride is reduced in sunlight, ferrous chloride, hydrogen chloride, and formaldehyde being the primary products, whilst methyl chloride and formaldehyde hydrochloride are obtained by secondary reactions.

If the light acts merely as a catalyst, the velocity of the reaction

should be proportional to the concentration. Experiments on methyl or ethyl alcoholic solutions of ferric chloride in quartz vessels of 1.3 cm. diameter, placed 12 cm. from a 110-volt. mercury vapour lamp, show, however, that the quotient t/c (where c is the concentration of the solution and t the time required for its decolorisation) is nearly constant, proving that the amount of light energy required to reduce a definite quantity of ferric chloride is nearly constant and independent of the concentration. The light acts, therefore, not as a catalyst, but as an actual generator of chemical energy. It follows that the reduction of the ferric chloride must proceed more rapidly the narrower the containing vessel; this is proved experimentally.

A method of determining the change of concentration of the solution after a definite exposure to the light is based on the fact that the change of the density of a reacting mixture is proportional to the change of concentration of the reacting substances. A 3% solution of ferric chloride in ethyl alcohol or a 4% solution in methyl alcohol is, exposed to the mercury vapour light for definite intervals of time t , and the density of the system is also determined; it is found that $\Delta \times 10^7/t$ is practically constant (Δ representing the change of density).
C. S.

Effect of Temperature on the Photodynamic Action and the Action of Light on Invertase. B. HANNES and ALB. JODBLAUER (*Biochem. Zeitsch.*, 1909, 21, 110—113).—Solutions of invertin were exposed to sunlight from which the heat rays were eliminated, with and without addition of eosin, at 10° and 30°. It was found that the increased temperature (20°) produced exactly the same amount of injury in both cases, the percentages being 11.2 and 36.1 at 10°, and 12.6 and 40.6 at 30°.
N. H. J. M.

Radioactive Minerals in Common Rocks. J. W. WATERS (*Phil. Mag.*, 1909, [vi], 18, 677—679).—Experiments have been made to determine in what minerals the radioactivity of igneous rocks is most concentrated. Cornwall granite, from which kaolin and mica had been previously removed, was fractionated by means of bromoform, and afterwards by means of a magnet. The radioactivity was found to be chiefly concentrated in a small fraction which spectroscopic examination indicated to be anatase or rutile.

Similar methods applied to a gneiss from the Inner Hebrides showed that the activity was concentrated in a very heavy, non-magnetic mineral occurring in very small crystals, which proved to be zircon.

H. M. D.

Radioactivity of Certain Lavas. JOHN JOLY (*Phil. Mag.*, 1909, [vi], 18, 577—586).—The radioactivity of Vesuvian and other lavas has been measured, and the proportions of radium and thorium which they contain are tabulated. The values of the radioactivity of Vesuvian lavas from 1631 up to the present day are abnormally high, and appear to show a progressive increase according as they are of more recent eruption. The value obtained for a very old leucitic rock

from the prehistoric eruption of Monte Somma was less than the normal for igneous rocks. The progressive increase in radioactivity suggests that, as time progresses, materials richer and richer in radium are being tapped. This may very well be the case in spite of the fact that the lavas have shown a remarkable constancy in chemical composition from the earliest times.

The question as to the connexion between radioactivity and vulcanicity is discussed, and an estimate is made of the intrinsic heating effect of the lavas on the basis of their content of radioactive materials. From the mean radium and thorium content of the Vesuvian lavas ejected since 1631, it is calculated that a rise of temperature of about 150° in one million years is produced, assuming no loss by conduction.

H. M. D.

The Radioactive Elements. II. DANIEL STRÖMHOLM and THE SVEDBERG (*Zeitsch. anorg. Chem.*, 1909, 63, 197—206. Compare this vol., ii, 200).—Of the actinium series, actinium-*X* belongs to the alkaline earth group, being isomorphous with barium. Actinium itself is isomorphous with lanthanum, and radioactinium with thorium.

Attempts which have been made to determine the coefficient of distribution of radioactive elements between crystals of barium nitrate and the mother liquor, indicate that the coefficient is constant over a considerable range of concentration, and is the same for thorium-*X*, actinium-*X*, and radium.

In the thorium, actinium, and radium series, the element immediately preceding the emanation is an alkaline earth metal. Before this comes an element isomorphous with thorium. A modification of the periodic table is suggested, in which the three radioactive series are arranged parallel with one another in the sixth period.

C. H. D.

Complex Nature of Radium-*C*. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1909, 10, 697—703).—Measurements have been made to ascertain whether the β -rays emitted by disintegration products of radium are homogeneous or not.

From a solution of the active deposit, radium-*C* is completely removed by repeated treatment with animal charcoal, and radium-*B* precipitated by means of barium sulphate. The absorption of the β -rays of the freshly prepared material by aluminium indicates that these rays are homogeneous. By the same process it is found that the β -radiation of radium-*C* is nonhomogeneous, and the conclusion is drawn that radium-*C* consists of two or more substances. By investigation of the decay curves of the radium-*C*, obtained by collecting the particles of matter set free when β -rays are expelled from radium-*B*, this conclusion is confirmed. The half-decay periods of the products obtained vary between one and 2.5 minutes, so that radium-*C* consists of at least two substances, radium-*C*₁ and radium-*C*₂. There is also some evidence that the latter is complex, one of its components having a period of a few seconds, the other a period of two to 2.5 minutes.

H. M. D.

Action of Radium Emanation on the Elements of the Carbon Group. Sir WILLIAM RAMSAY and FRANCIS L. USHER (*Ber.*, 1909, 42, 2930—2931. Compare *Trans.*, 1909, 95, 624).—Solutions of different salts of the carbon group of elements have been submitted to the action of radium emanation, which was collected in one week from a solution of radium bromide containing 0.2111 gram of metallic radium. After the emanation had been carefully freed from carbon dioxide, it was introduced into an evacuated glass vessel containing the solution to be experimented on, and the whole left for four weeks. The gases were then collected and analysed, with the following results :

Solution of	Vol. of emanation, c.mm.	N ₂ , c.c.	O ₂ , c.c.	CO ₂ , c.c.	CO, c.c.	Oxyhydrogen gas, c.c.	H ₂ , c.c.
H ₂ SiF ₆	0.0724	—	—	0.063	—	9.15	1.03
Ti(SO ₄) ₂	0.0912	0.210	—	0.054	0.096	—	0.69
Zr(NO ₃) ₄	0.0692	0.762	—	0.116	0.008	—	—
Zr(NO ₃) ₄	0.0865	0.456	—	0.124	0.002	—	—
Th(NO ₃) ₄	0.1120	3.686	—	0.551	—	—	—
Th(NO ₃) ₄	0.0765	0.639	—	0.124	—	—	—
Pb(ClO ₃) ₂	0.0649	—	2.655	0.007	0.006	2.531	—

Thus each of the elements of the carbon group, without exception, gives rise to carbon compounds under the action of radium emanation ; the quantities produced are, however, not equal. It is not improbable that elements with a high atomic weight are more easily broken down than those of lower atomic weight. Lead, however, seems to be especially stable, showing little tendency to change into carbon.

Mercurous nitrate gave no trace of carbon monoxide or dioxide.

T. S. P.

Secondary Radiation of X-Rays. PAOLO ROSSI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], 15, 67—75. Compare Townsend, *Proc. Camb. Phil. Soc.*, 1899, 10, 217).—The author finds that the fact that strata which are isotransparent for a given quality of X-rays, exercise in general different absorptions on the secondary radiations excited by them, has a marked influence on the intensity and nature of the secondary radiation leaving the radiating body. In this way can be explained, at least qualitatively, the facts that the secondary radiation is less intense but more penetrating for aluminium than for copper, and that with a thin plate of aluminium this secondary radiation is not only less copious, but also less penetrating than with a thick plate.

Marked increase of the hardness of the primary rays is accompanied by variation of the relations between the intensities of the secondary emissions of different substances, in some cases to such an extent as to change the order of these substances with respect to intensity of emission. It would appear, indeed, that the softer rays are the less active in exciting the secondary radiation of such substances, so that secondary X-rays obey a law similar to that of Stokes relative to fluorescence.

T. H. P.

Retardation of α -Rays by Metals and Gases. T. SMITH TAYLOR (*Phil. Mag.*, 1909, [vi], 18, 604—619.* Compare *Abstr.*, 1908, ii, 793).—Further examination of the retarding effect of metals on

* and *Amer. J. Sci.*, 1909, [iv], 28, 357—372.

α -rays has shown that for sheets of different metals of equal air equivalents, the rates at which the air-equivalents decrease with the speed of the α -particles are approximately proportional to the square roots of the respective atomic weights. The air equivalents of hydrogen layers increase as the speed of the entering particles decreases, whilst the air-equivalents of sheets of paper and celloidin remain constant. On the other hand, the hydrogen-equivalents of paper, celloidin, and air decrease as the speed of the α -particles decreases.

The observation, made by Bragg, that the total ionisation produced by the α -particle is the same in air and hydrogen, is confirmed by a more direct method. It seems probable that for large ranges the α -particle loses its energy more rapidly the higher the atomic weight of the substance through which it passes; this difference diminishes, however, and for low ranges the loss of energy is the more rapid the lower the atomic weight of the substance. A comparison of the Bragg curves for air and hydrogen indicates that the large ionisation at low ranges is due to some extent to the fact that the particle loses its energy more rapidly in this part of the range.

H. M. D.

γ -Rays of Uranium and Radium. FREDERICK SODDY and ALEXANDER S. RUSSELL (*Phil. Mag.*, 1909, [vi], 18, 620—649. Compare this vol., ii, 460).—A comparison of the γ -radiations of uranium-*X* and of radium has been made, and from the results the conclusion is drawn that the β - and γ -radiations are probably not interdependent. The ratio of the β - to the γ -rays of uranium-*X* is 62 when the same ratio for radium-*C* is taken as unity, the rays in each case being measured through 1 cm. of lead. When the absorption in the lead is allowed for, the value of the ratio for uranium is 50. The ratio for uranium is only 18 when the rays are measured through 0.6 cm. of aluminium, so as to admit any soft γ -radiation if present.

For thicknesses less than 1 cm. of lead or its equivalent, the absorption of the γ -rays of uranium does not follow any simple law. For greater thicknesses the absorption is exponential, and is proportional to the density of the absorbing material. The value of λ/d for all but the heaviest and lightest substances was found to be 0.047 for uranium and 0.040 for radium, the ratio being 1.18. Lead appears to behave abnormally, and the value of λ/d is 0.0636 for uranium γ -rays and 0.0434 for radium γ -rays, the ratio being 1.465.

The initial γ -radiation of that amount of uranium-*X* which is in equilibrium with one kilogram of uranium was found to be equal to that of 0.015 mg. of a sample of a radium compound containing 66.6% of radium.

H. M. D.

Absorption of Uranium-*X* by Charcoal. ALBERT RITZEL (*Zeitsch. physikal. Chem.*, 1909, 67, 724—761).—The measurements were made with solutions of uranium nitrate varying in concentration from *N*/10 to *N*. As the uranium was in radioactive equilibrium with uranium-*X*, the concentration of the solutions with reference to the latter was known. A method is described for estimating the

amount of uranium- X in a solution by measuring the β -radiation with an electroscope in the usual way.

When charcoal is shaken with a solution containing uranium- X the latter is taken up by the charcoal, at first rapidly, then more slowly, and equilibrium is only attained after shaking for about ten days. At equilibrium, the amount taken up by the charcoal, C_s , is proportional to that in the solution, C_l . It is considered that uranium- X is at first adsorbed on the surface of the charcoal, and then slowly diffuses into it. The magnitude of the ratio $C_l:C_s$ is the smaller the smaller the concentration of the uranium nitrate solution, and also depends on whether other radioactive substances besides uranium- X are present in solution.

Experiments have also been made on the partition of uranium- X between charcoal and solutions containing no uranium. For solutions of hydrochloric, nitric, and sulphuric acid, equilibrium is reached in a few hours, and the equation holds: $C_l = \text{const.}(C_s - k)$, where k is a constant. Uranium- X is also absorbed by alkalis, but not by water, salt solutions, or ether. In these respects it behaves just like the decomposition products of thorium investigated by von Lerch (Abstr., 1904, ii, 8).
G. S.

Ionium. BRUNO KEETMAN (*Jahrb. Radioaktiv. Elektronik.*, 1909, 6, 265—274).—The production of very active preparations of ionium from the residues obtained in working up uranium ores containing but little thorium is described. On addition of hydrofluoric acid to the strongly acid solution of the raw material, a mixture of fluorides of the rare earths, calcium and uranium, together with about 0.25% of thorium, is obtained. The fluorides are converted into sulphates, and from the aqueous solution of these, ionium and thorium are separated quantitatively by means of precipitated zinc hydroxide. The strongly acid solution of the precipitate is then treated with oxalic acid, when ionium thorium oxalate is thrown down. From 500 kilograms of raw material, 140 grams of the oxalate were obtained, with an activity 200 times as large as that of metallic uranium. Although a large number of methods were tried, it was not found possible to separate the ionium from the thorium.

The rate of formation of radium from ionium was determined with the above material, and the observations give 1800 years for the life of radium. This is in good agreement with the value given by Rutherford and Geiger.

Ionium was detected in a sample of uranyl ammonium carbonate prepared by Rammelsberg. Since the exact date of the preparation of this material is not known, the determined amount of ionium cannot be used to deduce accurately the life of ionium. The data indicate, however, that this is several thousand years.

The relationship of actinium to ionium has been examined, and, as a result, it is proved that actinium is not a direct product of the transformation of ionium.

By reason of its high and very constant activity, ionium-thorium oxalate is recommended as a suitable substance for testing the constancy of electrometers and for determining capacities. H. M. D.

Escape of Negative Electrons from Reacting Metals.

FRITZ HABER and G. JUST (*Ann. Physik*, 1909, [iv], 30, 411—415).—Experiments are described which show that negative electrons are given off by the alkali metals when these undergo oxidation in moist air. If the liquid alloy of sodium and potassium, contained in an insulated vessel, is connected with the negative pole of a high potential battery, and a metal disk, connected with an electroscope, is placed above the alloy at a distance of a few centimetres, it is found that the electroscope becomes negatively charged when the surface of the alloy is disturbed so as to expose the unaltered metals to the action of the air. When the alloy is connected with the positive pole of the battery, the electroscope is unaffected. Experiments in hydrogen and dry air gave no result.

The employment of an electrical field to remove the negative electrons from the surface of the oxidising metal is not essential. This can also be effected by passing a current of dry air over the freshly exposed surface. From this observation the authors draw the conclusion that the electrons move with small velocity. Apart from this small velocity of the emitted electrons, the reaction effect is very similar to the photo-electric effect.

H. M. D.

Kinetic Energy of the Positive Ions Emitted from Various Hot Substances. F. C. BROWN (*Phil. Mag.*, 1909, [vi], 18, 649—672. Compare this vol., ii, 368).—Measurements have been made of the kinetic energy of the positive ions emitted by gold, silver, palladium, tantalum, nickel, platinum, osmium, tungsten, iron, and aluminium phosphate at high temperatures.

The radiating surface of from 0.2 to 0.3 sq. mm. area was located in the centre of a disk of 13 mm. diameter, and the ions emitted impinged on a parallel disk less than 1 mm. distant. Different potentials were applied to the parallel disc, and the corresponding thermo-ionic currents were determined.

The experimental data indicate that the mean kinetic energy of the positive thermo-ions emitted from hot substances is independent of the material from which the ions are emitted, and varies directly as its absolute temperature. On the assumption that the translational kinetic energy of the ions has the same mean value as the molecules of a gas at the same temperature, the charge of the thermo-ions is found to 1.55×10^{-20} electrostatic units. This is approximately the same as the charge carried by ions from other sources.

H. M. D.

Extension of the Law of Corresponding States. HANS HAPPEL (*Physikal. Zeitsch.*, 1909, 10, 687—693).—From the relationship which according to the theory of Clausius and Mosotti exists between the dielectric constant, the volume of the molecules, and the specific volume of a substance, the author considers that substances in corresponding states should have the same dielectric constant. By reference to the data for carbon tetrachloride, benzene, and other aromatic hydrocarbons, hexane, octane, carbon dioxide, nitrous oxide, oxygen, nitrogen, and carbon monoxide, it is shown that this is approximately true if the substances compared show a certain degree of correspondence.

H. M. D.

Conductivity and Ionisation of Polyionic Salts. ARTHUR A. NOYES and JOHN JOHNSTON (*J. Amer. Chem. Soc.*, 1909, 31, 987—1009).—In an earlier paper (Abstr., 1908, ii, 347) an account was given of a study of the ionisation and conductivity of various salts in aqueous solution through a wide range of temperature. As these salts contained only univalent and bivalent ions, the investigation has now been extended to salts containing ions of higher valency as well as to other salts of the uni-bivalent type.

Measurements have been made of the conductivity of aqueous solutions of various concentrations and at temperatures ranging from 0° to 156°, of one uni-univalent salt, potassium nitrate; two uni-bivalent salts, potassium oxalate and calcium nitrate; two uni-tervalent salts, potassium citrate and lanthanum nitrate; and four salts of still higher types, namely, potassium, calcium, and barium ferrocyanides, and lanthanum sulphate. The results show that the principles previously derived (*loc. cit.*) from a study of the salts of uni-univalent and uni-bivalent types apply also to those of higher types.

The depression of the f. p. caused by most of the salts studied has also been determined. From these measurements, the mol. number, i (the number of mols. resulting from one formula weight of the salt), has been calculated, and compared with the mol. number derived from the conductivity by the expression: $i = 1 + (n - 1)(\Lambda/\Lambda_0)$. Between the two values thus obtained for i , considerable differences exist which cannot be explained. E. G.

Change of the Equivalent Conductivity of Ions with the Temperature. JOHN JOHNSTON (*J. Amer. Chem. Soc.*, 1909, 31, 1010—1020).—In a study of the conductivity of polyionic salts (preceding abstract), the values were required of the equivalent conductivity, Λ_0 , at zero concentration between 0° and 156°. Since actual measurements with extremely dilute solutions are not trustworthy, the values have been calculated on the assumption that at the higher temperatures the equivalent conductivities of the potassium and chloride ions are equal.

The results show that the equivalent conductivity of each of the ions of the salts studied (*loc. cit.*), except the hydrogen and hydroxyl ions, is a function of the fluidity, ϕ , of water, of the form $\Lambda = k\phi^m$, where m is a constant for each ion varying between 0.81 and 1.03 for the different ions. It is also shown that the relation between Λ and the temperature t can be expressed by the equation: $\Lambda = (1/k)(t + 43.25)^p$. Values of the constants p and of $\log k$ are given, so that the conductivity of any ion at any temperature can be calculated.

Values of the ratio Λ/ϕ are also given for the various ions at the different temperatures, and these indicate that the ratio decreases as the temperature increases, the decrease being greater the greater the conductivity, and also that the exceptional behaviour of some of the ions, especially those of higher valency, is due to a change in their state of hydration with the temperature.

It is shown, by means of the data published by Dutoit and Duperthuis (this vol., ii, 120), that analogous results obtain with solutions of sodium iodide in various organic solvents. E. G.

Electrical Conductivity and Plasticity of Isomorphous Mixtures of Lead with Indium and Thallium. NICOLAI S. KURNAKOFF and S. F. SCHEMTSCHUSCHNY (*Zeitsch. anorg. Chem.*, 1909, **64**, 149—183).—Lead and indium form a complete series of isomorphous mixtures. The electrical conductivity measured on drawn wires has been determined at 25° and 100°. The conductivity curve and the curve of temperature-coefficients of the resistance have the U-shape characteristic of isomorphous series. The plasticity is measured by determining the pressure required to produce flow through a given opening at the ordinary temperature. Using a cylinder 8.66 mm. in diameter and an aperture 2.81 mm., a pressure is required which varies from 10.6 kilograms per sq. mm. for pure lead and 3.06 for pure indium to 23.72 for a mixture of equal atomic proportions of the two metals. The curve is the reverse of the conductivity curve.

Lead and thallium (Kurnakoff and Pushin, *Abstr.*, 1907, ii, 262) form two series of solid solutions, α from 0 to 6.5 and β from 24.7 to 100 atomic % Pb. There is a maximum on the freezing-point curve at about 36 atomic % Pb, but this does not correspond with any compound, although Lewkonja (*Abstr.*, 1907, ii, 261) assumes the existence of PbTl_2 . The conductivity and temperature-coefficient curves are quite continuous throughout the β -range, indicating a continuous series of solid solutions without any compound. The conductivity of thallium is lowered by the addition of lead, reaching a minimum at 3 atomic % Pb, and then rising to a maximum near the original value. The existence of a third solid solution, γ , is thus indicated lying between the α and β ranges. A quite similar curve is given by the pressures required to produce flow.

Measurements of the plasticity of crystalline salts show that the pressure required to produce flow diminishes in the series: alkali chloride, bromide, iodide; and rubidium, potassium, ammonium, but increases in the series silver chloride, bromide, iodide. Salts containing water of crystallisation flow under a low pressure. Among metals, the pressure is found to increase in the order Na, In, Tl, Pb, Sn, Bi, Cd, Zn. The hardness, measured by Brinell's ball test, gives a curve closely parallel with that of the pressure, and either method may be used indifferently to measure hardness. C. H. D.

New Method for Measuring the Electrolytic Dissociation of Water. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1909, **31**, 1136—1138).—It has been shown (*Abstr.*, 1907, ii, 942) that the velocity coefficient, k , of the mutarotation of dextrose in aqueous, acid, or alkaline solution is given by the expression: $A + B(\text{H}^+) + C(\text{OH}')$, where A , B , and C are constants, and H^+ and OH' the concentrations of the hydrogen and hydroxyl ions in the solutions. If the velocity coefficient in aqueous solution is written k_w , and the hydrogen ion concentration, which in this case is equal to that of the hydroxyl ion, is written H^*_w , we have $k_w = A + (B + C)\text{H}^*_w$, which gives

$$\text{H}^*_w = (k_w - A)/(B + C).$$

This relation affords a new method for determining the electrolytic dissociation of water, since k_w , A , B , and C can be found experimentally by determining the rate of mutarotation of dextrose in aqueous,

acid, and alkaline solutions. The method is not very accurate, but it is probable that better results could be obtained from measurements with lævulose. E. G.

Electromotive Forces Produced by Acid and Alkaline Solutions Streaming through Glass Capillary Tubes. ALEXANDER T. CAMERON and ERICH OETTINGER (*Phil. Mag.*, 1909, [vi], 18, 586—603).—When aqueous solutions are caused to flow through a capillary tube containing electrodes, potential differences are established, and these have been measured for very dilute solutions of acids and alkali hydroxides. From the results the authors draw the conclusion that the value of 5 volts, given by Helmholtz and Dorn as the potential difference between glass and water, is approximately correct. For dilute solutions of acids and alkalis (1/1000 to 1/5000 normal), the corresponding potential differences are about 0·5 volt smaller or larger. Although the sign of the change in the potential difference is that predicted by Helmholtz's theory, the magnitude is about three times as large as that indicated by theory. H. M. D.

Electromotive Force of Iodine Concentration Cells, One Electrode of which is Saturated with Iodine. ARTHUR P. LAURIE (*Zeitsch. physikal. Chem.*, 1909, 67, 627—639. Compare Abstr., 1908, ii, 1007).—The proportion of iodine ions in solutions of potassium iodide of different concentrations, saturated with iodine, has been determined by measurements of the *E.M.F.* of iodine concentration cells. One electrode was surrounded by a solution of potassium iodide containing a little iodine, the other by solutions of potassium iodide of varying concentration, saturated with iodine, and the values of the I^- -ion concentration were calculated by substitution in Nernst's equation in the usual way. The contact differences of potential were corrected for by using a concentrated solution of ammonium nitrate. Measurements of the solubility of iodine in solutions of potassium iodide from 0·344*N* to *N* have also been made at 25°.

The results show that in solutions of potassium iodide from 0·025*N* to *N*, saturated with iodine, the number of molecules of the free potassium iodide and bound iodine is approximately equal to that of the total potassium iodide added, hence even in the stronger solutions there is very little formation of polyiodides higher than KI_3 . In a solution 3*N* with reference to potassium iodide, there is distinct evidence of polyiodide formation, although the proportion is still comparatively small.

In another series of measurements at 20·4°, the proportion of I^- -ions present in solutions containing iodine in varying proportions up to saturation has been determined, and certain conclusions are drawn from the results. In a normal solution of potassium iodide containing very little iodine, the dissociation constant for the equilibrium $I_3 \rightleftharpoons I_2 + I^-$ is the same as that in dilute solutions, but alters when more iodine is present, the I_3 molecules becoming more stable.

G. S.

Piezoechemical Studies. III. Influence of Pressure on the E.M.F. of the Weston Element. ERNST COHEN and L. R. SINNIGE (*Zeitsch. physikal. Chem.*, 1909, **67**, 513—537. Compare this vol., ii, 291, 641, 796).—It is shown that the influence of pressure on the E.M.F. of the Weston and Clark cells is satisfactorily represented by means of the equation: $E_{\pi} - E_0 = \pi(v_1 - v_2)(1)$, where v_1 and v_2 represent the volumes of a gram-equivalent of the cell-materials before and after the passage of 96,540 coulombs of electricity through the cell, and π is the pressure.

The total change of volume ($v_1 - v_2$) occurring in the Weston cell as a consequence of the passage of 96,540 coulombs is considered as regards its separate parts, which are calculated from known data, or have been determined specially. In the course of the experiments it has been found that D_4^{25} for cadmium is 8.643, and D_4^{25} for mercurous sulphate, 7.064. The value of $v_1 - v_2$ is -6.64 c.c. at 25° . When this value (with the sign reversed) is substituted in equation (1), $dE/d\pi = 6.97 \times 10^{-6}$ volts per atmosphere at 25° . $dE/d\pi$ has also been determined directly between 0 and 1000 atmospheres, as described in the previous paper, and the value 6.32×10^{-6} volts per atmosphere at 25° was obtained, in good agreement with the above value.

Similar measurements have also been made with the Clark cell. The value of $dE/d\pi$, obtained directly and according to equation (1), is in both cases 13.0×10^{-6} volts per atmosphere. G. S.

Oxide Theory of Oxygen Electrodes. VI. RICHARD LORENZ [and, in part, PERCY E. SPIELMANN and N. KONSTANTINOFF (*Zeitsch. Elektrochem.*, 1909, **15**, 661—666. Compare this vol., ii, 640).—The arrests in the discharge curve of a polarised platinum anode at higher potentials than 0.93 volt probably correspond with unknown higher oxides of platinum. An electrode immersed in solutions containing persulphuric acid showed potentials varying from 0.88 to 1.11 volts; these results cannot be interpreted at present. The curve representing the current as a function of the E.M.F. applied to a pair of platinum electrodes shows very indistinct indications of a change in the process occurring at the anode at 0.8 to 1, 1.4, 1.6, and 2.1 volts with sulphuric acid as electrolyte; when a concentrated solution of hydrochloroplatinic acid is used, the points at 1.0 and 1.6 volts become very sharply defined, indicating that platinum ions take part in the change.

In order to obtain an arrest on the discharge curve of a polarised lead anode, it is necessary to polarise with a certain minimum E.M.F., which is from 0.38 to 0.67 volt higher than the corresponding value found on discharging the electrode. Furthermore, the curve connecting current and applied E.M.F. during the change exhibits discontinuities, and in order to develop an arrest in the discharge curve it is necessary to pass one of these discontinuities on the charge curve. The author, therefore, assumes that these points on the charge curve are not, as Le Blanc thinks, due to the discharge of an ion in the solution, but rather to the formation of some compound at the electrode. Each such compound requires a definite E.M.F. to produce it, and yields a definite lower E.M.F. when it is decomposed during the discharge of the electrode. T. E.

The Metal Tungsten as Valve Electrode. L. H. WALTER (*J. Proc. Inst. Elect. Eng.*, 1909, 43, 547—552).—The tungsten anode was made from the filament of an Osram lamp; one end was embedded in Wood's metal, which served as a support; the cathode was a lead cylinder with about 30 sq. cm. area; the anode had an area of about 0.1 sq. cm. The tungsten anode has a very pronounced valve action, the insulating film being formed even with an alternating current. The maximum voltage which the tungsten anode will resist is higher than that found for aluminium, but lower than for tantalum. In sulphuric acid (D 1.2) at 15° it is about 90 volts, and it is not very much reduced by rise of temperature. The resistance falls off very quickly when the current is interrupted. T. E.

Modification of Ostwald's Bromide Voltameter. WARREN K. LEWIS (*J. Amer. Chem. Soc.*, 1909, 31, 1145—1146).—In the course of certain work, a voltameter was required for use with exceedingly small currents, the total precipitate being only a few milligrams. It was necessary that the instrument should be free from polarisation and *E.M.F.* due to concentration cell effects or other electrochemical action. The Ostwald bromide voltameter (Oswald-Luther, *Phys.-Chem. Messungen*, 430) appeared well adapted for the purpose, but the platinum point used as a cathode introduces polarisation and the possibility of a cell effect. This objection was overcome by means of the following modification.

The cathode was separated from the anode by a porous cell, and was surrounded by potassium bromide solution of the same strength as that around the anode. Precipitated silver bromide was added to the cathode compartment in sufficient quantity to cover the electrode. Since the potassium bromide solution in both compartments was saturated with silver bromide, the silver ion concentration about both electrodes was the same, and any possible cell effect was thus eliminated. Polarisation was avoided, since the current densities employed were exceedingly small and the solid bromide about the cathode therefore maintained the silver concentration of the solution. The electrodes employed were silver plates with silver or platinum leads. From four to eight separate anodes could be connected simultaneously with a common cathode in the porous cup. This voltameter gave excellent results with current densities precipitating not more than 1.5—2.0 mg. of bromine per hour. E. G.

Apparatus for the Determination of Transport Numbers. ALEXANDER FINDLAY (*Chem. News*, 1909, 100, 185).—The apparatus consists of three tubes, all of which are furnished with small glass taps, through which the solution can be run out. The two outer tubes contain the electrodes, and are connected to a U-tube by means of rubber tubing furnished with spring clips. During an experiment, the clips are kept open, but at the end thereof they are closed, and the anode liquid run off for analysis through the tap at the bottom of the appropriate tube into a weighed flask. This tube and the electrode are washed with a small quantity of the original solution, the washings

being also run into the same weighed flask. The solution in the connecting U-tube can then be run off for analysis.

For the determination of transport numbers in cases where a gas is evolved at the cathode, the cathode outer tube is replaced by a special tube containing a mercury electrode, similar to that used by Hopfgartner (Abstr., 1892, ii, 151).

The apparatus is simple to use, and can be employed in the case of all solutions. T. S. P.

Electrolytic Production of Silver Mirrors. RUDOLF LOHNSTEIN (*Physikal. Zeitsch.*, 1909, 10, 672—673).—When a current of electricity is passed through distilled water between silver electrodes, the formation of a silver mirror on the walls of the glass vessel in the neighbourhood of the cathode can frequently be observed. The mirror formation is appreciably facilitated if reducing substances, such as sugars, glycerol, gelatin, or sodium potassium tartrate, are added to the distilled water. In the case of the last substance, the amount added must be very small, for it is essential that the solution should have a small conductivity. Addition of very small quantities of alkali hydroxide or ammonia to the sugar solutions is also favourable to the production of a mirror.

The phenomenon is supposed to be due to the formation of silver hydroxide at the anode; this is then reduced to metallic silver, which is colloiddally dissolved, but separates out under the influence of the current. H. M. D.

Magnetic Properties of Alloys of Manganese, Aluminium and Copper. ALEXANDER D. ROSS and ROBERT C. GRAY (*Zeitsch. anorg. Chem.*, 1909, 63, 349—352. Compare Heusler and Richarz, this vol., ii, 240).—A Heusler's alloy, quenched from 400°, gave a very low hysteresis without reduction of the permeability. The compound Cu_3Al plays an important part in determining the magnetic properties of these alloys. C. H. D.

Magnetic Function of Oxygen in Organic Compounds. PAUL PASCAL (*Compt. rend.*, 1909, 149, 508—510. Compare this vol., ii, 487, 788).—The molecular magnetic susceptibility of a simple organic compound is equal to the sum of the susceptibilities of its atoms plus a certain constant when an ethylenic linking or benzene nucleus is present. Oxygen loses its distinctive magnetic character in combination, and may be diamagnetic or paramagnetic according to the distribution of its valencies. The average results obtained by the study of a large number of alcohols, acids, salts, aldehydes, ketones, etc., are as follows: oxygen combined with two other atoms is diamagnetic with susceptibility -50.10^{-7} ; combined (bivalent) to one carbon atom which is not in combination with any other oxygen it is paramagnetic ($+20.10^{-7}$); if a second oxygen atom is connected univalently to the carbon atom, the doubly linked oxygen is diamagnetic (-35.10^{-7}).

In addition to the atomic effects, the structure of an oxygenated molecule may influence its magnetic properties. Every tertiary

carbon atom has an extra susceptibility of -10.10^{-7} , whilst for a quaternary atom -15.10^{-7} must be added. Nitrogen has a susceptibility of -58.10^{-7} , except when combined with tertiary carbon, when it must be taken as -50.10^{-7} . By means of the rules given, the susceptibility of a substance of known constitution can be calculated with an error of less than 1%, and, conversely, the constitution of a new substance might be decided by its magnetic susceptibility with a precision approaching that of the refractive index method. In the case of several isodynamic compounds, the susceptibility falls between that calculated for the enol and ketonic forms. Ethyl acetoacetate is almost entirely enolic when fresh, but soon changes in contact with a trace of pyridine into the ketonic form. R. J. C.

Thermal Properties of Silver Nitrate. JOSEPH GUINCHANT (*Compt. rend.*, 1909, 149, 569—571. Compare this vol., ii, 790).—From the latent heat of fusion (17.6 cal.) and the melting point (209°) of silver nitrate, its cryoscopic constant, calculated in the manner previously given, should be 264. The values obtained by extrapolation of the cryoscopic constant with infinitely dilute solutions of the following substances are: lithium nitrate 262, potassium nitrate 260, thallium nitrate 260, lead nitrate 283, silver chloride 273, silver iodide 305, silver fluoride 249, silver iodate 290, silver sulphate 289. The experimental molecular lowering, which varies little with the concentration of the solute, is, therefore, normal. Silver nitrate is a practicable solvent for cryoscopic work provided that moisture is carefully excluded.

The eutectic point of thallium nitrate-silver nitrate mixtures (72°) occurs at approximately equimolecular proportions, but microscopic examination shows that the crystals of the two nitrates exist side by side.

On cooling silver nitrate from its melting point, a sudden expansion at about 160° invariably breaks the test-tube. The transformation of monoclinic into orthorhombic silver nitrate at 159° is accompanied by dilatation. This has been measured directly on rods of silver nitrate, and is about 0.22%, a value considerably below that calculated from Retger's results (*Abstr.*, 1889, 931), namely, 1.15%. The contraction of a crystal of silver nitrate at 159° varies, moreover, with the orientation, being greatest (0.6%) in a direction perpendicular to the plane of the optic axes. R. J. C.

Relations between the Cryoscopic Constants and Position Isomerism in Disubstituted Derivatives of Benzene: Influence of the Substituent Groups. TEMISTOCLE JONA (*Gazzetta*, 1909, 39, ii, 289—311).—The author has determined the molecular depressions (K) of the freezing points (F) of a number of ortho-, meta-, and para-disubstituted derivatives of benzene, using as solutes naphthalene, methyl salicylate, phenetole, toluene, and benzil. The results, together with the latent heats of fusion (W) calculated from van't Hoff's formula, $K = 0.02.T^2/W$, in cal. per one gram are given in the following table; the values of the m. p. are also given, these differing in some cases from the numbers previously given by different observers.

	Ortho.			Meta.			Para.		
	<i>F.</i>	<i>K.</i>	<i>W.</i>	<i>F.</i>	<i>K.</i>	<i>W.</i>	<i>F.</i>	<i>K.</i>	<i>W.</i>
Nitrotoluene	-4.14°	71.8	20.14	16.0°	68.4	24.36	54.0°	78.0	27.41
Bromonitrobenzene.	36.5	91.8	20.86	54.0	87.5	24.44	124.0	115.3	27.33
Chloronitrobenzene.	32.5	75.0	24.88	44.4	60.7	33.19	83.0	109.0	23.25
Chlorophenol.....	7.0	77.2	20.55	28.5	83.0	21.78	37.0	85.8	22.40
Dihydroxybenzene .	104.0	71.3	39.86	118.0	65.0	47.04	169.0	—	—

Quinol is unsuitable for use as a cryoscopic solvent, as its m. p. is altered by fusion and re-solidification, even in an atmosphere of hydrogen.

It will be seen that the cryoscopic constants of the para-derivatives are, in all cases, greater than those of the corresponding ortho- and meta-derivatives. Further, except with the chlorophenols, the constants for the meta-derivatives are less than those of the corresponding ortho-derivatives, in spite of the fact that the squares of the absolute m. p.'s are much greater for the meta-compounds than for the ortho-derivatives. As the molecular weights of the solvents increase, in either the ortho- or the meta- or the para-series, the cryoscopic constant exhibits a tendency to increase; the lowerings of the values of the constant for the three nitrotoluenes, even although the molecular weight increases, are probably related to the presence of a methyl group in the nucleus. The results are not in agreement with Raoult's "general law of freezing," which states that if 1 mol. of any substance is dissolved in 100 mols. of any solvent, it effects a depression of the freezing point which is approximately constant and equal to about 0.62°. T. H. P.

Internal Heat of Vaporisation. JAMES E. MILLS (*J. Amer. Chem. Soc.*, 1909, 31, 1099—1130).—The author has calculated the internal heat of vaporisation of thirty-eight substances by means of the equations of (1) Clausius, (2) Mills (Abstr., 1907, ii, 226), and (3) Crompton (Proc., 1901, 17, 61). The results afford conclusive evidence that these equations are in substantial agreement, and that the divergences in the values obtained are due to experimental error. The interpretation of each equation is fully discussed. E. G.

Partial Vapour Pressures of Binary Mixtures. MARTIN A. ROSANOFF and C. W. EASLEY (*J. Amer. Chem. Soc.*, 1909, 31, 953—987).—A new method of measuring the partial vapour pressures of binary mixtures has been described by Rosanoff, Lamb, and Breithut (this vol., ii, 379) which depends on the fact that if a mixed vapour of constant composition is passed through a liquid mixture of the same substances, the composition and temperature of the liquid will steadily change until complete equilibrium, as regards both temperature and pressure, has been established.

The present paper contains an account of the determination of the composition of the vapours in equilibrium with several typical binary mixtures, namely, carbon tetrachloride and benzene, carbon disulphide and acetone, chloroform and acetone, ethylene chloride and benzene, carbon disulphide and tetrachloride, and acetic acid and benzene. Most of these mixtures have been investigated isothermally by

Zawidzki (Abstr., 1901, ii, 6). The new measurements, however, have been carried out, not at constant temperature, as were Zawidzki's, but under the constant pressure of 760 mm. The apparatus employed is described with the aid of a diagram. The results are tabulated and plotted as curves, and are shown to agree fairly closely with those of Zawidzki (*loc. cit.*).

A discussion is given of certain theoretical considerations suggested by the results of this work. E. G.

Molecular Attraction. VIII. JAMES E. MILLS (*J. Physical Chem.*, 1909, 13, 512—531. Compare Abstr., 1906, ii, 216; 1907, ii, 226).—The equation $(L - E)/(\sqrt[3]{d} - \sqrt[3]{D}) = \text{const.}$, where L denotes the heat of vaporisation, E the energy spent in overcoming external pressure, and d and D are the densities of liquid and saturated vapour respectively, has now been further tested by means of very accurate data communicated to the author by Young, but not yet published. The values of the constant for each thirty-eight substances through a wide range of temperature are tabulated, and it is shown that, except at 0° and in the neighbourhood of the critical temperature, there is not a single deviation from the mean value of the respective constants greater than 2% for twenty-five of the substances examined. Certain associated liquids, such as water, the alcohols, and acetic acid, show larger deviations. Certain of the deviations for non-associated substances are probably due to errors in determining the physical constants.

The author points out that these results prove the correctness of the above equation quite independently of the validity of the assumptions on the basis of which it has been derived theoretically. It is shown to lead to the result that in any normal substance the heat given out as the molecules approach each other, multiplied by the distance apart of the molecules, is a constant. G. S.

Thermochemistry of the Halogens. JOHN C. THOMLINSON (*Chem. News*, 1909, 100, 185—186. Compare Abstr., 1908, ii, 1016).—Using the method previously described and assigning definite structural formulæ to the various compounds, the author calculates the heats of formation of chlorine monoxide, chloric acid in water, iodine pentoxide, and bromine pentoxide to be respectively -13·311, 47·880, 57·960, and 37·962 calories. The actual heats of formation in the first three cases are: -17·930, 48·000, and 60·244 calories respectively. T. S. P.

Heat of the Reaction of Formation of Quinone Dichloroimides. W. SVENTOSLAVSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 839—849).—From the values of the molecular heats of combustion, benzene, 779·2 Cal.; benzoquinone, 656·3 Cal.; naphthalene, 1233·6 Cal., and α -naphthaquinone, 1103·7 Cal., it would appear that the heat of formation of the linking 2 (C=O) and of the re-grouping of the naphthalene nucleus into the quinonoid configuration is greater by 7·00 (129·9—122·9) Cal. than the heat involved in the formation of the same linking 2 (C=O) and the rearrangement of the benzene nucleus into the paraquinone. The figures given above are, however,

not sufficiently exact to render this difference of 7 Cal. accurate to less than 3.0—4.0 Cal.

In view of this large possible error, the author has determined directly the heats of formation of benzoquinonedichloroimide and α -naphthaquinonedichloroimide from the hydrochlorides of the corresponding diamino-compounds. He finds that the presence of free hydrochloric acid is not necessary for the occurrence of this reaction, which is effected either by chlorine water or by calcium hypochlorite. The results of his measurements are expressed as follows:

$C_6H_4(NH_2)_2 \cdot 2HCl$ (diss.) + $3Ca(OCl)_2$ (diss.) = $C_6H_4N_2Cl_2$ (solid) + $3CaCl_2$ (diss.) + 90.00 Cal.; $C_{10}H_6(NH_2)_2 \cdot 2HCl$ (diss.) + $3Ca(OCl)_2$ (diss.) = $C_{10}H_6N_2Cl_2$ (diss.) + $3CaCl_2$ (diss.) + 96.86 Cal.; $C_6H_4(NH_2)_2 \cdot 2HCl$ (diss.) + $3Cl_2$ (diss.) = $C_6H_4N_2Cl_2$ (diss.) + $6HCl$ (diss.) + 68.08 Cal.; $C_{10}H_6(NH_2)_2 \cdot 2HCl$ (diss.) + $3Cl_2$ (diss.) = $C_{10}H_6N_2Cl_2$ (diss.) + $6HCl$ (diss.) + 74.82 Cal.; $C_6H_4(NH_2)_2 \cdot 2HCl$ (solid) + $3Ca(OCl)_2$ (diss.) = $C_6H_4N_2Cl_2$ (solid) + $3CaCl_2$ (diss.) + 83.31 Cal.; $C_{10}H_6(NH_2)_2 \cdot 2HCl$ (solid) + $3Ca(OCl)_2$ (diss.) = $C_{10}H_6N_2Cl_2$ (solid) + $3CaCl_2$ (diss.) + 89.13 Cal.; $C_6H_4(NH_2)_2 \cdot 2HCl$ (solid) + $3Cl_2$ (diss.) = $C_6H_4N_2Cl_2$ (solid) + $6HCl$ (diss.) + 61.39 Cal.; $C_{10}H_6(NH_2)_2 \cdot 2HCl$ (solid) + $3Cl_2$ (diss.) = $C_{10}H_6N_2Cl_2$ (solid) + $6HCl$ (diss.) + 67.09 Cal.

The heat of formation of solid α -naphthaquinonedichloroimide from the solid diamino-hydrochloride is hence found to be 5.82 Cal. (89.13—83.31) or 5.7 Cal. (67.09—61.39) greater than the heat of formation of solid benzoquinone dichloroimide. The heat of formation

of the grouping $ClN:\langle \text{benzene ring} \rangle:NCl$ in the naphthalene nucleus is hence 5.76 Cal. greater than its heat of formation in the benzene nucleus; the experimental error in this value is not more than 0.7—0.9 Cal.

T. H. P.

Thermochemical Investigations on Nitro-compounds. W. SVENTOSLAVSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 920—925).—The author has measured the molecular heats of combustion of the following compounds.

Nitromethane, 169.95 Cal. (*v* const.), 169.5 Cal. (*p* const.), 178.7 Cal. (gas, *p* const.). α -Nitropropane, 477.8 Cal. (*v* const.), 478.0 Cal. (*p* const.), 489.4 Cal. (gas, *p* const.) (compare Thomsen, *Thermochem. Untersuch.*, 1886, 4, 215; Berthelot and Matignon, *Abstr.*, 1894, i, 158).

Denoting the heats of formation of the various atomic linkings as follows: C—H, *x*; C—C, *y*; C—N, β ; N—O, μ ; O—O, ω ; H—O, *u*; C—O, *z*; and N—N, *n*, the author calculates the values of $[\beta - z + (\omega - n)/2 + 4\mu - n - 2\omega]$ for various nitro-derivatives to be: nitromethane, -20.0 Cal.; nitroethane, -15.3 Cal.; α -nitropropane, -14.2 Cal.; nitrobenzene, -14.0 Cal.; *o*-dinitrobenzene, -17.4 Cal.; *m*-dinitrobenzene, -14.1 Cal.; and *p*-dinitrobenzene, -13.1 Cal. (compare this vol., ii, 547).

The thermochemical value of the C—N^{III} linking in amines seems to be identical with that of the C—N^V linking in nitro-compounds.

T. H. P.

Calorimetric Investigation of the Formation of Azo-compounds. W. SVENTOSLAVSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 925—932).—The calorimetric measurements here described, dealing with the heats of formation of *p*-aminoazobenzene and naphthaleneazo- α -naphthylamine, were made with the object of arriving at values for the heat of formation of the linking (N:N) in azo-compounds. The results are expressed shortly as follows: $2\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ (solid) + NaNO_2 (solid) + $n\text{CH}_3\cdot\text{CO}_2\text{H}$ (liq.) = $\text{C}_{10}\text{H}_7\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ (solid) + $\text{CH}_3\cdot\text{CO}_2\text{Na}$ (diss.) + $2\text{H}_2\text{O}$ (diss.) + $(n-1)\text{CH}_3\cdot\text{CO}_2\text{H}$ (liq.) + 47.44 Cal.; $2\text{Ph}\cdot\text{NH}_2$ (liq.) + NaNO_2 (solid) + $n\text{CH}_3\cdot\text{CO}_2\text{H}$ (liq.) = $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (solid) + $\text{CH}_3\cdot\text{CO}_2\text{Na}$ (diss.) + $2\text{H}_2\text{O}$ (diss.) + $(n-1)\text{CH}_3\cdot\text{CO}_2\text{H}$ (liq.) + 43.20 Cal.

The heat of formation of the linking (N:N) in naphthaleneazo- α -naphthylamine is hence 4.24 Cal. greater than its heat of formation in *p*-aminoazobenzene. This result is similar to those found for the heats of formation of other atomic linkings in the naphthalene and benzene nuclei (compare this vol., ii, 862).

Further considerations lead to the conclusion that the heat of formation of the linking (N:N) is greater by 45.5 Cal. than the heat of formation of two linkings of nitrogen in the molecule of that element.

T. H. P.

Thermochemistry of Nitroso-compounds. W. SVENTOSLAVSKY (*J. Russ. Phys. Chem. Soc.* 1909, 41, 933—950. Compare this vol., ii, 547, and preceding abstracts).—From the results of measurements of the heats of formation of phenylethylnitrosoamine and diphenylnitrosoamine, namely, NHPhEt (diss.) + NaNO_2 (solid) + $\text{C}_2\text{H}_4\text{O}_2$ (liq.) = $\text{NPhEt}\cdot\text{NO}$ (diss.) + $\text{C}_2\text{H}_3\text{O}_2\text{Na}$ (diss.) + H_2O (diss.) + 11.66 Cal. and NHPh_2 (diss.) + NaNO_2 (solid) + $\text{C}_2\text{H}_4\text{O}_2$ (liq.) = $\text{NPh}_2\cdot\text{NO}$ (diss.) + $\text{C}_2\text{H}_3\text{O}_2\text{Na}$ (diss.) + H_2O (diss.) + 13.45 Cal. (compare this vol., ii, 794), it was concluded that the formation of the linking (N-N) in phenylethylnitrosoamine is less by 1.79 Cal. than the heat of formation of the same linking in diphenylnitrosoamine. This conclusion was based on the assumption that the difference between the heats of solution of phenylethylamine and its nitroso-derivative in acetic acid differed little from the difference between the heats of solution of diphenylamine and diphenylnitrosoamine in acetic acid, which assumption is now shown by the results described in the present paper to be erroneous.

The molecular heat of combustion of dimethylnitrosoamine has the value 394.3 Cal. (*v* or *p* const.) or 407.86 Cal. (gas). Denoting the heat of formation of the linking (N-N) by n , and that of (N:N) by $3n$, the value of $(n-n_1)$ is calculated to be 19.0 Cals.

The heat of formation of phenylethylnitrosoamine is found to be: NHPhEt (liq.) + NaNO_2 (solid) + $\text{C}_2\text{H}_4\text{O}_2$ (liq.) = $\text{NPhEt}\cdot\text{NO}$ (liq.) + $\text{C}_2\text{H}_3\text{O}_2\text{Na}$ (diss.) + H_2O (diss.) + 18.61 Cal., which gives the value 14.0 Cal. for $(n-n_1)$. In presence of excess of nitrous acid, this heat of formation is expressed by the equation: NHPhEt (liq.) + HNO_2 (diss.) = $\text{NPhEt}\cdot\text{NO}$ (liq.) + H_2O (diss.) + 18.97 Cal. The agreement between these two results shows that the formation of the nitroso-compound is quantitative as well when excess of nitrite as when excess of amine is present, and that the sum of the heats of the

accessory processes, namely, the solution of water in acetic acid and the solution of sodium nitrite in acetic acid with formation of sodium acetate and nitrous acid, is zero.

The heats of formation of diphenylnitrosoamine and $\beta\beta$ -dinaphthyl-nitrosoamine are as follows: NHPh_2 (diss.) + NaNO_2 (solid) + $\text{C}_2\text{H}_4\text{O}_2$ (liq.) = $\text{NPh}_2\cdot\text{NO}$ (diss.) + $\text{C}_2\text{H}_3\text{O}_2\text{Na}$ (diss.) + H_2O (diss.) + 13.45 Cal., or with NHPh_2 (solid) and $\text{NPh}_2\cdot\text{NO}$ (solid), + 14.92 Cal.; and $\text{C}_{20}\text{H}_{15}\text{N}$ (diss.) + NaNO_2 (solid) + $\text{C}_2\text{H}_4\text{O}_2$ (liq.) = $\text{C}_2\text{H}_3\text{O}_2\text{Na}$ (diss.) + H_2O (diss.) + $\text{C}_{20}\text{H}_{14}\text{ON}_2$ (diss.) + 14.62 Cal. So that, in this case, replacement of the phenyls by naphthyls results in an increase of the heat of formation by 1.17 Cal. (14.62—13.45). The heat of reaction of 1 mol. NaNO_2 on excess of diphenyl-*m*-phenylenediamine is 16.74 Cal., whilst the formation of diphenyl-*m*-phenylenedinitrosoamine is represented by: $\text{C}_6\text{H}_4(\text{NHPh})_2$ (diss.) + NaNO_2 (diss.) + $2\text{C}_2\text{H}_4\text{O}_2$ (liq.) = $\text{C}_6\text{H}_4(\text{NO}\cdot\text{NPh})_2$ (diss.) + $2\text{H}_2\text{O}$ (diss.) + $2\text{C}_2\text{H}_3\text{O}_2\text{Na}$ (diss.) + 2×19.56 Cal.

These results, which are discussed in relation with those previously obtained, indicate the identity of the heats of formation of the linkings ($\text{N}\cdot\text{N}^{\text{III}}$) and ($\text{N}\cdot\text{N}^{\text{V}}$), which shows that these heats of formation are subject to the influences of the atoms and radicles which surround them, and are independent of the chemical characters of the whole compounds.

T. H. P.

Heat of Combination of Acidic Oxides with Sodium Oxide.

IV. Heat of Formation of Trisodium Orthophosphate, Trisodium Orthoarsenate, the Oxides of Antimony and Bismuth Trioxide. WILLIAM G. MIXTER (*Amer. J. Sci.*, 1909, [iv], 28, 103—111. Compare this vol., ii, 644).—The heats of formation have been calculated from the thermal data obtained in the oxidation of the elements or lower oxides by means of sodium peroxide. The trustworthiness of the method is shown in the agreement of some of the constants with the values obtained by other methods: $3\text{Na}_2\text{O} + \text{P}_2\text{O}_5 = 2\text{Na}_3\text{PO}_4 + 233.392$ Cal.; $3\text{Na}_2\text{O} + \text{As}_2\text{O}_5 = 2\text{Na}_3\text{AsO}_4 + 202.8$ Cal.; $3\text{Na}_2\text{O} + 2\text{Sb} + 5\text{O} = 2\text{Na}_3\text{SbO}_4 + 393.3$ Cal.; $2\text{Sb} + 3\text{O} = \text{Sb}_2\text{O}_3 + 163.0$ Cal.; $2\text{Sb} + 4\text{O} = \text{Sb}_2\text{O}_4 + 209.8$ Cal.; $2\text{Sb} + 5\text{O} = \text{Sb}_2\text{O}_5 + 229.6$ Cal.

H. M. D.

Thermochemistry of Phosphorus Compounds. PAUL LEMOULT

(*Compt. rend.*, 1909, 149, 554—556. Compare this vol., ii, 936).—The heats of combustion of triphenylphosphine, triethylphosphine, *o*-phosphoranilide, and *o*-phosphor-*o*-toluidide have been determined by the bomb calorimeter. Combustion is not complete in absence of potassium nitrate (*loc. cit.*), but the decomposition of the latter introduces an uncertainty in the thermal values, and it has not been employed. The error from unburnt phosphorus is of the order 0.5%. Also, in the case of triethylphosphine, a small proportion distilled into the water at the bottom of the bomb and escaped combustion. The following values were obtained for the combustion of 1 gram of substance at constant pressure: triphenylphosphine, 2480.7 cal.; triethylphosphine, 1249.7 cal.; phosphoranilide, 2458.3 cal.; phosphor-*o*-

toluidide, 2927.7 cal. The corresponding heats of formation are 382.2, 142.1, 168.6, and 189.1 cal. respectively. The heats of formation of the three phosphoric acids being very similar and the ortho-acid constituting 85% of the product, it is assumed in calculating the heats of formation given above that this acid alone is produced. The author calculates that the contribution of the phosphorus atom to the heat of combustion of phosphine is 228.7 Cal., of triphenylphosphine 232.2 Cal., and of triethylphosphine 229.7 Cal., whereas the heat of combustion of white phosphorus is 308.5 Cal. Hence the heat of transformation of combined phosphorus into white phosphorus is - 78 Cal. per atom, or - 312 Cal. per molecule of P_4 .

The substitution of phenyl for hydrogen in phosphine increases the heat of combustion by 723.2 Cal. per phenyl group, a value in close agreement with the normal increment of 722 Cal. in compounds not containing phosphorus.

R. J. C.

Heat Effect and Free Energy of Chemical Action in Different Solvents. LEO PISSARJEWSKY and A. SCHELJAPIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 795—813).—In order to study the heat effect of the reaction $2AgCN + KBr \rightleftharpoons KAg(CN)_2 + AgBr$ (which proceeds slowly) in different solvents, the authors have measured the separate heat effects of the two reactions: $AgCN + KCN = KAg(CN)_2$ and $AgBr + 2KCN = KAg(CN)_2 + KBr$. The solvents employed were water and aqueous solutions, of various concentrations, of glycerol and methyl alcohol. Similarly, the heat effect of the reaction $2AgCN + KCNS \rightleftharpoons KAg(CN)_2 + AgCNS$ in water and in aqueous glycerol was arrived at from the measurements for the reactions $AgNO_3 + KCN = AgCN + KNO_3$, $AgNO_3 + 2KCN = KAg(CN)_2 + KNO_3$, and $AgNO_3 + KCNS = AgCNS + KNO_3$.

In the case of the former reaction, if the reacting substances are mixed in such concentrations that, immediately after mixing, the concentration of each is unity, the reaction will proceed in the direction of formation of $KAg(CN)_2$ and $AgBr$, and the measure of the affinity constraining the reaction in that direction will be the maximal work or diminution of free energy, which amounts to 1.118 Cal. in 9.8% aqueous glycerol, and 1.337 Cal. in 99.4% aqueous glycerol. The values of the heat effect, namely, - 0.055 Cal. in the first solution and - 2.667 Cal. in the second, indicate that the reaction should proceed in the opposite direction; such a result was, however, found only in these two instances, and in the majority of cases the heat effect may serve as an approximate measure of the maximal work, and consequently of the affinity. Between the diminution of free energy and the internal friction in the different solvents there exists no such simple relation as was observed by Pissarjewsky and Levites (*Abstr.*, 1908, ii, 570) for the reaction $Ca(OH)_2 + K_2SO_4 \rightleftharpoons CaSO_4 + 2KOH$. The results obtained also indicate that, when the solution contains excess of potassium cyanide, there are present, in addition to the ions $Ag(CN)_2'$, also ions $Ag(CN)_3''$, and possibly some still more complex (compare Bodländer and Eberlein, *Abstr.*, 1904, ii, 401).

The curve expressing the change of the heat effect of the reaction $2AgCN + KCNS \rightleftharpoons KAg(CN)_2 + AgCNS$ on addition of glycerol to

the aqueous solvent is, in general, similar to the curves for the reaction between 2AgCN and KBr in aqueous glycerol and aqueous methyl alcohol.

T. H. P.

Easy Method for Determining Vapour Densities. PHILIP BLACKMAN (*J. Physical Chem.*, 1909, 13, 532—537).—Into a graduated capillary tube (open at both ends, with a tap at one end), which may be bent several times, is sucked a little mercury, then a short thread of the liquid, the vapour density of which is to be determined, and, finally, a little more mercury; the tap is then closed. The length of the thread of liquid between the two threads of mercury is measured, the tube is enclosed in a jacket, heated at constant temperature above the point of vaporisation of the liquid, and the length of the vapour column measured. Some modifications of the method are also described. A formula for calculation and a table of results are given.

G. S.

Viscosity of Certain Gases and Gas Mixtures at Different Temperatures. KARL SCHMITT (*Ann. Physik*, 1909, [iv], 30, 393—410).—Measurements are recorded of the viscosity of helium, argon, hydrogen, oxygen, nitrogen, and air at temperatures ranging from -190° to $+183^{\circ}$. Mixtures of helium and argon, hydrogen and oxygen, hydrogen and nitrogen, and oxygen and nitrogen have also been investigated at different temperatures. The addition of helium to argon increases the viscosity, although the coefficient of viscosity of helium is less than that of argon. A maximum viscosity is reached when the mixed gas contains 40% of helium. Small quantities of oxygen and nitrogen increase the viscosity of hydrogen to a marked extent; on the other hand, the viscosities of oxygen and nitrogen are only slightly altered by the addition of small quantities of hydrogen. The viscosities of the various gas mixtures can in general be represented by means of Sutherland's formula.

H. M. D.

Viscosity of Liquids as a Temperature Function. MARCEL BRILLOUIN (*Ann. Chim. Phys.*, 1909, [viii], 18, 197—213. Compare Thorpe and Rodger, *Phil. Trans.*, 1894, A, 185, 397—710; 1897, A, 189, 71).—The hyperbolic formula of Graetz, $\eta = A(t - t_0)/(t - t_1)$, represents with satisfactory approximation the viscosities measured by Thorpe and Rodger in the case of those liquids the other properties of which (surface tension, density, etc.) are normal. If, however, the results are corrected by reference to a smooth curve plotted about the experimental points, the corrected values do not give such good agreement with the formula as the experimental ones. The author discusses at length the sources of error in drawing a smooth curve by the ordinary flexible laths, etc., and concludes that the "smoothed" results employed by Thorpe and Rodger cannot be so trustworthy as their experimental results. Moreover, the formula adopted by Thorpe and Rodger, namely Slotte's, has no simple theoretical meaning. In Graetz's formula, t_0 is a temperature somewhat above the critical temperature, where the viscosity (η) would be zero, t_1 is a temperature

somewhat below the solidifying point, where the viscosity would be infinitely great, A is the viscosity at a mean temperature $(t_0 + t_1)/2$.

Graetz's formula is in good agreement with the measured viscosities of sixteen hydrocarbons, four halogenated hydrocarbons, and carbon disulphide. In the case of substances like methyl alcohol and water, the surface tension of which is abnormal at low temperatures, the actual viscosity increases more rapidly than the calculated viscosity as the temperature falls. Methyl alcohol above 20° and water above 35° are almost normal, but below these temperatures there is a growing disagreement with the formula. With substances of higher molecular weight and more complicated structure, such as dimethylethylcarbinol, neither Slotte's nor Graetz's formula explains the course of the viscosity curve. The author obtains the best agreement by introducing two new constants, c and c_1 (making five constants in all), and writing the formula thus: $\eta = A \sqrt{T \{ (t - t_1)^2 + c \} / \{ (t + t_0)^2 + c_1 \}}$, where T is the absolute temperature. This formula requires a minimum viscosity at a certain temperature, the significance of which, should it be found to exist, is discussed from the point of view of the spheres of repulsive action of the liquid molecules.

R. J. C.

Adsorption of Colouring Matters. HERBERT FREUNDLICH and WALTER NEUMANN (*Zeitsch. physikal. Chem.*, 1909, **67**, 538—550. Compare Freundlich and Losev, *Abstr.*, 1907, ii, 534).—Further experiments on the scission of dyes, more particularly new magenta, by adsorbing substances, such as charcoal, soot, and arsenic sulphide, are described. When new magenta is shaken with charcoal (from blood) or soot, a considerable proportion of the chlorine (20—30% under the experimental conditions employed) remains in solution in the form of chlorine ions, and the dye is almost completely adsorbed by the charcoal. The solution, however, is neutral to litmus, and it has not been found possible to establish with certainty the nature of the cation or cations. Small proportions of H^+ ions and of Ca^{++} ions are present, but not nearly equivalent to the Cl^- ions in the solution. The main proportion of the cations probably originate from impurities on the surface of the charcoal.

In another series of experiments, solutions of colloidal arsenious sulphide were completely precipitated by new magenta. In this case practically all the chlorine remained in solution in the form of Cl^- ions, and an equivalent amount of H^+ ions was also present. The latter probably originate from arsenious acid or hydrogen sulphide, present as impurity in the colloidal arsenious sulphide solution. Similar results were obtained when morphine hydrochloride was substituted for new magenta.

It is pointed out that, contrary to the opinion expressed in the earlier paper, it is quite in accordance with the law of absorption, that an adsorbing agent which has taken up completely an adsorbable substance from solution does not give up any of the adsorbed substance to pure water.

G. S.

Capillary Phenomena. ZDENKO H. SKRAUP (*Monatsh.*, 1909, **30**, 675—680).—When a drop of dilute aqueous solution of an acid is

placed on filter-paper, it spreads out in the form of a circle, the acid being surrounded by a wider ring of water. Holmberg (this vol., ii, 25) has based on this phenomenon a method for estimating the strength of very dilute acid solutions, depending on the relative diameters of the rings. The author has repeated and confirmed Holmberg's work, but finds it more convenient to measure the capillary ascent on long strips of indicator paper dipped into the solutions. It is remarkable that the same values are obtained when the distances thus measured are substituted in Holmberg's quadratic formula (applied by him to spreading out in a circle).

The height to which the solute extends for a total rise of 100 mm. has been measured for a number of electrolytes in different dilutions. There is very little difference in the height to which equivalent solutions of strong acids ascend. In normal solution, strong bases ascend to the same height as acids in corresponding dilution, but in dilute solution bases ascend somewhat higher than acids. In general, weak bases and acids ascend somewhat higher than strong ones in equivalent dilution.

In the case of lead acetate, three zones are to be observed on the paper: the wet zone, below that an acid zone, and finally a basic zone. This phenomenon is due to hydrolysis, and is very suitable as a lecture experiment. Hydrolysis can also be shown in the case of copper sulphate, by treating the moistened paper with hydrogen sulphide, but the acid zone in this case is only a little above the darkened zone.

G. S.

Relations in Capillarity. R. D. KLEEMAN (*Phil. Mag.*, 1909, [vi], 18, 491—510).—Several relationships connecting the potential energy of the surface with other physical constants of a liquid have been deduced, and the relationships have been tested by applying to them the data for a considerable number of organic compounds.

H. M. D.

Gaps in Miscibility of Isomorphous Substances. Zinc Silicofluoride and Stannifluoride. WILLEM STORTENBEKER (*Zeitsch. physikal. Chem.*, 1909, 67, 618—626).—In a previous paper (Abstr., 1903, ii, 470) the author has maintained that limited miscibility in the case of isomorphous substances is rare or non-existent, whilst Gossner (Abstr., 1907, ii, 532) has given various instances of such limited miscibility, for example, the hexahydrates of zinc silicofluoride and zinc stannifluoride. The author has prepared the last two salts, and investigated their miscibility in the usual way. From solutions containing fairly large proportions of both components, small crystals have been obtained under certain conditions which appear to contain both components, and it is suggested that the two salts in question can be made to form a continuous series of mixed crystals, although under other conditions they show a tendency to crystallise separately, as found by Gossner.

G. S.

Liquid Mixed Crystals in Binary Systems. ADA PRINS (*Zeitsch. physikal. Chem.*, 1909, 67, 689—723).—The paper deals with the equilibrium relations in binary systems when one or both components

can be obtained as a crystalline liquid. In the theoretical part, the possible temperature-composition curves are figured and discussed, the occurrence of metastable liquid crystals (Lehmann) and of complete and partial miscibility in the solid state being taken into account. The temperature at which liquid crystals appear on heating is termed the transition point (*t. p.*), and that at which the liquid crystals give place to an isotropic liquid the melting point.

The systems *p*-azophenetole and *p*-azoxyphenetole, cholesteryl *isobutyrate*, propionate, and benzoate with *p*-azoxyphenetole, and *p*-methoxycinnamic acid and *p*-azoxyanisole with *p*-azoxyphenetole, have been investigated. The transition and melting points of the mixtures, contained in small tubes, were determined in the usual way, and in many cases the changes on gradually raising the temperature were observed microscopically. Special arrangements for making microscopic observations at known temperatures are described.

The m. p. of *p*-azophenetole is 162.4°; the t. p. of *p*-azoxyphenetole is 138.4°, the m. p. 167.3°. The m. p. of *p*-azophenetole is lowered by the addition of *p*-azoxyphenetole, solid mixed crystals (β -crystals) separating on cooling. Similarly, the m. p. of *p*-azoxyphenetole is lowered by adding *p*-azophenetole; in this case liquid mixed crystals (α -crystals) separate. The α - and β -crystals are not isomorphous, but on cooling they change to a continuous series of β -crystals, and on still further cooling probably into another form of mixed crystals. The eutectic mixture contains about 20 mols. % *p*-azophenetole. The recent work of Bogojawlensky and Winogradoff (Abstr., 1908, ii, 809) on this system is adversely criticised.

The freezing-point curve of the system cholesteryl *isobutyrate*-*p*-azoxyphenetole is somewhat similar to that just described. On one side of the eutectic point solid *isobutyrate*, on the other liquid mixed crystals, separate from the fused mass. Pure cholesteryl *isobutyrate* does not form liquid crystals, but on addition of *p*-azoxyphenetole a region of metastable liquid crystals appears; they become stable when more than 30% of *p*-azoxyphenetole is present.

Cholesteryl propionate and *p*-azoxyphenetole give rise to a continuous series of liquid mixed crystals. Lehmann (Abstr., 1906, ii, 836, 837) has stated that cholesteryl propionate exists in two liquid crystalline modifications, but the author's results render this doubtful. The t. p. of cholesteryl propionate is 96.2°, the m. p. 112.7°. The freezing-point curve of the system *p*-methoxycinnamic acid (t. p. 170.6°, m. p. 185.5°) and *p*-azoxyphenetole, both of which form a stable, liquid-crystalline modification, is continuous, and shows a very distinct minimum. The curve along which the solid and liquid-crystalline phases are in equilibrium consists of two branches meeting in a eutectic point, as is the case in most of the other binary systems dealt with in the paper.

The freezing-point curve of the system *p*-azoxyanisole (t. p. 118.5°, m. p. 135.5°) and *p*-azoxyphenetole falls regularly from the melting point of the latter to that of the former component. The melting point of the different mixtures is not sharp, but takes place over a range of about 0.6°. This phenomenon occurs also in most of the other systems, and is regarded as evidence that the liquid-crystalline

modification of a substance is to be regarded as a homogeneous phase.

Cholesteryl benzoate and *p*-azoxyphenetole also form a continuous series of liquid mixed crystals with a minimum in the melting-point curve. No evidence was obtained of the occurrence of two non-miscible liquid phases in this case, as suggested by Lehmann. G. S.

Nature of Precipitated Colloids. II. HARRY W. FOOTE, S. R. SCHOLES, and RALPH W. LANGLEY (*J. Amer. Chem. Soc.*, 1909, 31, 1020—1027).—In a previous paper (Abstr., 1908, ii, 821), experiments have been described which indicate that precipitated ferric and aluminium hydroxides may be regarded as solid solutions of water in the oxides or lower hydroxides. In drying the precipitates, a point was reached at which the product began to gain weight when placed over water, the composition at this point being that of the saturated solution.

This method of investigation has now been used to determine the composition of the saturated solutions of water in the mixed oxides of (1) iron and aluminium, (2) aluminium and silicon, (3) iron and silicon, and (4) aluminium and phosphorus, in order to ascertain the nature of the precipitates obtained when a solution of a soluble silicate or phosphate and an aluminium or ferric salt is treated with ammonium hydroxide. Precipitates of almost any desired composition can be obtained by varying the proportions of the salts employed. Many of these solutions have been described in the past as silicates or phosphates of aluminium or iron, but it is pointed out that there is no valid reason for regarding them as such.

The percentages of water in the mixed oxides when gain in weight first occurs are tabulated, and curves have been constructed in which the compositions of the mixed oxides are plotted as abscissæ and the amounts of water as ordinates.

The curve for the mixed oxides of aluminium and iron clearly suggests that the precipitate is a solid solution dissolving water, the mixture taking up more water than does either oxide alone. The curves for the precipitates containing the oxide of silicon or phosphorus are of the same type, and do not exhibit any break, thus affording evidence that all the precipitates should be regarded as solid solutions. The curve for aluminium oxide and phosphoric acid shows a decided drop at the point corresponding with AlPO_4 , and it seems not improbable that this salt is actually formed. E. G.

The Equilibrium of the Reaction $\text{H}_2\text{S} + 2\text{I} = 2\text{HI} + \text{S}$ and the Dissociation of Hydrogen Sulphide. F. POLLITZER (*Zeitsch. anorg. Chem.*, 1909, 64, 121—148).—The reaction between hydrogen sulphide and solid iodine takes place at the ordinary temperature, although the concentration of the hydrogen iodide produced is very small. Pure hydrogen sulphide, prepared from calcium sulphide and hydrochloric acid, is mixed with electrolytic hydrogen and brought into contact with solid iodine and sulphur contained in a U-tube at constant temperature, the whole being kept thoroughly dry. The escaping mixture passes through a vessel in which the iodine is con-

densed by cooling with solid carbon dioxide. Hydrogen iodide is absorbed in water and titrated, hydrogen sulphide absorbed in sodium hydroxide and weighed, and hydrogen measured by volume. The equilibrium constant is found to be 1.90×10^{-3} at 40° and 9.96×10^{-3} at 60° . The heat of reaction is calculated to be 17,200 cal., and the heat of formation of hydrogen sulphide to be 5000 cal., in agreement with the values determined calorimetrically. The heat of vaporisation of sulphur (forming S_2 molecules) at the ordinary temperature is found to be 28,500 cal.

Measurements have also been made of the solubility of hydrogen sulphide in water and in hydriodic acid at different concentrations and temperatures. The solubility increases considerably with the concentration of the hydrogen iodide. Measurements have also been made of the equilibrium in solution, and in the gas phase in contact with the solution.

C. H. D.

Isomorphism of Ternary Mixtures in which the Components are not Completely Miscible. ERNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1909, **67**, 641—688).—A theoretical paper, which deals with the equilibria in ternary systems when the three independent components are isomorphous, but are not completely miscible in the solid and liquid state. The ternary systems in which the miscibility is incomplete in only one of the binary systems are discussed completely. There are eight chief types, and the several cases occurring in each are illustrated graphically. The more complicated cases in which there is incomplete miscibility in more than one of the binary systems are only partly dealt with.

In the second part of the paper, the ternary alloys of the metals: copper, silver, gold, chromium, manganese, iron, cobalt, nickel, palladium, platinum, are considered on the basis of the experimental data for the respective binary systems, due mainly to Tammann and his co-workers, and are referred as far as possible to the different types figured in the earlier part of the paper.

G. S.

Equilibria in Quaternary Systems. The System: Water-Ethyl Alcohol-Sodium Chloride-Sodium Sulphate. FRANZ A. H. SCHREINEMAKERS and (Fräulein) W. C. DE BAAT (*Zeitsch. physikal. Chem.*, 1909, **67**, 551—560).—The equilibria in the above system have been determined by solubility measurements in the usual way. The results are complicated by the existence of sodium sulphate decahydrate, $Na_2SO_4 \cdot 10H_2O$, under certain conditions.

The four ternary systems have mostly been investigated by previous observers, and the available data are amplified in some respects. The equilibria in the quaternary system have been examined at 15° , 25° , and 35° . The composition of the saturated solutions in equilibrium with the different solid phases are given in tabular form, and are also represented graphically. The results of the analyses of the saturated solutions have been confirmed by the "residue" method. The relationships are comparatively simple at 35° , as under these conditions the decahydrate of sodium sulphate does not exist.

G. S.

Steric Hindrance. III. Relation between the Structure of the Aliphatic Alcohols and Their Rate of Esterification. ARTHUR MICHAEL and KARL WOLGAST (*Ber.*, 1909, 42, 3157—3176. Compare this vol., ii, 220).—The authors' researches on the nature of steric hindrance lead them to a re-examination of this question. The work of Menshutkin is open to criticism, because the percentages of alcohol esterified in the first hour, which he termed the "initial velocities," are not proportional to the rates of esterification, since in many cases an appreciable quantity of water is formed in that time. The method selected for measuring the velocity of esterification was to determine at definite intervals the decrease of the acid titration of an alcoholic solution containing a known amount of the acid. Trichloroacetic acid was chosen as the acid, and was titrated with ammonia, rosolic acid being used as indicator. The results are summarised as follows, the values given being for $k \times 10^5$, in which k is the constant of the reaction calculated from the equation of the second order: $k = 1/t \cdot x/A(a-x)$, A being the number of gram-molecules of acid to which 1 litre of alcohol is added, a the number of c.c. of $N/10$ -ammonia required to neutralise 2 g. or 2 c.c. at the beginning, $a-x$ the amount required to neutralise the same quantity at time t . The values of k are either means of the series obtained from any one experiment, or, in cases where a regular increase or decrease in the value found for successive times was observed, the values extrapolated graphically for $t = 0$.

Esterification with Trichloroacetic Acid at 25°.—Primary alcohols: Methyl alcohol, 3690; ethyl alcohol, 650*; propyl alcohol, 725; butyl alcohol, 1200; isobutyl alcohol, 740; heptyl alcohol, 1160; octyl alcohol, 1860; cetyl alcohol, 2500. Secondary alcohols: Dimethylcarbinol, 98; methylethylcarbinol, 90; methylpropylcarbinol, 76; methylhexylcarbinol, 109. Tertiary alcohols: *tert.*-Butyl alcohol, 118; *tert.*-amyl alcohol, 248.

Esterification with Trichloroacetic Acid at 50°.—Primary alcohols: Methyl alcohol, 24000; ethyl alcohol, 4210; cetyl alcohol, 16300.

In order to exclude the possibility that the results should be to any considerable degree dependent on the acid taken, a further series of measurements was made with acetic acid, the titration being effected with baryta and rosolic acid as indicator.

Esterification with Acetic Acid at 50°.—Primary alcohols: Methyl alcohol, 808; ethyl alcohol, 159; *n*-butyl alcohol, 234; cetyl alcohol, 436.

The figures show that the relative rates of esterification are not greatly different at 25° and at 50°. The velocity of esterification of the normal primary alcohols increases as the carbon chain becomes longer. The first member, methyl alcohol, has an abnormally high rate. Menshutkin found the velocity of esterification constant from ethyl alcohol onwards. The increase is not an additive one, but a constitutive influence depending on the position of the methyl group. This conclusion is borne out by the authors' results for secondary and tertiary alcohols given above; these also differ considerably from the values obtained by Menshutkin. The decrease in velocity on passing

* Mean from Kailan's experiments at 25° (compare Abstr., 1908, ii, 936).

from the primary series to the secondary is much greater than that observed by Menshutkin, whilst the velocities of esterification of tertiary alcohols, which Menshutkin found very much smaller than those of secondary alcohols, actually exceed them.

The authors consider that the hypothesis that the rate of esterification depends on the spacial extension of the atoms in the reacting molecules (*Hypothese der Raumerfüllung*) is not consonant with the relations between the structure of the alcohols and the rates of esterification, which indicate, on the other hand, that the influence of the atoms in the alcohol molecule is not purely mechanical, but is dependent on their nature and position relative to the hydroxyl group. Their former conclusions (*loc. cit.*) are thus confirmed.

For the discussion of numerous points connected with the observations and calculations, the original paper should be referred to. Especial care was taken in the purification of the alcohols used, and the following physical data, etc., were obtained. The boiling points are corrected. Methyl alcohol, b. p. $64.4^{\circ}/768.0$ mm. Ethyl alcohol, b. p. $78.0^{\circ}/762.0$ mm. *n*-Propyl alcohol, b. p. $97.1-97.2^{\circ}/760$ mm. *n*-Butyl alcohol, b. p. $116.8-117.2^{\circ}/755$ mm. *iso*Butyl alcohol, b. p. $107.5-107.6^{\circ}/759$ mm. *sec*-Amyl alcohol, b. p. $119.3-119.7^{\circ}/768.0$ mm. *tert*-Amyl alcohol, b. p. $101.7-102.2^{\circ}/763.8$ mm. Heptyl alcohol, b. p. $175.0-176.0^{\circ}/760$ mm. *n*-Octyl alcohol, b. p. $194.5-195.5^{\circ}/755$ mm. *sec*-Octyl alcohol, b. p. $179.5^{\circ}/769$ mm.

sec-Butyl alcohol, prepared by the method of Sabatier and Senderens by reducing methyl ethyl ketone, was freed from admixed ketone as follows. The alcohol was left with phenylhydrazine for some hours, then fractionated with a Hempel column in a vacuum, the distillate treated with three to four drops hydrochloric acid, and after a time twice fractionated. The hydrochloric acid was finally removed by heating for some hours with lime. In the case of *isopropyl* alcohol and methylpropylcarbinol, the troublesome removal of the phenylhydrazine may be avoided by using semicarbazide instead.

R. V. S.

Square Root of the Atomic Weights. ISIDOR TRAUBE (*Physikal. Zeitsch.*, 1909, 10, 667-670).—Bragg has shown that the stopping power of metals for α -rays is proportional to the square roots of the atomic weights, and that for gases it is proportional to the sum of the square roots of the weights of the atoms in the molecule. This stopping power is also approximately proportional to the molecular volumes of different substances at their respective boiling points. The relationship thus indicated between atomic weights and volumes has been investigated.

For a large number of organic and inorganic substances it is found that the molecular volume at absolute zero is proportional to the sum of the square roots of the atomic weights corresponding with the equation $v_0 = 2.6 \sqrt{\Sigma A}$. From dispersion and absorption measurements, Martens has shown that for a number of elements, the period of vibration of the atoms is proportional to the square root of the atomic weights. According to the above relationship, it then follows that

these periods of vibration are approximately proportional to the volumes of the atoms.

The paper also contains a series of numbers which indicate proportionality between the sum of the square roots of the atomic weights and the sum of the maximum valencies of the atoms in the molecules of different substances. This relationship, however, does not hold good unless abnormally high valencies are assumed in certain cases.

H. M. D.

Dependence of the Valency on the Temperature in Heterogeneous Systems. WILHELM BILTZ (*Zeitsch. physikal. Chem.*, 1909, 67, 561—593).—The dependence of valency on the temperature is discussed in the light of the available data for the dissociation equilibria of oxides, hydrates, and ammonia compounds at fixed pressures. In the case of the oxides, for example, the temperatures are given at which a higher and a lower oxide of the same metal are in equilibrium with oxygen at atmospheric pressure. When experimental data for atmospheric pressure are not available, the temperatures in question are calculated from the heat of the reaction, and the dissociation pressures at other temperatures by substitution in Nernst's equation connecting dissociation pressure and temperature. So-called valency isobars are then drawn, by taking the absolute temperatures as abscissæ and the valencies as ordinates. For example, the absolute temperature for the equilibrium PdO_2/PdO is 453° and for PdO/Pd 1148° , and a line drawn from the point representing valency four and 453° to that representing valency two and 1148° is the valency isobar. The points at which the valency horizontals meet the isobars are termed valency points of section. When more than two oxides exist, the isobars consist of two or more straight lines meeting at certain angles. Similar curves are constructed for the hydrates and ammonia compounds of certain salts, except that for the hydrates a dissociation pressure of 1/10 atmosphere is chosen.

From the results, the following rule is deduced. The valency isobars, independent of the absolute value of the valency and independent of its increase, ascend from the valency points of section the more steeply the lower the temperature. The tangents of the angles of inclination increase with falling temperature at first gradually, then more rapidly, and the relation between the temperature and the tangent of the angle of inclination of the isobars can be represented by a continuous curve for each of the three types of compound. When a substance shows more than two valencies, the isobar which joins the two lowest valency points of section is less inclined than the others. For compounds of the same type, the inclination of the valency isobars is constant for a definite temperature.

G. S.

Dependence of Valency on Volume in Certain Tervalent Elements. ALBERT LUDWIG (*J. Amer. Chem. Soc.*, 1909, 31, 1130—1136).—The author has observed (*Abstr.*, 1902, ii, 451) that during the fusion of carbon under a high gaseous pressure the electrical conductivity ceases, and this he has regarded as an

indication of a change of the carbon into the denser form of diamond. A fuller study of this change offers considerable difficulty on account of the high inversion temperature (over 3000°) and the extremely high pressure required. Experiments have therefore been made in order to investigate the volume changes of more easily fusible substances, and bismuth, antimony, and aluminium have been selected for the purpose.

The fused metal was placed in a heavy nickel-steel cylinder, fitted with a hardened steel piston. The metal was lightly covered with a magnesia plug, moistened with water, and a pressure of from 6000 to 17,000 atmospheres was suddenly brought to bear upon it. A rapid generation of gas immediately occurred. When the cylinder had cooled to the ordinary temperature, the pressure was released and the gas allowed to escape. In the cases of bismuth and antimony, after removing the metal by amalgamation with mercury, black powders were obtained, consisting of the oxides BiO and SbO . In the case of aluminium, the metal appeared but little changed. On breaking up the aluminium, however, the particles of metal immediately became covered with a peculiar, white, feathery substance, which is isotropic, has n 1.542, is easily soluble in acetic acid, and on ignition is converted into the oxide Al_2O_3 . It is probable, therefore, that, like bismuth and antimony, aluminium is bivalent under high pressures, and forms the oxide AlO . It is also probable that, on account of its high m. p., the metal does not revert immediately to the less dense form, but only returns slowly after vigorous shaking or pounding, the pressure developed by the change causing the oxide to appear in the form of fine threads. E. G.

Sensitive Micro-balances and a New Method of Weighing Minute Quantities. BERTRAM D. STEELE and KERR GRANT (*Proc. Roy. Soc.*, 1909, A, 82, 580—594).—Two types of constant-load vacuum gravity micro-balance are described. The first is designed for the measurement of small alterations in weight, and is sensitive to one two-hundred and fifty-thousandth of a milligram; the second for absolute measurements of masses not exceeding 0.1 gram, with an accuracy of one ten-thousandth of a milligram.

The balances are enclosed in a brass case, consisting of base and cover, which are both provided with flanges carefully ground so as to make a vacuum tight joint. A side-tube, soldered into the case and provided with a manometer, enables the case to be connected with the atmosphere or with a vacuum pump. The beam, which is made of fused quartz, carries a small mirror, which is illuminated by a Nernst lamp through a plate-glass window in the cover. The zero position of the instrument is obtained by realigning the position of the image on a millimetre scale. The beam has the form of a double triangle, which in the first type of balance oscillates about a central knife-edge ground upon the end of a quartz rod. Attached to one end of the beam is a small quartz bulb of known internal volume, containing air sealed up at known temperature and pressure. At the other end is a quartz counterpoise, the shape of which depends on the purpose for which the balance is intended. The final adjustment for balance and for the

position of the centre of gravity is rendered possible by the fact that quartz is appreciably volatile in the oxygen coal-gas flame. To give an idea of the dimensions of the balance of the first type used by the authors, it may be mentioned that the total weight of the beam with attached mirror, bulb, and counterpoise is only 0.177 gram, the length of the arm 5.1 cm., and the volume of the bulb 0.00865 c.c.

The method of weighing, which depends for its successful application on the possibility of attaining perfect homogeneity in the beam of the balance, consists in employing as counterpoise the whole or any fraction of the weight of the air in the sealed quartz bulb. By adjusting the pressure in the balance case, it is obvious that the effective weight of the enclosed air can be made to vary between zero and the vacuum weight, and that at a given temperature a change in pressure of, say, 1 mm. of mercury will correspond with a definite variation of the effective weight and with a definite shift in the scale reading.

The balance of the first type was designed with the special object of measuring the loss of weight of radium salts during disintegration.

H. M. D.

Modified Form of Gooch Crucible. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1909, 31, 1146).—When material is transferred from a flask or large beaker into a Gooch crucible, there is a danger that some of the substance may fall outside and thus be lost. This can be obviated by welding on to the crucible a flange or brim, sloping at an angle of about 45°. The diameter of the top of the crucible may thus be doubled. The flange also serves to stiffen the crucible and thus enable it to retain its form better.

E. G.

Automatic Filter Funnel. HERBERT S. BAILEY (*J. Amer. Chem. Soc.*, 1909, 31, 1144—1145).—The apparatus described has been found very convenient as a substitute for the ordinary filter flask or bell-jar and beaker usually employed in filtering with suction.

The stem of the funnel containing the Gooch crucible passes through a rubber stopper, which is fitted into the mouth of a glass tube. This tube may be of any convenient size, and terminates in a narrow tube, which is constricted and provided with a small movable plug placed below the constriction and kept from falling out by two or three small projections on the inside of the tube. The plug is ground so as to close the constriction when pressed against its lower surface. The large tube is provided with a side-arm in order to connect it with the pump. When the action of the pump is discontinued and air is admitted through the side-tube, the plug drops and the filtrate is discharged into a suitable vessel placed to receive it.

E. G.

Constant Level Reservoir. D. BASIL W. ALEXANDER (*J. Amer. Chem. Soc.*, 1909, 31, 1052—1053).—An apparatus is described which has been found useful for filtering solutions of bitumen in carbon tetrachloride. The liquid to be filtered is placed in a separating funnel, which is closed at the top by a stopper, and is so supported that the lower end is about half an inch above the felt of a Gooch

crucible. As the liquid passes through the crucible, air ascends into the separating funnel, and further quantities of the liquid flow out until the whole has been filtered. E. G.

Lecture Experiment to Show the Rate of Chemical Action.
WALTHER NERNST (*Ber.*, 1909, 42, 3178—3179).—The experiment depends on the following facts : (1) The different indicators show their characteristic colour changes at definite and different concentrations of hydrogen or hydroxyl ions ; (2) when a solution of an ester is treated with a little alkali, the alkalinity quickly vanishes, and, as a result of the hydrolysis of the ester, a gradually increasing acid reaction makes its appearance. If, therefore, 50 c.c. of boiled water are treated with enough barium hydroxide to make the solution about $N\cdot0\cdot001$, and then with 1 c.c. of methyl formate, an almost instant decoloration will be observed on addition of a trace of phenolphthalein. On addition of litmus, cyanine, *p*-nitrophenol, or methyl-orange, the times required for decoloration are respectively about 1, 15, 30, 120 minutes. The experiment may conveniently be shown with the different indicators simultaneously, the indicators being introduced into all the flasks at the same instant by being poured from a row of test-tubes fastened on a rod. R. V. S.

Inorganic Chemistry.

Absorption of Hydrogen by Colloidal Platinum and Palladium Solutions. GIUSEPPE KERNOT and F. DE SIMONE NIQUESA (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], 15, 168—175).—Pure colloidal platinum and palladium solutions absorb much larger quantities of hydrogen than are taken up by the metals in any other physical condition, even by colloidal suspensions prepared by chemical means. A rough proportionality is found between the concentration of the colloidal metal and the volume of hydrogen absorbed. The absorption of hydrogen is considerably diminished by the presence of gum, dextrin, or albumin, but is not sensibly influenced by sucrose.

T. H. P.

Ice [Modification] III. GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1909, 63, 285—305).—Phases stable only at higher temperatures may be obtained in a metastable state at lower temperatures by sufficiently rapid cooling. It is now shown that phases stable only under high pressures may be obtained under low pressures by compressing isothermally, cooling to a temperature at which the velocity of transformation becomes negligible, and reducing the pressure. This method has been applied to water to obtain ice III, stable only under high pressures, under atmospheric pressure.

Ice I contracts on melting, and the equilibrium temperature of

ice I and water therefore falls with increase of pressure. Ice III expands on melting, so that its melting point rises with increase of pressure. The difference in the specific volumes of ice I and III is very large, and the heat of transformation very small, passing through zero at -43° . The internal heat of transformation at this temperature is 9.4 cal., being exactly balanced by the external work. At -190° ice III can be obtained even when the pressure has fallen to that of the atmosphere, the transformation not setting in until -120° is reached.

The water in the experiments is enclosed in a paper cylinder, surrounded with light petroleum, in connexion with the pressure apparatus. The quantity of water used in each experiment is about 3.2 grams. The pressure is raised to 3000 kilograms, and, after cooling to the ordinary temperature, the vessel is cooled with solid carbon dioxide, causing freezing to ice III, with a corresponding fall of pressure. After cooling with liquid air, the pressure is lowered to 100 kilograms. On warming to -120° , an increase of pressure is observed corresponding with the transformation to ice I. It has been found possible to open the vessel under atmospheric pressure at -190° and to transfer the ice to liquid air, removing the paper. Ice III is clear and colourless, being built up of coarse crystallites. It has a porcelain-like appearance when undergoing transformation into ice I. It sinks at once in liquid air, whilst ice I floats. When removed from the liquid air, the transformation takes place rapidly, the mass falling into a bulky, white powder, which melts at 0° . Abnormal behaviour is observed when the paper cylinder is omitted, the whole vessel being filled with water, as in this case the uniform transmission of pressure is hindered.

Ice I, formed from water under ordinary pressure, must consist of polymerised molecules. Nordenskiöld's tetragonal ice is only a crystalline modification of this. Ice III, formed at high pressures, must consist of simple molecules. Ice II must have the same molecular weight as ice III. There are thus two polymerised and two simple forms. Equilibrium can only exist between two modifications of different molecular weight. Modifications having the same molecular weight differ only in their space-lattice systems, not more than one of which can be stable.

C. H. D.

Anodic Formation of Hydrogen Peroxide. E. H. RIESENFELD and B. REINHOLD (*Ber.*, 1909, 42, 2977—2981).—The formation of hydrogen peroxide in the electrolysis of aqueous solutions has hitherto only been noticed at the cathode, its production being due to a secondary reaction. All attempts to prove its formation at the anode have failed. Theoretical considerations indicate that, if formed at all, it should be produced by the electrolysis of strongly alkaline solutions at low temperatures.

The authors find that there is no anodic formation of hydrogen peroxide when sodium hydroxide is electrolysed at any temperature down to -25° , the lowest temperature at which sodium hydroxide is liquid. On the other hand, when potassium hydroxide is used, there is an appreciable formation of hydrogen peroxide at all temperatures between 0° and -60° , the maximum amount being

formed at -40° . The experiments were carried out in a U-tube, the anode consisting of a platinum wire, the cathode, of platinum foil, being surrounded by parchment paper.

The different action of the two alkalis is probably due to the fact that hydrogen peroxide is decomposed catalytically much more rapidly by sodium hydroxide than by potassium hydroxide. This is proved by experiments on the catalytic decomposition of hydrogen peroxide by these alkalis.

In all the experiments the solution at the anode became yellow in colour. This is not due to the formation of potassium ozonate (compare Baeyer and Villiger, *Abstr.*, 1902, ii, 650), which then decomposes with the formation of hydrogen peroxide, since the intensity of the yellow colour continually increases with fall in temperature, whereas there is an optimum temperature for the formation of the hydrogen peroxide. Moreover, it is shown that the decomposition of potassium ozonate does not give rise to any appreciable quantities of hydrogen peroxide.

There is no formation of hydrogen peroxide at nickel electrodes, neither is a yellow colour produced. This is in accordance with the electrochemical behaviour of nickel as compared with platinum.

T. S. P.

Action of Colloidal Iridium Solutions on Hydrogen Peroxide. GIUSEPPE KERNOT and F. ARENA (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], 15, 125—132).—When colloidal solutions of iridium in $N/1000$ sodium hydroxide are prepared, according to Bredig's method, the sodium hydroxide undergoes dissociation, and part of the hydrogen liberated is absorbed by the colloidal iridium, and causes a marked acceleration in the action of the latter on hydrogen peroxide. It is therefore preferable to employ pure water in place of the dilute alkali. The catalytic action of such solutions is intensified by the presence of an acid, and is greatly diminished or entirely destroyed by small proportions of mercuric chloride or potassium cyanide.

T. H. P.

Influence of Potassium Persulphate on the Catalytic Decomposition of Hydrogen Peroxide by means of Colloidal Iridium Solutions. GIUSEPPE KERNOT (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], 15, 145—150. Compare preceding abstract).—The velocity of decomposition of hydrogen peroxide by colloidal iridium solutions is increased considerably by the presence of potassium persulphate, the increase being greater in neutral than in acid solution, and possibly proportional to the amount of persulphate. It may be that the latter acts only catalytically, the increase of the constant of the decomposition reaction being due to the formation of a compound, such as the potassium salt of Caro's acid, $OK \cdot S_2O_5 \cdot O_2K$, more highly oxygenated and less stable than the persulphate or hydrogen peroxide; in such case, the following three reactions would be superposed: (1) catalytic decomposition of hydrogen peroxide; (2) reaction between the oxygen evolved from the peroxide and the persulphate, and (3) decomposition of the product of reaction (2).

T. H. P.

Action of Colloidal Rhodium Solutions on Hydrogen Peroxide. GIUSEPPE KERNOT and F. ARENA (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], 15, 157—166).—By means of Bredig's method, the authors have prepared colloidal solutions of rhodium in pure water (conductivity $1.5-3.0 \times 10^{-6}$), a current of 2 amperes at 110 volts being employed, and the capsule containing the water kept cooled. Such solutions, which have a reddish-brown colour and are extremely unstable, exert a marked catalytic activity towards hydrogen peroxide. Potassium persulphate or percarbonate accelerates the catalytic action, apparently owing to the formation of a highly oxygenated product more readily decomposable than hydrogen peroxide. Potassium perchlorate, perchloric acid, ammonium persulphate, and most other electrolytes exert a retarding influence on the catalysis. T. H. P.

Liquid Chlorine. FREDERICK M. G. JOHNSON and DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1909, 31, 1138—1144).—A study has been made of the vapour pressure, density, and molecular surface energy of liquid chlorine, and also of its behaviour as a conducting solvent. The apparatus employed is described with the aid of diagrams.

The vapour pressure has been determined at temperatures ranging from -105.7° to -32.0° . The results are almost identical with those obtained by Knietzsch (*Abstr.*, 1891, 14). The b. p., under atmospheric pressure, is -33.7° . At the f. p. the vapour pressure is 9.2 mm., showing the temperature to be -101.5° . By means of the Clausius formula, the heat of vaporisation at 760 mm. for 1 gram-mol. is found to be 21.1×10^{10} ergs.

The densities have been determined between -93.7° and -29.4° , and it is shown that the density at any temperature can be calculated by means of the formula $1.725 - 0.00243(100 + t)$. At the b. p. the density is 1.568, and hence the molecular volume is 22.6, which agrees with the value obtained by Kopp from organic compounds.

The molecular surface energy, determined by means of a modification of Ramsay and Shields' apparatus, is recorded for temperatures between -61.5° and -28.7° . Between these temperatures $d(MV)^{2/3}/dT = 2.04$, and hence liquid chlorine has the formula Cl_2 . The curve exhibiting the variation of molecular surface energy with temperature shows that the value of the molecular surface energy is zero at 129.4° .

No inorganic substance could be found which becomes ionised in liquid chlorine, but a mixture of ether and hydrochloric acid enables the liquid to conduct well, probably owing to the formation of the compound $\text{Er}_2\text{O} \cdot \text{HCl}$. E. G.

Formation of Ozone by the Ultra-violet Rays. FREDERICK M. G. JOHNSON and DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1909, 31, 1146—1147).—Experiments have been made which show that Bardier and Nogier's statement (*Compt. rend.*, 1908, 147, 354), that the odour observed in the neighbourhood of the mercury arc enclosed in quartz is not due to ozone, is incorrect. In all cases in which the odour is perceptible, the presence of ozone can be detected by means of potassium iodide and starch paper. E. G.

Specific Gravity and Percentage Strength of Selenic Acid. M. E. DIEMER and VICTOR LENHER (*J. Physical Chem.*, 1909, 13, 505—511).—Two methods for the preparation of pure selenic acid from selenium dioxide are described. A large number of density determinations of aqueous solutions containing the acid in proportions from 0 to 99.4% have been made, and the results are represented graphically and also in tabular form. Some of the interpolated results are as follows: 10.44%, D_4^{20} 1.080; 25.30%, D_4^{20} 1.215; 40.06%, D_4^{20} 1.385; 60.18%, D_4^{20} 1.680; 80.10%, D_4^{20} 2.120; 99.36%, D_4^{20} 2.595.
G. S.

Some Complex Selenium Anions. ARTHUR ROSENHEIM and MAX PRITZE (*Zeitsch. anorg. Chem.*, 1909, 63, 275—281).—*Mercuric selenocyanate*, $\text{Hg}(\text{SeCN})_2$, prepared from potassium selenocyanate and mercuric chloride, forms white needles, decomposed by hot water. When only half the quantity of the potassium salt is used, pale yellow crystals of *mercuric chloroselenocyanate*, $\text{HgCl}(\text{SeCN})$, are obtained, and may be recrystallised rapidly from water. Two other double salts, $\text{KHg}(\text{SeCN})_3$ and $\text{K}_2\text{Hg}(\text{SeCN})_4$, may be obtained in a crystalline form. A *cobalt* salt, $\text{CoHg}(\text{SeCN})_4$, greenish-blue, microscopic crystals, and a white *zinc* salt, $\text{ZnHg}(\text{SeCN})_4 \cdot \text{H}_2\text{O}$, have been prepared.

Mercuric oxide is insoluble in selenious acid, but *mercuric selenite*, HgSeO_3 , may be obtained from mercuric oxide and sodium hydrogen selenite, or from mercuric nitrate and sodium selenite, in white crystals, insoluble in water or dilute nitric acid. For analysis, it is dissolved in hydrochloric acid, warmed with ammonium persulphate, and then boiled with sulphuric acid. After adding an excess of a solution of hydrogen sulphide and expelling the gas with carbon dioxide, the precipitated mercuric sulphide is free from selenium.

Two double salts, $\text{Na}_2\text{Hg}(\text{SeO}_3)_2$ and $\text{HgCl} \cdot \text{SeO}_3 \cdot \text{Na} \cdot 2\text{H}_2\text{O}$, were prepared. The solubility of mercuric selenite in sodium selenite solutions was determined, and a constant calculated for the complex formation.
C. H. D.

New Compounds of Nitrogen with Hydrogen and Metals. FRANZ W. DAFERT and R. MIKLAUX (*Monatsh.*, 1909, 30, 649—654. Compare Haber and Van Oordt, *Abstr.*, 1905, ii, 159, 384, 814).—When calcium nitride is heated, within certain limits of temperature, in a stream of hydrogen, the latter is rapidly absorbed, and a lemon to orange-yellow substance is obtained, the approximate composition of which is: calcium 80.3%, nitrogen 17.1%, and hydrogen 2.6%. Although the analytical results are not quite conclusive, the new substance is probably tricalciumamide, $\text{Ca}_3(\text{NH}_2)_2$. It is scarcely affected by heating in nitrogen or hydrogen, but changes slowly in diffused light, rapidly in sunlight, to a greyish-black substance, probably a mixture of calciumimide and calcium hydride, formed according to the equation $\text{Ca}_3(\text{NH}_2)_2 = 2\text{CaNH} + \text{CaH}_2$. The amide, in an impure form, has also been prepared by heating calcium hydride in nitrogen.

Lithium nitride also absorbs hydrogen on heating, forming a white compound, probably trilithiumamide, Li_3NH_2 . In sunlight it decom-

poses rapidly, giving rise to a red substance. The change is probably represented by the equation $\text{Li}_3\text{NH}_2 = \text{Li}_2\text{NH} + \text{LiH}$, the red compound being the previously unknown lithiumimide, Li_2NH .

Magnesium nitride does not show any tendency to unite with hydrogen. G. S.

Reductions with Phosphorous and Hypophosphorous Acids.

ADOLF SIEVERTS [with MORIZ MAJOR] (*Zeitsch. anorg. Chem.*, 1909, **64**, 29—64).—Ferric alum reacts with hypophosphorous acid at the temperature of the water-bath, whilst phosphorous acid is not attacked after several hours. A separation of the two acids by titrating the ferrous salt thus formed with permanganate is, however, impossible, as phosphorous acid is readily oxidised by permanganate in presence of a ferrous salt. The author has therefore only determined the iodine value of the solutions by means of iodine and arsenious acid. Both acids are only very slowly oxidised by air, and it is not necessary to exclude air during titration. By oxidising with bromine to phosphoric acid, and estimating this and comparing the result with the iodine value, the two acids may be estimated when present together.

Gold chloride is reduced by both acids to metallic gold. The precipitate oxidises a boiling solution of hypophosphorous acid slowly, evolving hydrogen.

[With WILHELM KRUMBHAAR.]—Silver behaves similarly when the phosphate is used, dissolved in phosphoric acid; the nitrate causes complications, owing to reduction of the anion. Even in ammoniacal solution, the precipitate consists of metallic silver, and not of a suboxide, and there is no evidence of the formation of silver hydride (Bartlett and Rice, *Abstr.*, 1897, ii, 212). Phosphorous acid reduces copper sulphate to copper; phosphates are without action. Cupric chloride is reduced to cuprous chloride. The acid is readily oxidised by air in presence of a cupric salt. Hypophosphorous acid, with the copper in excess, precipitates metallic copper without evolution of hydrogen; with an excess of sodium hypophosphite, cuprous hydride, CuH , is precipitated. In all cases the reduction is first to a cuprous salt.

Platinum salts are not reduced by hypophosphites, even on boiling, and the oxidation caused by platinum-black is due only to retained oxygen. Palladium salts, on the other hand, are reduced by both acids in the cold. Even a cold solution of sodium hypophosphite is oxidised by precipitated palladium to phosphite, and even further on boiling. Alcoholic sodium hypophosphite does not react with palladium.

Nickel and cobalt salts are not reduced, but the metals prepared by the action of hydrogen on the oxides behave like palladium. Reduced iron dissolves readily in sodium hypophosphite solution on heating.

C. H. D.

Reducing Action of Silicon. ÉMILE VIGOUROUX and F. DUCELLIEZ (*Bull. Soc. chim.*, 1909, [iv], **5**, 868—869).—In an attempt to free amorphous silicon from aluminium, with which it was contaminated,

the substance was heated to dull redness, or slightly beyond, with twice its weight of potassium hydrogen sulphate. A vigorous action took place, and the resulting product when cold had a strong odour of hydrogen sulphide, and contained yellow crystals of potassium sulphide, silica, alumina, potassium silicate, and unchanged silicon. In using potassium hydrogen sulphate to remove aluminium from crude silicon, the two products should be kept at a temperature below a red heat.

T. A. H.

The Silicic Acids. GUSTAV TSCHERMAK (*Zeitsch. anorg. Chem.*, 1909, 63, 230—274).—The method of determining the velocity of dehydration of the silicic acids (Abstr., 1905, ii, 816) has been applied to the study of a number of such acids, a vessel containing water being placed under similar conditions to the specimen, and its loss of weight also determined, in order to eliminate accidental changes in the rate of evaporation.

The rate of loss of water depends on the physical condition of the preparation, powdery and gelatinous silicic acids behaving differently. The absolute weight is also of influence, a large mass losing water relatively more slowly than a smaller mass. After the break in the dehydration curve has been passed, all the preparations behave similarly. This break occurs at a quite definite water-content, which is characteristic of each silicic acid. It is not identical with the break in Van Bemmelen's vapour-pressure curves (Abstr., 1908, ii, 838), and the trustworthiness of the author's method is maintained. Water-glass, which is an indefinite mixture of silicates, yields silicic acids with variable critical points on the dehydration curves.

The gel obtained from silicon tetrachloride and water consists of orthosilicic acid, and not of anhydrous silica, as suggested by Le Chatelier (Abstr., 1908, ii, 1033). Its hardness is only that of gypsum. The density of the silicic acids is also greater than that calculated on the assumption that they are mechanical mixtures of silica and water. Water is taken up by the dehydrated acids, but not to the amount of that originally present. If previously dehydrated over sulphuric acid, the silicic acid develops heat in becoming hydrated, but if ignited, no measurable heat development takes place, although a hydrate is slowly formed. The different silicic acids are unequally reactive towards alkalis, but quantitative relations have not been established. A combination of the hydrate and adsorption hypotheses is proposed to account for the behaviour of the silicic acids. The break in the dehydration curve indicates the composition of the acid derived from the silicate, except that differences of molecular weight, indicated by differences of physical structure, may also occur. Thus the acid from anorthite is represented as H_2SiO_3 , and that from leucite as $(\text{H}_2\text{SiO}_3)_2$. Diopside may resemble leucite in this respect, and these minerals are not to be regarded as simple metasilicates. The place of aluminium in complex silicates is also discussed. C. H. D.

Search for the Heavier Gases of the Helium Groups in Minerals. C. F. HOGLEY (*Phil. Mag.*, 1909, [vi], 18, 672—677).—The inert gases evolved on heating certain minerals either alone or

with potassium hydrogen sulphate have been examined. The gas obtained from malacone consists almost entirely of helium, the volume of argon present being less than 1%. The search for krypton in the helium evolved from fergusonite shows that, if present at all, the amount of krypton is less than one-millionth of the helium content.

H. M. D.

Acid Sulphates. IV. JOH. D'ANS (*Zeitsch. anorg. Chem.*, 1909, 63, 225—229. Compare this vol., ii, 139).—The examination of solutions containing potassium sulphate and sulphuric acid at 25° shows that a salt, crystallising in needles, exists between $K_3H(SO_4)_2$ and $KHSO_4$, having the composition $K_2SO_4 \cdot 6KHSO_4 \cdot H_2O$, losing the water readily and completely at 180°. It appears to be identical with Stortenbecker's salt (Abstr., 1903, ii, 143). No other intermediate salt exists at 25°. A second definite salt, unstable at 25°, has a small region of stability at 18°, extending at lower temperatures. It probably has the composition $K_2SO_4 \cdot 3KHSO_4$ (compare Arzallier, Abstr., 1908, ii, 763).

C. H. D.

Application of Electrolysis in Inorganic Chemical Manufactures. BERNHARD IEPISIUS (*Ber.*, 1909, 42, 2892—2916).—A lecture before the German Chemical Society dealing with the history of the practical application of electrolysis to the manufacture of sodium hydroxide and chlorine and allied products on a large scale.

E. F. A.

The Fittig Reaction and the Dark Blue Sodium Bromide Resulting from Sodium and Bromobenzene. ERNST MOHR (*J. pr. Chem.*, 1909, [ii], 80, 315—319).—The dark blue substance which is usually produced in the Fittig reaction has been isolated and examined. Sodium wire (1 atom) is pressed into a large test-tube half-filled with dry ether, dry bromobenzene (>3 mol.) is added, and the mixture is heated on the water-bath for eight hours at 45—55°. The liquid is decanted, and, with as complete exclusion of air as possible, the dark blue, heavy powder is washed with dry ether, dried at the pump for fifteen minutes, and kept in dry air, in which it remains unchanged for weeks. Two estimations of the bromine in different specimens showed the presence of 98.3 and 91.3% of sodium bromide; the remaining percentage is attributed to organic matter which cannot be removed by ether. The suggestion is advanced that the colour may be due to finely-divided sodium or to sodium sub-bromide, Na_2Br . The question whether sodium phenyl is an initial product of the Fittig reaction is also discussed.

C. S.

Formation and Decomposition of Mixed Crystals of Alkali Nitrates and Nitrites. GIUSEPPE BRUNI and D. MENEGHINI (*Zeitsch. anorg. Chem.*, 1909, 64, 193—199).—The freezing-point curve of mixtures of sodium nitrate and nitrite has a minimum at 50% $NaNO_3$ and 221.5°. The salts form two series of solid solutions, and there is a break in the curve at 37% $NaNO_3$. The end of the crystallisation is not readily determined by thermal means, but by

isolation of the solid phase by means of van Eyck's apparatus (Abstr., 1900, ii, 403) and analysis, the limits of the gap are found to be 29.5 and 35% NaNO_3 . The minimum thus falls within the region of the second series of mixed crystals.

Mixed crystals of sodium nitrate and nitrite are not formed by crystallisation from a solution of the mixed salts in water. The heat of solution of the mixed salts in water is that calculated from the heats of solution of the pure salts, whilst that of the rapidly cooled mixed crystals is considerably different, indicating that decomposition of the mixed crystals into their compounds takes place at temperatures below the freezing point. This resolution is hastened by the presence of moisture. C. H. D.

True Atomic Weights. Stas' Determinations. III. LOUIS DUBREUIL (*Bull. Soc. chim.*, 1909, [iv], 5, 852—859, 860—865).—In these two papers the investigations already outlined (Abstr., 1908, ii, 936, 1035; this vol., ii, 475, 563, 654) are extended to the cases of silver iodide and silver bromide, and Stas' methods and results are critically reviewed. From the data obtained by Stas in the synthesis of silver iodide by three different methods, it is shown that the recalculated values of the apparent atomic weights of silver are 108.032, 108.0262, and 108.0278, whilst those for iodine are 126.9928, 126.9769, and 126.9756 respectively.

In the case of silver bromide, Stas employed two methods, and the recalculated apparent atomic weights deduced from these results are: for silver, 107.9933 and 107.9943, and for bromine, 80.0091 and 80.0077 respectively. T. A. H.

Solubility of Silver and of its Alloys in Mixtures of Acids. ERNESTO PANNAIN (*Gazzetta*, 1909, 39, ii, 234—239).—Pure silver is insoluble in dilute sulphuric acid, and the same is the case with an alloy of 5 parts of silver with one part of copper, whilst pure boiling sulphuric acid does not dissolve silver except when it has the density 60°Bé. The presence of impurities may, however, determine the attack of the metal, even by dilute acids. For the industrial separation of silver and gold, sulphuric acid of density less than 60°Bé should not be employed, the action of this acid on the silver being facilitated by the presence of nitric acid. If a mixture of these two acids is used, the silver dissolves at a comparatively low temperature, and the amount of nitric acid used up is only one-half of that required to dissolve the silver in absence of sulphuric acid. In the treatment of alloys of silver with dilute sulphuric acid, either for the whitening of coins or manufactured articles, or for the separation of silver from base metals, it is essential that such impurities as occur in commercial sulphuric acid or well-water should be absent from the acid, otherwise the action of the latter will not be confined to the base metals. T. H. P.

Investigation of the Eutectic Mixture of Silver and Ammonium Nitrates by the Method of Melting. FLAVIAN M. FLAWITZKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 739—743).—The author has studied the eutectic mixture of silver and ammonium

nitrates by the method previously employed in investigating cryohydrates (*ibid.*, 1896, 28, 424). The eutectic mixture contains 48.75% AgNO_3 , and was collected at the temperature 102.4° ; Zawidzki (Abstr., 1904, ii, 389) found that the eutectic mixture of these two salts solidified at 100.8 — 101.5° .

The mean composition of the eutectic mixture is $\text{AgNO}_3 + 2.232\text{NH}_4\text{NO}_3$, corresponding with 30.94 mol. % of silver nitrate. The ratio of the molecular depressions of melting point for the two salts in the mixture is calculated to be 1.43 or nearly 1.5, and, assuming that the salts polymerise to $(\text{AgNO}_3)_3$ and $(\text{NH}_4\text{NO}_3)_2$, the mixture should consist of $\text{AgNO}_3 + 2.283\text{NH}_4\text{NO}_3$, corresponding with 30.46 mol. % of silver nitrate. This complex composition, which approximates to $4\text{AgNO}_3, 9\text{NH}_4\text{NO}_3$, may be explained by the existence of the double salts, $\text{AgNO}_3, \text{NH}_4\text{NO}_3$, $\text{AgNO}_3, 2\text{NH}_4\text{NO}_3$, and $\text{AgNO}_3, 3\text{NH}_4\text{NO}_3$, the conditions of stability of these being different in the solid and fused states; in the solid state only the compound $\text{AgNO}_3, \text{NH}_4\text{NO}_3$ is known. The m. p. of $\text{AgNO}_3, 3\text{NH}_4\text{NO}_3$ is calculated to be 145.7° , and that of $\text{AgNO}_3, 2\text{NH}_4\text{NO}_3$, 8.6° . T. H. P.

Preparation of Silver Dimercurous Arsenate and Phosphate.

JULES JACOBSEN (*Bull. Soc. chim.*, 1909, [iv], 5, 947—950).—*Silver dimercurous arsenate*, $\text{AgHg}_2\text{AsO}_4$, forms orange-red crystals, each consisting of four associated monoclinic crystals approaching rhombic symmetry. It is obtained by adding hydrogen peroxide solution, freed from chlorides, to a solution of silver nitrate, mercurous nitrate, and potassium arsenite in dilute nitric acid.

Silver dimercurous phosphate, AsHg_2PO_4 , occurs in yellowish-white, hemimorphic, rhombic prisms or rhombic tablets, and is obtained by adding disodium hydrogen phosphate to a solution of mercurous nitrate and silver nitrate in very dilute nitric acid. The precipitate first formed is crystallised by dissolving in the minimum quantity of nitric acid and then diluting with water. Both salts are blackened by ammonia, and liberate free mercury.

Attempts to replace (1) the silver, and (2) the mercury by lead in these salts were unsuccessful. T. A. H.

Complex Salts of Glucinum and Zirconium.

SEBASTIAN M. TANATAR and E. K. KUROVSKI (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 813—815).—The action of sodium tungstate on glucinum chloride or nitrate leads to the precipitation of complex salts of more or less basic character, depending on the conditions. Two such salts have been prepared, containing (1) 14.55% GlO and 79.30% WO_3 , and (2) 24.61% GlO and 57.26% WO_3 , and both having formulæ of the type: $x\text{GlX}_{2,y}\text{GlWO}_4, z\text{GlO}$. The following complex salts have also been prepared: (1) $\text{ZrCl}_4, 2\text{Zr}(\text{WO}_4)_2, 2\text{ZrO}_2$; (2) $x\text{GlCl}_2, y\text{Gl}_2(\text{VO}_4)_2, z\text{GlO}$; (3) $x\text{Gl}(\text{NO}_3)_2, y\text{Gl}_2(\text{VO}_4)_2, z\text{GlO}$; (4) $x\text{ZrCl}_4, y\text{Zr}_3(\text{VO}_4)_3, z\text{ZrO}_2$, together with glucinum and zirconium molybdates, GlMoO_4 and $\text{Zr}(\text{MoO}_4)_2$. T. H. P.

Hydrates of Magnesium and Zinc Nitrates. ALEXIS VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 744—748. Compare Funk, Abstr., 1899, ii, 209).—Magnesium nitrate forms hydrates containing

2, 6, and, probably, $9\text{H}_2\text{O}$, whilst with zinc nitrate there exists, in addition, a hydrate with $4\text{H}_2\text{O}$. This observation is in harmony with the less marked metallic character of zinc compared with magnesium, which explains the fact that zinc nitrate readily loses nitric acid even at the ordinary temperature, whilst $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ does not decompose, but, on heating, loses 4 mols., possibly more, of water. The dihydrates of these salts correspond with the first anhydride of orthonitric acid, $\text{NO}(\text{OH})_3$, and may be represented thus: $\text{Zn}[\text{O} \cdot \text{NO}(\text{OH})_2]_2$, whilst the tetrahydrates correspond with orthonitric acid, $\text{N}(\text{OH})_5$, for example, $\text{Zn}[\text{O} \cdot \text{N}(\text{OH})_4]_2$. T. H. P.

Investigation of the Interactions between the Hydrates of Zinc or Magnesium Nitrate by the Method of Cooling Mixtures. ALEXIS VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 748—753).—The author has investigated the interactions occurring between the two members of each of the following pairs of hydrates: (1) $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$; (2) $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; (3) $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. The results are as follows:

(1) In this case, interaction took place at the constant temperature, $54 \cdot 5^\circ$, the mixture flowing away at this temperature containing 18.16% MgO , corresponding with $\text{Mg}(\text{NO}_3)_2 \cdot 4 \cdot 1\text{H}_2\text{O}$. The break in the curve hence occurs at about 55° , and not at 67° as stated by Funk (*Abstr.*, 1899, ii, 209). According to Flawitzky's law (*Abstr.*, 1906 ii, 152), which states that in cryohydrates or eutectic alloys the depressions of the melting points of the constituent parts are inversely proportional to their chemical masses, the composition of the mixture, m. p. $54 \cdot 5^\circ$, should be $\text{Mg}(\text{NO}_3)_2 \cdot 4 \cdot 193\text{H}_2\text{O}$, which is in good agreement with the experimental result.

(2) With hexa- and tetra-hydrated zinc nitrates the temperature of interaction is $35 \cdot 4^\circ$, and the composition of the product obtained, $\text{Zn}(\text{NO}_3)_2 \cdot 5 \cdot 5\text{H}_2\text{O}$; the composition calculated by means of Flawitzky's law being $\text{Zn}(\text{NO}_3)_2 \cdot 5 \cdot 496\text{H}_2\text{O}$.

(3) Here the temperature of interaction is $38 \cdot 4^\circ$, and the composition of the mixture, $\text{Zn}(\text{NO}_3)_2 \cdot 3 \cdot 138\text{H}_2\text{O}$, the calculated composition being $\text{Zn}(\text{NO}_3)_2 \cdot 3 \cdot 173\text{H}_2\text{O}$. T. H. P.

Alloys of Lead and Tin. P. N. DEGENS (*Zeitsch. anorg. Chem.*, 1909, 63, 207—224. Compare Rosenhain and Tucker, *Abstr.*, 1908, ii, 1038).—The lead-tin eutectic point is found to lie at 181° and 24.4 atomic % Pb. Tin retains only 0.21 atomic % of lead in solid solution, whilst lead retains 1.2 atomic %, or possibly more, of tin. A transformation at 146° is found, having a maximum duration at 57 atomic % Pb. Experiments with an air dilatometer confirm the thermal results, the transformation being observed in all alloys containing 0—88 atomic % Pb. Microscopically, the occurrence of the transformation in cooling is marked by the appearance of a constituent distributed through the lead. The existence of a compound formed from solid lead and tin at 146° is suggested, but the formula is unknown. C. H. D.

Red Lead. II. JAROSLAV MILBAUER (*Chem. Zeit.*, 1909, **33**, 950—951, 960—961. Compare this vol., ii, 574).—More rapid rotation of the containing tube reduces the yield of red lead, owing to the formation of lumps. The previous heating of the air or oxygen supplied is practically without influence. The presence of impurities (alkalis, lead, silver, or copper oxides) has practically no effect on the velocity of reaction; bismuth and zinc retard the oxidation. Dilution with an inactive substance reduces the velocity, the action being mechanical. The yield of red lead from lead carbonate amounts to 89.9% after three hours' heating, and is not increased when the heating is continued for seven hours; the reaction occurs, however, at lower temperatures than when lead oxide is used, the maximum velocity being at 450°. Decomposition of the red lead sets in above 470°. C. H. D.

Action of Lead Oxide and some Lead Salts on Concentrated Solutions of Magnesium Chloride and a New Process for Making White Lead. HANS HOF (*Chem. Zeit.*, 1909, **33**, 1077—1078. Compare Abstr., 1887, 446; 1891, 151; 1904, ii, 336; 1908, ii, 946; this vol., ii, 668).—A boiling concentrated solution of magnesium chloride dissolves considerable quantities of lead oxide; for example, 1 litre of a solution of specific gravity 1.32 will dissolve 50 grams of lead oxide. If the oxide contains carbonate, a pasty mass of basic carbonate of magnesium is precipitated at the same time. Lead carbonate and also the basic carbonate will dissolve in a cold concentrated solution of magnesium chloride; if the solution so obtained is heated to 80° the lead carbonate decomposes with the evolution of carbon dioxide and precipitation of basic carbonate of magnesium. The filtrate, on cooling, deposits a double chloride of lead and magnesium, which has the composition $2\text{MgCl}_2, \text{PbCl}_2, 13\text{H}_2\text{O}$, and is decomposed by water. The same double chloride is at first deposited when the hot saturated solution of lead oxide in concentrated magnesium chloride is allowed to cool, but after some days the whole solidifies to a mixture of the double chloride and a magnesium oxychloride, $\text{MgCl}_2, 5\text{MgO}, 13\text{H}_2\text{O}$.

In order to make white lead from this mixture, it is suspended in water and heated to such a temperature that the magnesium oxychloride is decomposed, being well stirred meanwhile. Lead oxychloride is formed at the same time, and this treatment is continued until the filtrate from a cooled portion of the mixture shows only a trace of lead. The mixture of lead oxychloride and magnesium hydroxide is then filtered from the mother liquors, again suspended in water, and the suspension treated with carbon dioxide at steam heat, until a neutral reaction is obtained. The reaction is complete in about four hours, and with proper precautions a pure white, chlorine-free basic carbonate of lead is produced, which has a high covering power. The process can be used with litharge containing the oxides of iron or copper, since these are without action on the solution of magnesium chloride; the copper must not be present as cuprous oxide.

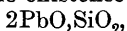
Zinc oxide is slightly soluble in a hot concentrated solution of magnesium chloride, but zinc carbonate has no effect on the colour of white lead, so that litharge containing zinc may be treated in the

above manner. Lead sulphate also dissolves in hot concentrated magnesium chloride solution, but on cooling the double chloride of lead and magnesium separates. By appropriate treatment, after the addition of milk of lime in order to produce the necessary quantity of magnesium hydroxide, this double chloride may also be converted into white lead.

T. S. P.

Lead Silicates. SIEGFRIED HILPERT and PAUL WEILLER (*Ber.*, 1909, 42, 2969—2977. Compare Abstr., 1907, ii, 870).—The freezing-point curve of mixtures of lead oxide and silica in varying proportions has been investigated. Lead oxide melts at 776° , and the increasing addition of silica lowers the melting point until the eutectic temperature, 675 — 685° , is reached, corresponding with 24 mols. % SiO_2 . Over this portion of the curve the melting points were readily obtained from the cooling curves, but immediately the eutectic composition was passed, crystallisation took place so slowly that the method of thermal analysis was of no value; with the ordinary rate of cooling, the fused mass solidified to a glass. When the cooling took place sufficiently slowly, however, the point at which crystallisation occurred could be told by direct observation of the fused mass; the results thus obtained were checked by observing the behaviour of the crystallised substance on heating.

The curve does not show the existence of an orthosilicate,



but gives a maximum (770°) corresponding with the metasilicate, PbO,SiO_2 . A second eutectic past this maximum could not be observed, since with more than 52 mols. % of silica the fused mass always solidified as a glass. This glass zone exists, at all events, as far as the composition $2\text{PbO},3\text{SiO}_2$, and in order to obtain thin-fluid fusions, it is necessary to raise the temperature to above 1000° . These silicates with high melting points become cloudy on cooling, and take on the appearance of enamel. Only in the case of the silicate $2\text{PbO},3\text{SiO}_2$ could crystals be detected; these crystals were not silica, and it is therefore probable that a lead silicate exists which is richer in silica than the metasilicate.

The specific volumes of the lead silicates investigated were always higher than according to the ordinary rule of mixing. The crystallised metasilicate has $D\ 6.36$; the amorphous has $D\ 5.93$; the crystals are biaxial, and belong either to the rhombic or the monoclinic system. The refractive indices of glasses rich in lead are very high; for example, that of a glass with the composition $2\text{PbO},\text{SiO}_2$ is 2.07 for sodium light. The glasses also show complete absorption in the violet and ultraviolet. The orthosilicate glass is dark yellow, the metasilicate, light yellow; the colour darkens with rise in temperature.

All the basic fusions up to and including the metasilicate easily dissolve in mineral acids and in acetic acid, silica being deposited. With increasing content of silica, they are less readily attacked, so that one of the composition $\text{PbO},2\text{SiO}_2$ must be dissolved in hydrofluoric acid.

Lead oxide and silicates richer in lead than the metasilicate are

reduced by hydrogen at 240° . With the meta and higher silicates, reduction only begins above 300° .
T. S. P.

The Solubility of Cuprous Iodide. MORITZ KOHN (*Zeitsch. anorg. Chem.*, 1909, 63, 337—339).—It is stated in several text-books that cuprous iodide is insoluble in cold potassium bromide solution. This is erroneous; cuprous iodide dissolves readily in solutions of potassium bromide, to an extent increasing considerably with the concentration. The solutions undergo change in the course of a few days, iodine being set free, the solubility of the cuprous iodide not being markedly affected.
C. H. D.

The Supposed Copper Quadrantoxide. L. MOSER (*Zeitsch. anorg. Chem.*, 1909, 64, 200—214).—The green precipitate obtained by Rose by the reduction of copper sulphate with an alkaline stannous solution, and regarded by him as the oxide Cu_4O , consists of cuprous oxide and copper. The precipitate is analysed after washing with warm water out of contact with air by dissolving in dilute nitric acid and estimating the total copper electrolytically. The cuprous copper is estimated by dissolving in dilute sulphuric acid.

Similar results are obtained by the action of alkaline stannous sulphate on copper sulphate or on precipitated cuprous oxide, and also by the action of sodium hyposulphite on cupric salts. It is also impossible to prepare a suboxide by igniting copper oxalate in a current of carbon dioxide.
C. H. D.

The Resolution of Ytterbium. FRANZ WENZEL (*Zeitsch. anorg. Chem.*, 1909, 64, 119—120).—A statement in support of Welsbach's priority in the resolution of ytterbium into two elements, as against Urbain.
C. H. D.

Liquidus Curves of the Ternary System: Aluminium-Copper-Tin. JOHN H. ANDREW and C. A. EDWARDS (*Proc. Roy. Soc.*, 1909, A, 82, 568—579).—From the form of the liquidus curves, it is clear that no ternary compound is deposited from any liquid alloy containing aluminium, copper, and tin. The behaviour of the aluminium and copper towards tin indicates, in fact, that the system may almost be considered as a binary series of alloys. This is seen by a comparison of the freezing-point curves of alloys which contain a constant percentage of tin.

Independently of the tin concentration, the curves are very similar to that which represents the behaviour of copper aluminium alloys. The data indicate further that the compound Cu_3Al is quite stable in presence of tin, and that this is insoluble in the majority of the alloys
H. M. D.

The Amount of Sulphur in Electrolytic Iron. AUGUST PFAFF (*Zeitsch. Elektrochem.*, 1909, 15, 703—705).—Three samples of electrolytic iron were made by electrolysis of 6, 12, and 13% ferrous sulphate solutions at 70 — 95° , using iron containing 0.03% of sulphur as anode and a cathodic current density of 2 amperes per sq. dm. Two other

samples were made from 2% ferrous ammonium sulphate solution at 30°. The quantity of sulphur found by dissolving the deposit in hydrochloric acid and collecting the hydrogen sulphide evolved in ammoniacal hydrogen peroxide varied from 0.0002 to 0.0008%.

T. E.

Influence of Foreign Substances on the Diagram of Condition of the Alloys of Iron and Carbon. PAUL GOERENS (*Zeitsch. Elektrochem.*, 1909, 15, 617—634).—The construction of three dimensional models showing, not only the temperatures at which crystallisation begins in mixtures of three components, but also the secondary changes in the solid is discussed, Charpy's results for the system lead-tin-bismuth being taken as an example. When manganese, silicon, chromium, nickel, or tungsten is added to a mixture of iron and carbon, the arrests on the cooling curve are merely displaced; the addition of phosphorus, tin, arsenic, or antimony, on the other hand, gives quite a new set of arrests on the cooling curve. The systems manganese-iron-carbon and phosphorus-iron-carbon are discussed very fully with the help of a number of diagrams and microphotographs of sections. The greater part of the data used have already been published (compare Abstr., 1908, ii, 1041, 1042, and this vol., ii, 241).

T. E.

Electrical Conductivity of Ferric Sulphate Solutions. ROGER C. WELLS (*J. Amer. Chem. Soc.*, 1909, 31, 1027—1035).—When a solution of ferric sulphate is diluted, a precipitate gradually forms, which is usually regarded as a basic salt. Cameron and Robinson (Abstr., 1908, ii, 112) have shown that such precipitates have not a definite composition. The present investigation was undertaken with the object of tracing the changes which take place when a solution of ferric sulphate is diluted.

The results show that at low dilutions the conductivity is abnormally low, whilst at high dilutions it is abnormally high. As the dilution increases, a precipitate is produced, the rate of its formation increasing enormously with rise of temperature. The conductivities of the solutions at 0°, 25°, and 30° before the production of the precipitate have been determined by direct measurement at low dilutions and by extrapolation at high dilutions. The values obtained indicate that ferric sulphate begins to undergo hydrolysis at a dilution of a few litres. It is suggested that the hydrolysis takes place in two stages, the first occurring with great rapidity, but without the formation of a precipitate, and the second at a measurable rate and accompanied with the production of the so-called "basic salt."

E. G.

Phosphorus Compounds of Cobalt. S. F. SCHEMTSCHUSCHNY and I. SCHEPELEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 862—875).—The authors have investigated the melting-point curve of alloys of cobalt and phosphorus, and also the microstructure of several of the solidified products. The results obtained indicate the existence of dicobalt phosphide, Co_2P , which has a hardness of about 6, those of cobalt and phosphorus being 4 and 0.5 respectively; this increased

hardness may be connected with the considerable contraction which occurs on formation of the compound. The values of D are for Co_2P , 6.3—6.6; for Co , 8.5—8.9, and for P , 1.8—2.3. The compound exhibits magnetic properties, which are less intense than for cobalt or the alloys intermediate to Co and Co_2P . Increase of the proportion of phosphorus beyond that corresponding with Co_2P leads to the formation of non-magnetic compounds, such as Co_2P_3 . T. H. P.

Nickel and Cobalt Chromates. SAMUEL H. C. BRIGGS (*Zeitsch. anorg. Chem.*, 1909, **63**, 325—329. Compare Abstr., 1908, ii, 113; Gröger, *ibid.*, 690; Schulze, Abstr., 1896, ii, 24).—Nickel and cobalt chromates are insoluble in water, like the chromates of copper, zinc, and cadmium, and are not precipitated from nickel and cobalt solutions; they must therefore be polymerised.

Nickel chromate, NiCrO_4 , is obtained by heating a solution of 6.5 grams of nickel carbonate and 10 grams of chromium trioxide in 10 c.c. of water in a sealed tube to 260° for several hours. The solid is collected and washed with water, alcohol, and ether. It forms black crystals, insoluble in hot dilute nitric acid, and only slowly attacked by concentrated nitric acid or aqua regia. For analysis, it is fused with sodium and potassium carbonates, forming nickel oxide and alkali chromate.

Cobalt chromate, CoCrO_4 , prepared in a similar manner at 185° , forms greyish-black crystals, readily soluble in hot dilute nitric acid. For analysis, mercurous nitrate is added, and the cobalt precipitated from the filtrate by alkali.

Cobalt chromate dihydrate, $\text{CoCrO}_4 \cdot 2\text{H}_2\text{O}$, obtained from cobaltic acetate and potassium chromate in an attempt to prepare complex cobaltic chromates, forms bronze-coloured prisms or leaflets, always mixed with some double chromate. C. H. D.

Stability and Reactions of Uranyl Chloride. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1909, 836—837).—Uranyl chloride is stable in a perfectly dry atmosphere. An aqueous solution, if air is excluded, slowly deposits a small quantity of uranic hydroxide, which after some time partly redissolve. The decomposition is more rapid in presence of air. No evidence has been obtained of the formation of chlorouranic acid, $\text{UO}_2\text{Cl} \cdot \text{OH}$.

W. O. W.

Action of Uranic Sulphate on Calcium Carbonate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1909, 838—843).—Uranic sulphate and calcium carbonate interact when covered with water, or when a mixture of the two salts is fused, triturated in a mortar, or compressed. Analytical details of experiments are given, from which it appears that 19.97—29.33% of the calcium carbonate is converted into calcium sulphate under these conditions.

W. O. W.

Nature of Certain Sodium Uranium Compounds. FLOYD J. METZGER and M. HEIDELBERGER (*J. Amer. Chem. Soc.*, 1909, **31**, 1040—1045).—This investigation was undertaken with the object of

ascertaining whether the final product obtained in the estimation of uranium by Patera's method (*K. k. Geol. Reichsanstalt, Sitzungs Verhandl.*, March 20, 1866) is correctly represented by the formula $\text{NaO}(\text{U}_2\text{O}_5)_2$. This formula is still employed, although it ought to have been changed to $\text{Na}_2\text{U}_2\text{O}_7$ when the formula for water was altered from HO to H_2O . The results of the experiments show that, although sodium uranate may actually be precipitated of the composition $\text{Na}_2\text{U}_2\text{O}_7$, on washing with water to remove the excess of alkali, it gradually undergoes partial hydrolysis, so that pure sodium uranate, obtained by adding sodium hydroxide to a solution of uranyl nitrate, has the composition $\text{Na}_4\text{U}_5\text{O}_{17}$, and Patera's precipitate the composition $\text{Na}_9\text{U}_{10}\text{O}_{35}$.
E. G.

[Preparation of] Uranates by a Wet Method. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1909, 835—836).—A solution of calcium, strontium, barium, or magnesium chloride is added to a solution of uranyl chloride and the mixture treated with excess of ammonia (free from carbonate). The uranate is precipitated in the hydrated condition. The reaction is represented by the equation: $\text{UO}_2\text{Cl}_2 + \text{MCl}_2 + 4\text{NH}_3 + 2\text{H}_2\text{O} = \text{MUO}_4 + 4\text{NH}_4\text{Cl}$. W. O. W.

Reduction of Titanium Chloride by Hydrogen. HANS GOERGES and ARTHUR STÄHLER (*Ber.*, 1909, 42, 3200—3218. Compare *Abstr.*, 1905, ii, 40, 595).—The object of the present investigation was to determine the course of the reduction of anhydrous titanium tetrachloride by hydrogen, in order, if possible, to find the best methods of making the anhydrous trichloride and dichloride, and also the metal. It also presents other points of interest, in that titanium trichloride decomposes into the tetrachloride and dichloride at 440° , whereas in order to make it from the tetrachloride and hydrogen a temperature above 600° is necessary.

The anhydrous tetrachloride was prepared by chlorinating the carbide obtained from rutile, and was distilled in a special apparatus which contained no rubber connexions; the joints were all of glass, and any necessary seals were made with mercury, which is attacked to a very slight extent only by the tetrachloride.

In the first sets of experiments a dry mixture of titanium tetrachloride and hydrogen was passed through a porcelain tube, which was heated electrically to different definite temperatures. The amount of decomposition which took place was determined by measuring the amount of hydrogen and hydrogen chloride formed, and also the amount of tetrachloride remaining unchanged; the trichloride formed remained as a solid deposit in the porcelain tube. It was found that as the temperature rises, the amount of decomposition increases. At 785° the percentage decomposition was 21.7%, whereas at 1200° it was 94.3%. Experiments were made at eleven other temperatures lying between these two extremes. In all probability a state of equilibrium was reached while the gases were in the hot zone of the porcelain tube. When the concentration of the hydrogen is increased relatively to that of the titanium tetrachloride, the percentage decomposition increases. At constant temperature the ratio $[\text{TiCl}_3]^4/[\text{TiCl}_4]^3$ was approximately constant, but no explanation of this could be given. When hydrogen

chloride was added to the mixture of titanium tetrachloride and hydrogen, the percentage decomposition was considerably diminished.

A new method is described, by means of which large quantities of anhydrous titanium trichloride can be prepared. The principle used is that of the hot-cold tube. A porcelain tube, which is electrically heated by means of a wire spiral inside it, is surrounded by a glass tube, which is externally cooled by a rapid stream of cold water. A mixture of titanium tetrachloride and hydrogen is passed through the space between these tubes, and the trichloride collects in large quantities on the surface of the cold tube as a fine, reddish-violet powder, which rapidly decomposes on exposure to moist air.

The anhydrous trichloride possesses an appreciable vapour tension of the tetrachloride, even at the ordinary temperature, so that it undergoes decomposition to some extent according to the equation: $2\text{TiCl}_3 \rightleftharpoons \text{TiCl}_2 + \text{TiCl}_4$. The dichloride was prepared from it according to the method of Friedel and Guérin (this Journ., 1876, i, 190), and was obtained as a black substance which dissolved in fuming hydrochloric acid with the formation of a green solution. This solution contained bivalent titanium, and gave the following reactions. On boiling in the air, it became violet, with the formation of tervalent titanium. Nitric acid oxidised it first to the tervalent condition (violet), and then to the quadrivalent (colourless). With titanium tetrachloride: violet colour, due to the formation of the trichloride. Ammonium hydroxide, carbonate, or sulphide gave first a dark brown precipitate, which decomposed after a short time with the rapid evolution of hydrogen. Potassium thiocyanate gave a green solution, and sodium acetate a green precipitate of the titanous acetate. On heating with mercuric chloride, calomel was precipitated.

Indications were obtained that when the trichloride is reduced by hydrogen at a bright red heat, some metallic titanium is formed.

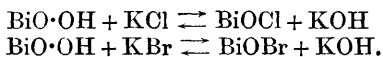
T. S. P.

Colloidal Thorium. EDGAR WEDEKIND and HEINRICH BAUMHAUER (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 191—193).—This material is of special interest, as it is a radioactive element in a colloidal condition. The technique of its preparation was suggested by that of the authors' previous work with zirconium (compare Abstr., 1908, ii, 501). Finely-divided thorium metal (95—96%) is thoroughly rubbed up in a mortar with cold dilute acetic acid (a stronger acid would act on the metal). The paste is brought on to a filter, and the acetic acid washed out with cold water. At a certain point a colloidal solution passes through. It shows grey opalescence by reflected light, and appears brown when light is transmitted through it. The hydrosol of thorium is fairly stable in the presence of certain electrolytes, but alkalis readily bring about its precipitation, presumably because of the decomposition of thorium acetate, which exerts a protective action on the colloid. It is stable against mineral acids. Freezing invariably brings about coagulation, the precipitate being readily observable on thawing. A freshly dialysed colloidal thorium solution was examined in an electrolytic cell. It was free from electrolytes. The space round the anode rapidly became clear when a difference of potential of

18 volts was set up between the electrodes, the particles moving to the cathode. Colloidal thorium, therefore, like colloidal zirconium, carries a positive charge. In a very dilute solution, particles can be resolved ultramicroscopically. They appear colourless, smaller than those of zirconium, and to be in violent commotion. A comparison of the radio-activities of thorium as metal and as hydrosol showed that 0.0235 of the latter were equivalent to 0.111 of the former. It is remarkable and not explained that although metallic thorium has a radio-activity of 15.4 uranium-potassium-sulphate units, and that of thorium oxide prepared from it is 8.6, yet that of the thorium hydrosol is smaller than that of thorium nitrate solution. The gel dried in a high vacuum, and at a high temperature was found to contain thorium 20.5%, and thorium oxide 78%.

G. S. W.

Equilibrium Reactions with Bismuth Hydroxide. WALTER HERZ and ALFRED BULLA (*Zeitsch. anorg. Chem.*, 1909, 63, 282—284).—The experiments of Herz and Muhs (*Abstr.*, 1904, ii, 413) have been repeated, using the pure compound $\text{BiO}\cdot\text{OH}$ prepared by Moser's method (this vol., ii, 320). The two following reactions were studied :



The values obtained for the equilibrium constants were 0.082 and 0.57 respectively, differing considerably from those formerly found from the reverse reactions. There are probably several distinct bismuth hydroxides.

C. H. D.

Preparation of Colloidal Gold Solutions by means of Hydrogen Peroxide. FRIEDRICH DOERINGKEL (*Zeitsch. anorg. Chem.*, 1909, 63, 344—348).—A solution containing 6 grams $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$ per litre is used, 2 c.c. being added to 100 c.c. of water, followed by five drops of hydrogen peroxide solution, stirring continuously. Reduction sets in after a minute, and is complete in a few seconds, giving a deep wine-red solution with slight opalescence. Perfectly clear solutions may be prepared by the addition of Zsigmondy's "nucleus" solution to the above mixture.

In alkaline solutions, hydrogen peroxide gives only turbid suspensions, unless about 1 c.c. of the "nucleus" liquid is added, when a deep blue solution, clear in transmitted or reflected light, is obtained.

Several of the solutions have been compared ultra-microscopically with those prepared by reduction with phosphorus.

C. H. D.

Gold-Magnesium Alloys. RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1909, 63, 169—183).—Alloys of gold and magnesium are best prepared by melting the magnesium in a current of hydrogen and adding the gold in small quantities, the reaction being violent. Alloys containing less than 27% Mg do not attack porcelain even at 1300°, but those richer in magnesium attack it, dissolving magnesium silicide.

Gold and magnesium form three compounds, each of which is

indicated by a maximum on the freezing-point curve, AuMg melting at 1160° , AuMg_2 at 796° , and AuMg_3 at 830° . The first forms solid solutions with both components, and the last with small quantities of gold, but the latter solid solution breaks up into AuMg_2 and AuMg_3 at about 715° .

The alloys containing up to 18 atomic % Mg are yellow; all others are silver-grey. Those containing 30–66 atomic % Mg are brittle, with a maximum hardness 5 and glassy fracture; the other alloys are more or less malleable, with granular fracture. All are stable in air at the ordinary temperature, and only those containing free magnesium tarnish in moist air. With 66–75 atomic % Mg, swelling and disintegration takes place at 600° . From 0 to 50 atomic % Mg, only aqua regia attacks the alloys; from 50 to 60%, concentrated nitric acid; above this, dilute acids dissolve the magnesium.

Eutectic structures are well developed in the series. The compound AuMg_3 separates in large and regularly formed crystals from its alloys with magnesium.

C. H. D.

Decomposition of Silver Tetrachloroplatinate by Water and the Preparation of Fulminating Platinum. JULES JACOBSEN (*Compt. rend.*, 1909, 149, 574–577).—Silver tetrachloroplatinate is decomposed by water at 100° in three hours, or on the water-bath in eight hours, thus: $\text{Ag}_2\text{PtCl}_4(\text{OH})_2 + \text{H}_2\text{O} \longrightarrow 2\text{AgCl} + \text{H}_2\text{PtCl}_2(\text{OH})_4$. The silver chloride is contaminated with some platinum compound containing less chlorine than tetrachloroplatinate, but the yield of dichloroplatinic acid is 80–90% of the theoretical. The solution of dichloroplatinic acid containing only platinum and chlorine was decomposed by heating to 80 – 90° , and passing a slow stream of hydrogen sulphide for one hour, boiling, and treating with hydrogen sulphide for ten minutes. The platinum was entirely precipitated by this means, and the filtrate, having been boiled to remove hydrogen sulphide, was analysed for chlorine.

On pouring excess of ammonia into a solution of dichloroplatinic acid, the liquid turns a dark colour, and finally precipitates a brown, flocculent mass containing no chlorine and resembling ferric hydroxide. Washed with boiling water until free from ammonia and dried, this precipitate presents a conchoidal structure. If dried at 100° and then over sulphuric acid, it rehydrates with such avidity that the particles jump about. When it is heated gently above 250° , the compound blackens, and finally explodes with some violence, giving spongy platinum, nitrogen, oxygen, and water vapour. The fulminating compound, which is easily soluble in hydrochloric acid, contains 67.57% of platinum and 2.944% of ammonia. It loses water when heated, until at 220° 18.47% (6 molecules) have been removed. The formula $\text{NH}_3[\text{Pt}(\text{OH})_5]_2$ corresponds with these properties.

If pyridine, instead of ammonia, is added to dichloroplatinic acid, an exactly similar detonating compound is obtained, to which the formula $\text{C}_5\text{NH}_5[\text{Pt}(\text{OH})_5]_2$ is ascribed. The carbon and hydrogen contents are 8.893 and 2.188 respectively, instead of the calculated 9.397 and 2.349.

R. J. C.

Decomposition of Ammonium Platinichloride and Ammonium Platinibromide by Heat. PRAFULLA CHANDRA RÂY and ATUL CHANDRA GHOSH (*Zeitsch. anorg. Chem.*, 1909, **64**, 184—188).

—Ammonium platinichloride decomposes when heated according to the equation: $3(\text{NH}_4)_2\text{PtCl}_6 = 3\text{Pt} + 16\text{HCl} + 2\text{NH}_4\text{Cl} + 2\text{N}_2$. The formation of di-imide (Maumené, *Abstr.*, 1890, 262) does not take place. Collecting the ammonium chloride in a tube packed with asbestos, and the hydrogen chloride in a tube packed with glass beads moistened with potassium hydroxide solution, the ratio of the chlorine in the two tubes is found to vary, owing to the absorption of hydrogen chloride by the glass and asbestos. If the salt is very dry, traces of chlorine are set free.

Ammonium platinibromide decomposes partly in the same way: $3(\text{NH}_4)_2\text{PtBr}_6 = 3\text{Pt} + 16\text{HBr} + 2\text{NH}_4\text{Br} + 2\text{N}_2$, and partly with liberation of bromine: $(\text{NH}_4)_2\text{PtBr}_6 = \text{Pt} + 2\text{NH}_4\text{Br} + 4\text{Br}$. The quantity of bromine diminishes as the salt is more thoroughly dried.

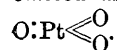
C. H. D.

Platinum Trioxide. A New Oxide of Platinum. LOTHAR WÖHLER and F. MARTIN (*Ber.*, 1909, **42**, 3326—3333).—The hydrate of platinum dioxide was dissolved in 2*N*-potassium hydroxide, and the yellow solution submitted to anodic oxidation, being well cooled meanwhile. The anode was in the shape of a crucible, and the platinum wire cathode was contained in a porous cell filled with potassium hydroxide. Soon after the electrolysis was started, the anode became covered with a golden-coloured deposit, and this peeled off after a time in the form of thin plates, which had a silky sheen; this deposit was amorphous. After being well washed with ice-cold water, it was analysed and found to have the composition $3\text{PtO}_3 \cdot \text{K}_2\text{O}$, that is, it was an alkali salt of platinum trioxide. The trioxide itself was obtained from the salt by treatment with ice-cold *N*/2-acetic acid. A reddish-brown substance was obtained, which contained slightly less oxygen than that necessary for the trioxide, owing to the fact that it readily parts with some of its oxygen as soon as all the alkali has been removed. On keeping, the percentage of oxygen gradually decreases, but it never falls to that necessary for the dioxide, probably because a solid solution of the trioxide in the dioxide is formed.

Platinum trioxide is not acted on by dilute sulphuric, nitric, or acetic acids. It slowly liberates chlorine from dilute hydrochloric acid. Sulphurous acid dissolves it with the formation of a colourless complex. Concentrated sulphuric and nitric acids slowly decompose it with the formation of the dioxide. On gently heating, it gives the dioxide.

In the cold it has no action on alcohol or acetic acid. The oxidation which takes place on warming is due to the dioxide which is formed.

It does not decompose hydrogen peroxide, and must therefore be classed as a polyoxide or peroxide of platinum of the constitution



The formation of platinum trioxide explains a number of phenomena which have been observed by other investigators when working with

platinum. In particular, it may be mentioned that the anodic passivity of platinum is probably due to the formation of this oxide.

T. S. P.

Platinum Selenides. ARNALDO MINOZZI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 150—154).—The action of formaldehyde on a solution containing a platinichloride and a selenite in presence of excess of an alkali hydroxide yields *platinum triselenide* as a black, flocculent precipitate, thus: $K_2PtCl_6 + 3SeO_2 + 8H \cdot CHO + 12KOH = PtSe_3 + 6KCl + 8H \cdot CO_2K + 10H_2O$. When heated to dull redness in a current of carbon dioxide, the triselenide is converted into the *diselenide*, $PtSe_2$, which forms a greyish-black powder.

T. H. P.

Preparation and Composition of Double Compounds of $Pd(NH_3)_2X_2$ with $Pd(NH_3)_4X_2$. Preparation of $Pd(NH_2 \cdot NH_2)Cl_2$. W. A. BURDAKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 757—759).—The compound, $Pd(NH_3)_2Br_2 \cdot 4Pd(NH_3)_4Br_2$ or $PdBr_2 \cdot 3\frac{2}{3}NH_3$, forms yellow crystals belonging to the quadratic system [I. TANATAR: axial ratio for the form {111}, 1:1.1487, and for the pyramid {112}, 1:0.5835]. On reduction with hydrogen, it decomposes according to the equation: $PdX_2 \cdot nNH_3 + H_2 = Pd + 2NH_4X + (n-2)NH_3$. This compound is analogous to the chloro-compound previously obtained (*ibid.*, 1897, 29, 739), which is now shown to have the formula $PdCl_2 \cdot 3\frac{2}{3}NH_3$, and not $PdCl_2 \cdot 3\frac{1}{3}NH_3$. The iodo-compound (compare *ibid.*, 1908, 40, 742) is not analogous with the chloro- and bromo-compounds, as it has the composition $PdI_2 \cdot 3\frac{1}{3}NH_3 \cdot \frac{2}{3}H_2O$.

In the precipitation of palladium from solutions of palladium chloride by means of hydrazine hydrochloride, reduction to the metal takes place only in hot solutions. In the cold, the compound, $PdN_2H_4Cl_2$, separates as an abundant, yellowish-white precipitate; this compound is decomposed to some extent by water at the ordinary temperature, whilst on boiling with water, complete decomposition takes place according to the equation: $3PdN_2H_4Cl_2 = 3Pd + 2NH_4Cl + 4HCl + 2N_2$.

T. H. P.

Mineralogical Chemistry.

Optical Activity of Mineral Oils in an Optically Transparent State. Paraffin Content of Mineral Oils as Criterion for Judging their Relative Geological Age. LEO UBBELOHDE (*Ber.*, 1909, 42, 3242—3247).—Polemical. A criticism of Rakusin's views (compare this vol., ii, 490, 586). W. H. G.

A New Occurrence of Lautite. LUCIEN DÜRR (*Mitt. Geol. Landesanst. Elsass-Lothringen*, 1907, 6, 249—252).—This mineral, previously known only from Marienberg, in Saxony, has been found as imperfect crystals and radial aggregates in association with native

arsenic, tetrahedrite, smaltite, proustite, etc., at the Gabe Gottes mine in Rauenthal, near Markirch, Elsass. It is light steel-grey with a reddish-tinge; the streak is black. Brittle; $H = 3-3\frac{1}{2}$; $D = 4.53$. There are good cleavages, and the mineral thus shows some resemblance to enargite. (Measurements of the angles between three co-zonal cleavages appear to indicate that the mineral is monoclinic.) Analysis agrees with the formula $CuAsS$.

Cu.	As.	S.	Total.
37.07	44.53	18.30	99.90

V. DÜRRFELD (*op. cit.*, 1909, 7, 121—126) describes a single crystal of lautite from this locality; it is orthorhombic, with $a:b:c = 0.69124:1:1.0452$, and a perfect basal cleavage. L. J. S.

The Occurrence of Ammonia and Nitrates in Potash Deposits. WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1909, 64, 215—216. Compare this vol., ii, 571).—A specimen of salt-clay from Schönebeck showed an average ammonia content near that of samples from Stassfurt and Vienenburg, but a regular increase from the surfaces to the middle of the deposit could not be observed.

The value 0.2 mg. per litre for the ammonia in sea-water is too high; the value in the oceans more nearly approaches 0.05 mg.

C. H. D.

Pyromorphite from British Columbia. O. BOWLES (*Amer. J. Sci.*, 1909, [iv], 28, 41—44).—Crystals of pyromorphite are found, together with cerussite and galena, in the Society Girl mine in south-eastern British Columbia. A crystallographic description is given of this material, and analysis (I) of wax-yellow crystals and (II) of green crystals. These analyses agree with the usually accepted formula, $Pb_5Cl(PO_4)_3$.

	PbO.	CaO.	FeO.	P ₂ O ₅ .	As ₂ O ₅ .	Cl.	CaF ₂ .	Insol.	Total, less O for F.	Sp. gr.
I.	80.20	0.59	0.86	16.12	0.41	2.52	trace	0.08	100.21	7.013
II.	80.13	0.56	0.46	15.65	0.90	2.59	—	0.05	99.75	7.051

L. J. S.

Vashegyite, a New Basic Aluminium Phosphate from Hungary. KARL ZIMÁNYI (*Math. és Természettud. Értesítő, Budapest*, 1909, 27, 64; *Zeitsch. Kryst. Min.*, 1909, 47, 53—55).—The mineral occurs in some abundance in limonite in the iron mine of Vashegy in comitat Gömör, where it forms compact, dull, white masses, with the appearance of meerschäum. It is porous, and adheres to the tongue. Hardness 2—3; $D = 1.964$. Analysis I agrees with the formula $4Al_2O_3, 3P_2O_5, 30H_2O$:

	Al ₂ O ₃ .	Fe ₂ O ₃ .	K ₂ O.	Na ₂ O.	P ₂ O ₅ .	CO ₂ .	H ₂ O.	Insol.	Total.
I.	28.33	1.19	0.16	0.05	31.32	0.12	33.97	0.24	100.33
II.	29.44		—	—	27.28	—	29.15	14.62	100.49

With this new mineral are associated diadochite and a loose,

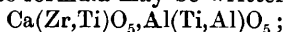
crumbling mineral; the latter gave analysis II, corresponding with $3\text{Al}_2\text{O}_3(\text{Fe}_2\text{O}_3), 2\text{P}_2\text{O}_5, 17\text{H}_2\text{O}$. Other aluminium phosphates from this locality are evansite and variscite. L. J. S.

The Keilhauite-Zirkelite Group, and a New Mineral of that Group. OTTO HAUSER (*Zeitsch. anorg. Chem.*, 1909, 63, 340—343).—A new mineral, *uhligite*, regarded at first as perowskite, has been found in a strongly altered nepheline rock from East Africa.

The analysis shows:

Cb_2O_5 .	TiO_2 .	ZrO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	Total.
Trace	48·25	21·95	10·50	trace	19·00	99·70

The mineral forms black, glistening octahedra, with conchoidal fracture; H 5—6. Its formula may be written



it is thus an aluminous zirkelite, in which titanium predominates over zirconium.

Keilhauite is regarded as being derived from the monoclinic form of sphene by isomorphous replacement of Ti and Ca by Al, Y, Fe, etc., whilst zirkelite and uhligite are derived from the regular form of the same mineral. C. H. D.

Pyrogenetic Epidote. B. S. BUTLER (*Amer. J. Sci.*, 1909, [iv], 28, 27—32).—A review is given of the previous descriptions of presumably primary epidote in igneous rocks; in these instances the epidote is often intergrown with allanite in granite. Porphyritic crystals of epidote (anal. I, D=3·29) are sparingly scattered through the porphyry (anal. II) of dykes cutting an extensive mass of soda-granite in Shasta Co., California. These crystals have a maximum length of 12 mm., and, like the porphyritic crystals of quartz, have been corroded by the magma. In addition to this porphyritic epidote, which appears to be a primary constituent of the rock, there is also some secondary epidote, present as minute granules, which has been derived from the biotite and felspar.

	SiO_2 .	TiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MnO .	MgO .	CaO .	Na_2O .	K_2O .	H_2O at 105°.	H_2O above 105°.	Total.
I.	38·22	0·33	25·12	8·75	1·25	0·19	trace	22·77	0·11	0·06	0·52	3·04	100·36
II.*	68·75	0·27	16·75	0·43	1·72	0·04	0·83	0·89	6·95	0·80	0·84	1·52	100·06
III.†	80·09	0·16	10·80	1·07	0·83	0·02	0·58	0·38	5·60	nil	0·24	0·52	100·34

* Also P_2O_5 , 0·16; BaO, 0·03; SrO, 0·03.

† Also ZrO_2 , 0·01; P_2O_5 , 0·04; BaO, SrO, nil.

L. J. S.

Nephrite and Magnesium Rocks from South Island, New Zealand. ALEXANDER MONCRIEFF FINLAYSON (*Quart. Journ. Geol. Soc.*, 1909, 65, 351—380).—A description is given of the intrusive peridotites which extend as a belt along the western side of South Island. Analyses are given of the following minerals. Tourmaline (anal. I), occurring as large, dark green to black crystals with corundum and magnetite in a matrix of chlorite and serpentine at the contact of serpentine with schists at Parapara. Epidote (anal. II), pale yellow

to colourless, columnar crystals, forming with some serpentine an epidote-rock at the contact of serpentine and limestone near Dun Mountain. Amphibole (anal. III), forming a serpentine-amphibole rock at the same contact as No. II. Nephrite (jade or New Zealand "greenstone"); analyses of a series of specimens selected to show the difference in composition (especially as regards the amount of iron) with the range in colour: IV, deep green; V, medium green; VI, olive-green; VII, pale green; VIII, greenish-white. The small amounts of alkalis shown in these analyses are no doubt due to the intermixture of glaucophane and riebeckite with the tremolite-actinolite molecules. When found *in situ*, the nephrite is associated with the peridotite and serpentine rocks. It may have had more than one mode of origin: (1) urealisation of the pyroxenes of the peridotites; (2) metamorphic action at the contact of serpentine and limestone; (3) direct change of olivine to nephrite; (4) deep-seated metamorphism of serpentine-talc-carbonate rocks. These changes were accompanied by great earth pressures and shearing, to which the compact and matted fibrous structure of the nephrite is ascribed.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
I.*	36.80	25.37	0.13	6.12	—	2.31	12.91	1.20	0.45	3.95	99.65
II.	42.45	23.27	7.91	1.22	—	21.52	1.45	—	—	2.62	100.44
III.	48.20	1.35	4.67	10.96	—	12.62	19.58	—	0.66	1.43	99.47
IV.	56.25	0.42	1.67	5.61	0.33	12.67	20.55	0.35	—	1.89	99.74
V.	56.01	0.65	1.88	5.02	0.29	13.41	20.65	0.45	0.28	2.03	100.67
VI.	55.89	2.34	2.39	2.34	0.41	13.97	18.72	0.51	—	2.21	98.78
VII.	57.45	1.09	0.24	1.35	0.28	15.41	20.61	—	0.51	2.65	99.59
VIII.	58.28	0.88	0.29	0.35	trace	14.98	22.08	0.42	0.38	1.98	99.64

* Also B₂O₃, 10.41; and traces of lithia and fluorine.

L. J. S.

Presence of Selenium in Mineral Waters from La Roche-Posay. FELIX TABOURY (*Bull. Soc. chim.*, 1909, [iv], 5, 865—867).—The composition of the soluble matter contained in the waters from the three springs at La Roche-Posay is given. They each contain traces of lithium and 0.2% of selenium, both these constituents being found in that portion of the residue soluble in a mixture of alcohol and water. Arsenic, which has been recorded previously as occurring in these waters, could not be detected, and it is suggested that selenium may have been mistaken for arsenic.

T. A. H.

Physiological Chemistry.

The Gaseous Exchange in Insects, and its Relation to the Temperature of the Air. B. SLOWTZOFF (*Biochem. Zeitsch.*, 1909, 19, 497—503).—The experiments were carried out chiefly with dung-beetles. The carbon dioxide output increases with rise of temperature

to a certain maximum, at which it remains constant on a further rise over an interval of about 12° . The point at which this occurs varies with different insects. The respiratory quotients for different species of insects were determined. S. B. S.

The Light Extinction, the Capacity to Unite with Gases, and the Percentage of Iron in Human Blood-pigment in Normal and Pathological Conditions. E. E. BUTTERFIELD (*Zeitsch. physiol. Chem.*, 1909, 62, 173—225).—In various diseased conditions, including the different kinds of anæmia, human hæmoglobin remains unchanged as regards the physical and chemical constants investigated. W. D. H.

Agglutination and Hæmolysis of Red Blood-corpuscles by Salts of Heavy Metals. J. DUNIN-BORKOWSKI and Z. SZYMANOWSKI (*Bull. Acad. Sci. Cracow*, 1909, 746—758).—There is no connexion between the agglutinating and hæmolysing power of the salts of the heavy metals and the valency and chemical relationship of these metals. G. B.

The Significance of the Cataphoresis of Blood-corpuscles. RUDOLF HÖBER (*Biochem. Zeitsch.*, 1909, 19, 494—496).—Some theoretical remarks on the nature of the phenomena observed when blood-corpuscles are treated with carbon dioxide; a criticism of the views of Spiro and Henderson on this subject. S. B. S.

Total Sugar in the Plasma and Globules of Blood. RAPHAEL LÉPINE and R. BOULUD (*Compt. rend.*, 1909, 149, 583—586. Compare Abstr., 1906, ii, 868; 1908, ii, 957; this vol., ii, 68).—Sugar in the blood estimated in the ordinary way is called by the author "immediate sugar," whilst the maximum amount of sugar obtained after treatment with hydrogen fluoride as already described is called "total sugar." An investigation is described on the estimation of sugar in the plasma and the corpuscles of blood from dogs in a normal condition and after deprivation from food. The sum of the immediate sugar of the plasma and clot is slightly higher than the immediate sugar of the blood before centrifugalisation; the total sugar, however, is the same in each case. W. O. W.

The Amount of Peptolytic Enzymes in Rabbit's Serum under Varying Conditions. II. EMIL ABDERHALDEN and WOLFGANG WEICHARDT (*Zeitsch. physiol. Chem.*, 1909, 62, 120—128. Compare this vol., ii, 816).—In a previous research it was shown that normal rabbit's serum contains no peptolytic enzyme capable of decomposing glycyl-*l*-tyrosine into its constituents, but this enzyme appears when the rabbit has been intravenously treated with certain proteins—horse-serum and egg-white. In the present research, it is shown that the same result follows the intravenous administration of certain protein cleavage products, namely, certain peptones obtained by the partial acid hydrolysis of silk. W. D. H.

The Amount of Peptolytic Enzymes in Dog's Blood-serum under Various Conditions. III. EMIL ABDERHALDEN and LUDWIG PINCUSOHN (*Zeitsch. physiol. Chem.*, 1909, 62, 243—249).—The peptolytic power of the normal blood-serum of the dog is nil, or almost so, but it appears on the parenteral administration of certain proteins and "peptones." This is not due to an enzyme specific in relation to the protein injected. It may be elicited by the subcutaneous injection of gliadin. This power of the serum is lost on heating to 60—65°.

W. D. H.

The So-called Artificial Complements. E. VON KNAFFL-LENZ (*Biochem. Zeitsch.*, 1909, 20, 1—9).—Comparisons were made between the action of artificial complements (oleic acid, etc.) and natural complements from serum, etc. It was found that hæmolysis caused by oleic acid, bile salts, or saponins could be inhibited equally strongly both by normal and immune sera. There was only a difference in the time of reaction. By heating the hæmolysing mixture to 56°, there was a very slight weakening of the hæmolysis in great dilutions, although the reaction time was lengthened. By heating highly diluted immune serum, it loses its activity. Blood-corpuscles, sensitised with a specific serum, are hæmolysed by soaps more quickly and as strongly as normal corpuscles. Mixtures of serum with solanin or sapotoxin act like the corresponding mixtures containing soaps; they differ in one respect only, in that hæmolysis undergoes neither weakening or slowing after heating to 56°. Oleic acid and bile salts behave differently to complements, with which they cannot, therefore, be regarded as identical.

S. B. S.

Metabolism of Different Classes of Animals. II. EMIL ABDERHALDEN and CARL BRAHM (*Zeitsch. physiol. Chem.*, 1909, 62, 133—135).—Young dogs who have taken nothing but milk resemble rabbits in excreting pyridine as such. After they are fed on meat, they acquire the power of excreting pyridine as a methyl compound, but later in life even prolonged feeding on milk does not alter the metabolic habit when it is once developed. Rabbits, on the other hand, never form methylpyridine, even when fed on milk or on meat.

W. D. H.

The Digestion of Fat in the Animal Body. S. J. LEVITES (*Biochem. Zeitsch.*, 1909, 20, 220—223).—Only very slight saponification of beef-fat occurs in the stomach, although very marked liberation of fatty acids from the fat in yolk of egg may be observed. These experiments bring into harmony the apparently contradictory results of Volhard (compare Abstr., 1903, ii, 494) and Levites (compare Abstr., 1908, ii, 960).

G. S. W.

The Accelerating Effect of Potassium on Sugar Degradation. Alimentary Glycosuria. JULIUS STOKLASA (*Zeitsch. physiol. Chem.*, 1909, 62, 47—57).—Attention is called to certain experiments of the author which show that in plants the oxidation processes, as determined by the quantity of expired carbon dioxide, are more

energetic in the presence of larger quantities of potassium than in the presence of small quantities or absence of this element. It is claimed that potassium plays an equally important part in the oxidation of sugar in the animal organism, and it is surmised by the author that the substance secreted by the pancreas which influences sugar metabolism contains potassium.
S. B. S.

Can the Dog Digest Cellulose or Raw Fibre? ARTHUR SCHEUNERT and ERNST LÖTSCH (*Biochem. Zeitsch.*, 1909, 20, 10—21).—The authors consider that the dog is incapable of digesting either cellulose or raw fibre, and that the previous statements to the contrary effect are due to faulty technique. Previous workers have failed to take account of the water and ash in the cellulose used for feeding, and the method of analysis (that of Simon-Lohrisch) gives false results, in that hydrogen peroxide, which is added to decolorise the mixture of alkali and substance, under analysis, readily destroys the fibre. The authors recommend a method of analysis in which the organic matter other than the cellulose is destroyed by alkali (100 parts of hydroxide to 100 parts of water), and no peroxide is employed.
S. B. S.

Influence of Silver Hydrosols and Salts on Nitrogen Metabolism. GUIDO IZAR (*Biochem. Zeitsch.*, 1909, 20, 266—291).—Female dogs were injected by the jugular vein. The diet was constant, and systematic examination of urine and fæces was made. Solutions of silver, whether in the form of nitrate, thiosulphate, albuminate, or as hydrosol, rendered stable by the addition of a dilute dialysed gelatin solution, raise the amounts of "total nitrogen" and of "purine-nitrogen" excreted in the urine. The nitrogen excreted in the fæces is diminished by stable silver hydrosol, but to obtain the same result with nitrate, thiosulphate, or albuminate much larger doses are needed. This influence on the nitrogen metabolism could not be obtained by the injection of quite considerable quantities of "collargol" or of colloidal silver that had not been rendered stable.
G. S. W.

Protein Metabolism. EMIL ABDERHALDEN and E. S. LONDON (*Zeitsch. physiol. Chem.*, 1909, 62, 237—242).—It seems to be accepted that an animal can construct its own protein out of proteins administered parentally. This has been accounted for by supposing that the injected protein is first excreted into the intestine, and thus undergoes digestion. The examination of the intestinal contents in a fistula dog after the subcutaneous administration of 200 grams of caseinogen dissolved in dilute sodium hydrogen carbonate solution, lend no support whatever to this hypothesis. A far more probable explanation is that the peptolytic and other ferments of the blood and other tissues perform the act of cleavage.
W. D. H.

Peptic Digestion of Casein from the Standpoint of the Acidity of its Cleavage Products. SIEGMUND KÜTTNER (*Pflüger's Archiv*, 1909, 129, 557—602).—By peptic digestion, casein is first decomposed into a phosphorus-free and a phosphorus-rich constituent.

The latter, paranuclein, on further digestion yields about equal parts of a phosphorus-free and a phosphorus-rich cleavage product. The former resists further gastric digestion and corresponds with Kühne's anti-complex; the latter yields peptides, and acid compounds which contain phosphorus (paranucleic acids); their presence increases the acidity of the digest. W. D. H.

The Cleavage of Histidine in the Dog's Organism EMIL ABDERHALDEN and HANS EINBECK (*Zeitsch. physiol. Chem.*, 1909, 62, 322—332).—The importance of histidine arises from the fact that it is an abundant cleavage product of globin, and so when red corpuscles are destroyed it may be important from the metabolic point of view. In the present research it was prepared from horse's red corpuscles. Its constitution suggests that it may play a part in purine metabolism, and Wiechowski's recent work shows that a necessary part of any such study is an estimation of allantoin in the urine. Examination of the faeces shows that histidine is well absorbed; when added to the diet, urea and ammonia increase in the urine, and this is followed later by a small rise in purine bases and uric acid. Using the best methods for the estimation of allantoin, the amount is increased on the days histidine is given, but the effect is certainly very small. W. D. H.

The Metabolic Changes of Nucleic Acid in the Organism of the Dog under Normal and Pathological Conditions. ALFRED SCHITTENHELM (*Zeitsch. physiol. Chem.*, 1909, 62, 80—99).—The sodium salt of α -thymonucleic acid was employed in the experiments. The total nitrogen, uric acid, purine bases, and allantoin were estimated in the urine, and the total and basic nitrogen in the faeces. If the nucleic acid is added to the normal diet of a dog, it undergoes the same changes as the endogenous nitrogen. The increased nucleic acid is excreted chiefly in the form of allantoin. Before ingestion of the additional nucleic acid, 96.8% of the purine derivatives were excreted as allantoin; after ingestion the amount was 95%. The injection of nucleic acid does not lead to the same result. Similar results were obtained when nucleic acid was administered to a starving animal. In the case of animals receiving large quantities of alcohol, the excretion was somewhat delayed. S. B. S.

Fate of the Non-hydroxylated Benzene Ring of Protein in the Animal Body. Phenaceturic Acid as an Important Constituent of Urine. HARALAMB VASILIU (*Bied. Zentr.*, 1909, 38, 644—645; from *Mitt. landw. Inst. Univ. Breslau*, 1909, 4, 703. Compare this vol., ii, 250).—Further experiments showed that the non-hydroxylated benzene ring is mostly destroyed by a carnivorous animal, but not by a non-carnivorous animal, about two-fifths being recovered in the form of hippuric acid and three-fifths is phenaceturic acid. Consequently, the protein (containing 4—5% of non-hydroxylated benzene) is less completely utilised by non-carnivorous than by carnivorous animals.

The destruction of the benzene ring depends, not on the animal, but on the nature of the food, and most probably on the reaction by which the combustion of the food in the cells proceeds. N. H. J. M.

The Comparative Physiology of Hunger Metabolism. V. B. SLOWTZOFF (*Biochem. Zeitsch.*, 1909, 19, 504—508).—The starvation metabolism of dung-beetles (*Geotrupes stercoralis*) was investigated. The insects in question die of starvation in five to eleven days, losing 21.73% of their original weight. This loss is due chiefly to water and fat. The energy utilised was calculated at 39.41 Cal. per kilo. per twenty-four hours. The amount of proteins utilised during starvation was only about one-fifth of the original quantity. The amounts of pentose and of chitin in the bodies did not change during starvation. S. B. S.

The Glycolytic Enzymes of the Pancreas. JULIUS STOKLASA (*Zeitsch. physiol. Chem.*, 1909, 62, 36—46).—The enzyme preparation was made by precipitating the expressed juice of the pancreas by alcohol-ether mixture, and rapidly drying the precipitate. The product thus obtained was found capable of producing carbon dioxide, lactic acid, and alcohol from sucrose, lactose, and maltose. Very appreciable quantities were produced within eight hours; the presence of antiseptics considerably slowed the reaction. From the monosaccharides, on the other hand, only minute quantities of carbon dioxide were obtainable under the same conditions and in the same interval of time. Monosaccharides, however, evolved considerable quantities of the gas after forty-eight hours. The latter action is due to bacteria.

S. B. S.

The Question of Pancreas Lactase (Investigations on Human New-born Children and Sucklings). J. IBRAHIM and L. KAUMHEIMER (*Zeitsch. physiol. Chem.*, 1909, 62, 287—295).—The pancreas, either of new-born children or of those in the suckling period, contains no lactase.

W. D. H.

The Occurrence of Peptolytic Enzymes in Invertebrates. EMIL ABDERHALDEN and ROBERT HEISE (*Zeitsch. physiol. Chem.*, 1909, 62, 136—138).—Extracts of the alimentary canal of nearly all the invertebrates examined (including coelenterates, echinoderms, worms, arthropods, and molluscs) liberate tyrosine from glycyl-*t*-tyrosine.

W. D. H.

Action of Arsenic on Autolysis. GUIDO IZAR (*Biochem. Zeitsch.*, 1909, 21, 46—50).—The way in which arsenic affects autolysis depends on the quantity. Small amounts inhibit, larger amounts accelerate it.

W. D. H.

Action of Silver Salts on the Autolysis of Liver. GUIDO IZAR (*Biochem. Zeitsch.*, 1909, 20, 249—265).—The accelerating action of silver hydrosols on liver autolysis led to this investigation. A number of salts and soluble compounds of silver were tested in this respect, and, in addition, their influence on the capacities of liver-extract to degrade and build up uric acid was examined. With the exception of collargol and protargol, for small concentration of the silver salt the increase of non-precipitable nitrogen in liver autolysis accompanies the increase of silver salt. This process soon

reaches a maximum, which differs for different salts, and larger doses inhibit the action. The yields of purine bases and monoamino-acids vary concordantly with the "total-autolysis" as measured by the method employed. With regard to the albumoses, the reverse would appear to be the case. The formation of uric acid is favoured by silver sulphate, acetate, nitrate, or citrate, and it is the more so with increasing amounts. The decomposition is favoured by small doses of the same salts, but is hindered by larger doses. Traces of potassium cyanide, nitric acid, and carbon monoxide have no influence on liver-autolysis that has been stimulated by silver nitrate.

G. S. W.

Production of Sugar in the Perfused Liver of Diabetic Animals. LEONE LATTES (*Biochem. Zeitsch.*, 1909, 20, 215—219. Compare Abstr., 1904, ii, 829).—The formation of sugar by artificially-perfused glycogen-free livers of dogs was not markedly raised by the extirpation of the pancreas or poisoning by phloridzin some days before killing. On the other hand, the formation of acetoacetic acid is, under these conditions, increased.

G. S. W.

Lactic Acid Formation in the Body. I. RUDOLF TÜRKEL (*Biochem. Zeitsch.*, 1909, 20, 431).—During the aseptic autolysis of liver, formation of lactic acid is followed by its rapid destruction, and after some days, it disappears from the mixture. A sugar- and glycogen-free liver does not produce appreciably less autolytic lactic acid than one having normal carbohydrate content. Added inositol does not increase the lactic acid formation. Following the addition of dextrose and alanine, an increased acid production was in some cases observed, but in other cases a negative result was obtained. The combined researches of workers on this subject indicate that there is a cell-constituent of unknown nature which gives rise to the lactic acid produced during liver autolysis.

G. S. W.

Decomposition of β -Hydroxybutyric Acid and Acetoacetic Acid by Enzymes of the Liver. ALFRED J. WAKEMAN and HENRY D. DAKIN (*J. Biol. Chem.*, 1909, 6, 373—390).—The liver cells, or aqueous extracts of the liver, contain an enzyme (β -hydroxybutyrase) which converts β -hydroxybutyric acid into acetoacetic acid. Its action is increased by the addition of blood or of crystallised oxy-hæmoglobin, which furnish the necessary oxygen readily. Serum causes some acceleration, but the addition of other tissues causes inconstant results. The liver tissue also decomposes acetoacetates, but here the addition of blood produces no increase in the action.

W. D. H.

Lecithin and Jecorin in the Liver of Normal Dogs and those Poisoned with Alcohol. A. BASKOFF (*Zeitsch. physiol. Chem.*, 1909, 62, 162—172).—Alcohol poisoning has a destructive influence on the lecithin, but not on the jecorin of the liver. The latter remains unaltered in amount and composition.

W. D. H.

Uric Acid Formation. II. Regeneration of Destroyed Uric Acid in the Artificially-perfused Liver. C. BEZZOLA, GUIDO IZAR, and LUIGI PRETI. **III. Uric Acid Formation in Liver Extracts after the Addition of Dialuric Acid and Urea.** MARCEL ASCOLI and GUIDO IZAR. **IV. LUIGI PRETI** (*Zeitsch. physiol. Chem.*, 1909, 62, 229—236, 347—353, 354—357).—II. By perfusing the dog's liver with arterialised blood containing uric acid, a marked decrease of the uric acid occurs in the perfusing fluid; but by perfusing the same with blood saturated with carbon dioxide, the uric acid which had disappeared appears again.

III. A large number of the decomposition products in various combinations was added to finely minced liver, and usually no formation of uric acid occurred; the only positive result was obtained by the addition of dialuric acid and urea.

IV. The restoration of uric acid noted in II. above is due to the action of an enzyme which occurs in blood and blood-serum, but not in the blood-free liver.

W. D. H.

The Action of Calcium and Strontium Salts on the Heart and Blood-vascular System. K. RUTKEWITSCH (*Pflüger's Archiv*, 1909, 129, 487—505).—Weak solutions of calcium and strontium salts increase the excitability and contractility of the cardiac muscle. Stronger solutions increase the contractility, but lessen the excitability. The rise of blood-pressure in the case of calcium salts is due mainly to the action on the heart; in the case of strontium, principally to an action on the vessels. The brachycardia sometimes seen is secondarily produced by stimulation of the vagus centre by the high blood-pressure.

W. D. H.

Influence of Calcium on the Pupil. JOHN AUER and SAMUEL J. MELTZER (*Amer. J. Physiol.*, 1905, 25, 43—65).—Intravenous injection of an $m/8$ -calcium chloride solution causes in rabbits a maximal contraction of the pupils, and the iris loses its excitability. The muscle mainly, and the motor nerve-endings probably, are affected; the sympathetic nerve fibres are also less excitable. The pupil slowly recovers after many hours. Atropine only slightly antagonises the effect; adrenaline and cocaine are rather more powerful antagonists. The action of adrenaline is more marked after removal of the superior cervical ganglion. Ether and asphyxia (to a less extent) retard the development of the myosis and hasten its disappearance.

W. D. H.

Internal Secretion of Chromaffine Tissue. RUD. EHREMANN (*Pflüger's Archiv*, 1909, 129, 402—406).—Polemical. The chief question discussed is one of priority, namely, whether Meltzer or the author first described the action of adrenaline on the pupil.

W. D. H.

The Lipoids of the Lung. NADINE SIEBER. **The Composition of the Lung.** NADINE SIEBER and W. DZIERZGOWSKI. **The Purines of the Lung.** NADINE SIEBER and W. DZIERZGOWSKI. **The Enzymes of the Lung.** NADINE SIEBER and W. DZIERZGOWSKI (*Zeitsch. physiol. Chem.*, 1909, 62, 250—253, 254—258,

259—262, 263—270).—The first paper relates to the preparation of lecithin and jecorin from lung tissue; the proportion between the two phosphatides was 6:1. A crystalline material, identified as *iso*-cholesterol, was also obtained. The second paper gives analytical details of water, solids, ash, phosphorus, sulphur, iron, nitrogen, fat, etc., in the lungs.

The percentage of the purine bases comes out differently according to the method employed; xanthine, however, was always the least abundant.

The horse's lung contains a catalase, a peroxylase, a glucase, and a diastase. W. D. H.

Formation of Dextrorotatory Lactic Acid during the Autolysis of Animal Organs. IV. TAKEO SAITO and JUNJI YOSHIKAWA (*Zeitsch. physiol. Chem.*, 1909, 62, 107—112).—In previous work it has been shown that on the autolysis of spleen, testis, and flesh, *d*-lactic acid appears, and this is to some extent destroyed on further action. In the present research, the appearance of the acid during autolysis of the thymus is described, but it is at present uncertain whether any disappears later, or whether such disappearance is of enzymic origin. The same is true for the lungs, but fresh lung contains a small amount of the acid before autolysis sets in. W. D. H.

Extractives of Fish Muscle. UMETARO SUZUKI and K. YOSHIMURA [with M. YAMAKAWA and Y. IRIE] (*Zeitsch. physiol. Chem.*, 1909, 62, 1—35; *J. Coll. Agr. Tōkyō*, 1909, 1, 21—58).—The aqueous extracts of the muscle of the lobster and of a number of fishes, including the salmon and the fresh-water eel, have been examined. In Japan, fish is an important article of diet, and a knowledge of the extractives may throw some light on cases of poisoning which not infrequently occur. Fish-extract appears to differ from meat-extract in containing appreciable quantities of monoamino-acids; in addition, carnosine, histidine, arginine, and lysine may occur in relatively large amounts. It is thought that eventually almost all protein fission-products will thus be met with, and that they are not simply waste products, but are used in metabolism. In one dried variety of fish ("Tka") a large quantity of a base was found, probably δ -amino-valeric acid, previously isolated by Salkowski from putrid pancreas. G. B.

The Cutaneous Fats. P. G. UNNA and L. GOLODETZ (*Biochem. Zeitsch.*, 1909, 20, 469—502).—Fats from the sebaceous glands, the fat of perspiration, the horny layer, etc., were investigated, and the content in cholesterol, oxycholesterol, *iso*cholesterol, and cholesterol esters determined. The three former substances were estimated in small quantities of fat by means of a spectrophotometrical method, using the acetic anhydride-sulphuric acid reaction, in which each substance gives characteristic bands. The amount of esters was ascertained by determining the increase in the amount of cholesterol caused by hydrolysis of the fat. It was found that both the intra- and extra-cellular fats of the skin are free from *iso*cholesterol, and in this respect differ from wool-fat (lanolin). The cutaneous fats contain,

however, cholesterol esters. There are various quantitative differences between the skin-fats of various origin, which are specified by the author.

S. B. S.

The Occurrence of Silicic Acid in the Organism. CARL CERNÝ (*Zeitsch. physiol. Chem.*, 1909, 62, 296—314).—The substance described by Drechsel as an orthosilicic acid ester in birds' feathers is a mixture of fatty acid esters of a high molecular alcohol, possibly of several such alcohols. It probably originates in the glands in connexion with the feathers. The occurrence of silicic acid in it is probably accidental; the amount found is never more than a trace, and it is often absent.

W. D. H.

The Significance of the Tissue as a Chlorine Depôt. VALDEMAR WAHLGREN (*Arch. exp. Path. Pharm.*, 1909, 61, 97—112).—The chlorine and water were estimated in the organs both of normal animals and of animals which had been injected with hypertonic sodium salt solutions, and were killed while the organisms still retained some of the excess chlorine. It was found that in normal animals the skin, blood, kidneys, and lungs contain the largest percentage amount of chlorine, and the muscles the smallest. The average percentage for the whole body was 0.17%. A third of the total exists in the skin. After intravenous injection, the largest increased percentage is found in the lungs, then in the intestine, blood, skin, and kidneys. The largest absolute increase is found in the muscles, intestine, and skin. After intravenous injection of hypertonic sodium chloride solutions, the water requisite for blood dilution comes chiefly from the muscles. The water content of the connective tissue also increases.

S. B. S.

Distribution of Iodine [in the Body]. R. VON DEN VELDEN (*Biochem. Zeitsch.*, 1909, 21, 123—130).—Drugs act endogenously by uniting with chemical groups in tissue protoplasm, or exogenously. Iodine appears to have affinities for many tissues, and this varies in disease as compared with health. According to Loeb, iodine which is not neurotropic becomes united with lipoid and fatty groups in the nervous system, and this view is confirmed by experiments on rabbits with iodival (iodoisovalerylcarnamide), given either by the mouth or subcutaneously. The amount of iodine which acts endogenously is small; the percentage of the element in the brain, for instance, is low, or it may be absent; nevertheless, it is slightly neurotropic and lipotropic; but in man this action appears to be negligible, and the excretion of iodine is rapid.

W. D. H.

Preformed Hypoxanthine. V. N. LEONARD and WALTER JONES (*J. Biol. Chem.*, 1909, 6, 453—460).—It seems to have been established that muscular exercise contributes to uric acid formation, and the most important purine base which contributes to the endogenous uric acid is muscular preformed hypoxanthine; this is not directly connected with nuclein metabolism, since it may occur in the absence of adenase, an essential factor in the passage from nucleic acid to hypoxanthine.

W. D. H.

The Action of Cells of Different Organs on Bacterial Extracts. H. TOYOSUMI (*Biochem. Zeitsch.*, 1909, 20, 39—55).—The cells of the organs of a normal guinea-pig possess the capacity of making the extract of cholera vibrios inactive, in that the same lose their precipitability and power of acting as complement. The organs of guinea-pig act more strongly in this respect than those of rabbits. The action of leucocytes and liver cells is stronger than the cells of other organs. S. B. S.

The Permeability of Cells for Dyes. RUDOLF HÖBER (*Biochem. Zeitsch.*, 1909, 20, 56—99).—Ruhland has called attention to the fact that certain aniline dyes do not behave in accordance with Overton's theory that dyes which stain cells on *intra vitam* application are soluble in lipoids, whereas those which behave differently in this respect do not. Thus, methylene-green, malachite-green, thionin, and others are soluble only with difficulty in lipoids, yet they stain spirogyra, whereas cyanosin, erythrosin, Bengal-pink, and others are soluble in lipoids, and will not stain this organism. Other contradictions to the Overton theory were discovered in experiments on the intestinal epithelium of frogs and the blood-corpuscles of the fish-salamander. The author calls attention to the fact that the exceptions to the Overton theory are not as numerous as would appear from Ruhland's work. Thus, no single case is known with certainty where a lipid-soluble basic dye fails to stain *intra vitam*, and only one case in which a sulphonic acid dye, which is lipid-soluble, does not colour. The acid dyes, which are exceptions to the Overton theory, are hardly ever sulphonic acids. More in accordance with facts, however, than the Overton theory is the statement that basic dyes act as *intra vitam* stains, whereas the acid dyes, as a rule, do not. The kidney epithelium does, however, possess the capacity to take up acid dyes, and this property depends on the colloidity of the dye. Thus, a non-colloidal or slightly colloidal dye is readily taken up, as is also a hydrophil colloid (a property determined experimentally by precipitability by zinc or calcium chloride). If a dye, on the other hand, is not readily taken up by the kidney cells, it is of suspension-colloidal nature. The liver of a frog does not possess the capacity of eliminating highly colloidal dyes. Indigo-carmin is the only dye eliminated with certainty in the bile-passages. S. B. S.

Does a Change of Fat into Glycogen Occur in the Silkworm during Metamorphosis? Y. KOTAKE and Y. SERA (*Zeitsch. physiol. Chem.*, 1909, 62, 115—117).—During the chrysalis stage, the amount of glycogen in the pupa is markedly lessened, and there is no ground for Couvreur's statement (*Compt. rend. Soc. biol.*, 1895, 796) that fat is transformed into glycogen. W. D. H.

An Enzyme in the Silkworm which produces Ammonia as a Cleavage Product of Amino-compounds. T. TAKEUCHI and R. INOUE (*J. Coll. Agr. Tōkyō*, 1909, 1, 15—20).—The larva, pupa, and moth of the silkworm (*Bombyx mori*) contain an enzyme which

readily liberates ammonia from asparagine, but only to a slight extent from other amino-compounds (urea, biuret). G. B.

The Situation of Kynurenic Acid Formation in the Dog's Organism. EMIL ABDERHALDEN, E. S. LONDON, and LUDWIG PINCUSOHN (*Zeitsch. physiol. Chem.*, 1909, 62, 139—141).—The administration of tryptophan, the parent substance of kynurenic acid, produces an increased excretion of that acid, not only in normal dogs, but also in those with an Eck's fistula. The liver is therefore certainly not the only place where kynurenic acid is formed from tryptophan.

W. D. H.

The Condition of the Calcium in Milk. I. PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1909, 21, 114—122).—In order to determine the proportion of calcium in milk which is in solution, as opposed to that in a colloidal state, the method of dialysis was employed. Milk was dialysed against rennet-whey, and also against the filtrate after precipitation of the protein by colloidal iron hydroxide; in the case of rennet-whey, the calcium in it rises, whilst that in iron-whey falls. From such experiments it is found that from 40 to 50% of the total calcium is diffusible. The percentage of calcium in "iron-whey" is higher than in rennet-whey, and this is diffusible; the treatment with colloidal iron peroxide, therefore, converts a part of the indiffusible into diffusible calcium. This was confirmed by electrical conductivity and cryoscopic methods. Sterilisation produces no change. The amount of phosphoric acid in iron-whey is small, and reasons are given in support of the view that a good deal of calcium is united to protein. The addition of pure caseinogen to milk de-ionises the calcium present, and prevents the subsequent action of rennet.

W. D. H.

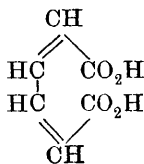
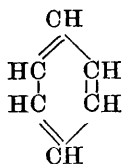
The Ingestion and Excretion of Radium Emanations by the Human Organism. F. L. KOHLRAUSCH and ERICH PLATE (*Biochem. Zeitsch.*, 1909, 20, 22—38).—The measurements were made by means of a Schmidt electrometer, of which the authors give a complete description. The urine was examined for radium emanations after drinking or bathing in emanation-containing water, generally after an interval of half an hour. No emanation could be detected after drinking water containing 100,000 units, nor after bathing in water containing 700,000 units, whether the patient was free to breathe the air of the bath-room or not; in the latter case a special form of helmet was worn.

S. B. S.

Physiology of Glands. XIII. Excretion of Total Nitrogen and Uric Acid during feeding with Proteoses. LEON ASHER and KARL REICHENAU (*Biochem. Zeitsch.*, 1909, 21, 76—102. Compare Abstr., 1909, ii, 1503).—Feeding on milk somatose has little or no influence on uric acid excretion. Tannin in small doses increases it, and this may be due to increased formation or diminished destruction. If a large dose (50 grams) of somatose is added to a nitrogen-rich diet, the effect is in no way different as regards total nitrogen and uric acid from that produced by any other protein.

W. D. H.

The Scission of the Benzene Ring in the Organism. I. The Appearance of Muconic Acid in the Urine after Doses of Benzene. MAX JAFFÉ (*Zeitsch. physiol. Chem.*, 1909, 62, 59—67).—The residue, after distilling off the alcohol, of an alcoholic extract of evaporated urine of animals which had received large quantities of benzene was dissolved in water. The aqueous solution was extracted with ether. The ethereal solution deposited, on concentration, first



gummy matter; the filtrate from this, on further concentration, deposited crystals, which were shown to be muconic acid, m. p. 289—290° (decomp.). Further crops of crystals were obtained on concentrating the filtrates. It was identified by the preparation of the methyl ester, m. p. 151—152°, and the tetrabromo-additive product, which darkened on heating at 230° and charred at 250°. The yield, calculated on the ingested benzene, was only 0.3%. Dogs and rabbits were the animals used for experiment, and the muconic acid was obtained also after ingestion of pure benzene prepared from benzoic acid. Its relationship to benzene is indicated in the annexed formulæ. This acid is the first direct scission product of benzene isolated in the urine. S. B. S.

Formation of Tribenzamide by the Action of Benzoyl Chloride on Urine. ALEXANDER ELLINGER and OTTO RIESSER (*Zeitsch. physiol. Chem.*, 1909, 62, 271—275).—The product described by Garrod and Hurtley (*Abstr.*, 1906, ii, 471) as a benzoyl derivative of tryptophan, probably benzoylkynurine, is shown to be tribenzamide (*Curtius, Abstr.*, 1901, 58). Kynurine cannot be benzoylated by means of benzoyl chloride. J. J. S.

Carbohydrates in Pathological Fluids and the Question of Residual Nitrogen. OTTO SITTIG (*Biochem. Zeitsch.*, 1909, 21, 14—34).—Twenty-three specimens of various pathological body-fluids were examined, and in six of these the carbohydrate percentage was high. Pentose was never found, the usual sugar is dextrose; lævulose was found in a few cases. Lævorotation was sometimes observed in fluids freed from both proteins and carbohydrates; this is attributed to amino-acids, and in one case tyrosine was isolated. Transudations are rich in sugar; exudations (that is inflammatory fluids) are poor in, or free from, sugar. W. D. H.

Alcaptonuria. OSKAR ADLER (*Biochem. Zeitsch.*, 1909, 21, 5—13).—No support was found for the hypothesis that another alcapton acid occurs in the urine in addition to quinolacetic acid. The existence of the so-called uroleucic acid is problematical. Administration of sodium iodide leads to no rise in nitrogen excreted, or to an alteration in the homogentisic acid: N ratio. On the following days, however, there is a slight increase in the homogentisic acid. The uric acid excretion and purine metabolism appear to be unchanged, but in alcaptonuria the administration of ammonium chloride leads to the appearance of much free ammonia. W. D. H.

The Peptolytic Enzymes in Different Forms of Cancer and other Tumours. II. EMIL ABDERHALDEN, A. H. KOELKER, and FLORENTIN MEDIGRECEANU (*Zeitsch. physiol. Chem.*, 1909, 62, 145—161). Compare this vol., ii, 688).—This is a portion of a large projected investigation on the enzymes of tumour cells, the object being to determine what differences are to be found between these and those obtained from the expressed juices of normal tissues. The present paper relates to peptolytic enzymes, and the tumours investigated were mainly those obtained from inoculated mice. No qualitative differences were found between the tumour extracts and those of normal tissues, but the former appear to be more energetic in their action.

W. D. H.

The Occurrence of Different Urinary Sugars and their Origin from Different Organs. FREDERIC LANDOLF (*Biochem. Zeitsch.*, 1909, 21, 108—109).—A few cases of different kinds of diabetes are briefly described; the nature of the osazones differs, and in cases of pancreatic origin numerous osazones are sometimes obtained. The conclusion drawn is that the nature of the carbohydrate differs according to the organ or organs, which atrophy and degenerate in the body.

W. D. H.

Is the Difference in the Behaviour of Lævulose and Dextrose as Glycogen Formers in Diabetes Characteristic only for this Condition? E. NEUBAUER (*Arch. exp. Path. Pharm.*, 1909, 61, 174—185).—It has been shown that administration of phosphorus causes disappearance of glycogen from the liver. Sugars were given to starving animals which had been poisoned by phosphorus. It was found that the absence of glycogen in phosphorus poisoning is due to the diminished ability to fix this carbohydrate; this happens, however, only in the case of dextrose, just as in the case of pancreatic diabetes; if lævulose or sucrose is employed as the carbohydrate, glycogen will be found in the liver. This ability to fix glycogen from these carbohydrates is also, as in the case of diabetes, only transient. The peculiar action in the formation of glycogen from lævulose, as opposed to dextrose, is not therefore characteristic of diabetes.

S. B. S.

Adrenaline Diabetes. LEO POLLAK (*Arch. exp. Path. Pharm.*, 1909, 61, 149—173).—I. *The differences in the behaviour of liver glycogen formed from dextrose and lævulose on treatment with adrenaline.*—Rabbits from the same litter were starved for four days, and then the same quantity of either dextrose or lævulose was administered by the stomach-tube. After sixteen hours, adrenaline was administered, and, eight hours later, the animals were killed and the glycogen in the liver was estimated. It was found that the resistance of the glycogen in the adrenaline action, whether formed from dextrose or lævulose, was the same when large doses of the drug were employed. If small doses, however, be employed, the lævulose glycogen was more resistant.

II. *Adrenaline glycosuria.*—Intravenous injection of adrenaline causes hyperglycæmia, which is not sufficient to cause glycosuria

unless increased diuresis is brought about simultaneously. A single subcutaneous adrenaline injection can, however, cause both hyperglycæmia and glycosuria, and the former symptom is more pronounced than in the case of intravenous injection, and sufficient to produce the latter symptom without increasing the diuresis. Repeated subcutaneous injections produce hyperglycæmia without glycosuria, and it is assumed that chronic adrenaline employment must in some way influence the kidneys. To produce glycosuria, the sugar-content in the blood should exceed 0.25% in the case of rabbits.

III. *The formation in starving rabbits of glycogen produced under the influence of adrenaline action.*—Repeated administration of adrenaline in increasing doses to starving rabbits (even those in which the liver has been entirely deprived of glycogen by strychnine convulsions) causes glycogen formation in the liver, in quantities such as have been observed only after feeding with carbohydrates. S. B. S.

Gout. Solubility of Uric Acid and Sodium Urate in Serum. Influence of Inorganic Electrolytes on the Separation of Uric Acid and Urates from Serum. Influence of Radium Emanation. HEINRICH BECHHOLD and J. ZIEGLER (*Biochem. Zeitsch.*, 1909, 20, 189—214).—The authors investigated the conditions determining solution and precipitation of uric acid and sodium urate in blood-serum. If for one hour serum is kept in contact with uric acid at 37° and filtered, a filtrate is obtained in which no uric acid crystals can be discovered microscopically. If this filtrate is left for twenty-four hours at 37°, a thick layer is deposited. Further, such a serum as this can be treated again with uric acid in a similar manner so as to become "overfilled," and it will again deposit its excess of acid as before. No explanation of this phenomenon is forthcoming, and as the operations are carried out at constant temperature it cannot be considered to be one of supersaturation. The term "overfilling" (*überfüllung*) is applied to this operation for this reason, and it is suggested that an exact study of the medium will provide a solution of the problem. Microscopically examined the white, crystalline precipitate is in the form of fine needles, and in no way resembles ordinary uric acid. Recrystallisation from a little water yields the well known rhombic crystals, and an analysis shows that at most small quantities of alkaline urates are present. This is of special interest in its bearing on the multitudinous forms of slightly impure uric acid crystals observed microscopically. With respect to the phenomenon of overfilling with uric acid, fresh serum, and serum inactivated by heating at 58°, behave differently. Fresh serum precipitates the excess of uric acid again in twenty-four hours under all conditions. From inactivated serum, precipitation depends on certain obscure factors. Sometimes inactivated serum "overfilled" with uric acid, and contained in a flask full to the top so that there is no air-bubble between the paraffined cork and the serum, or in a flask in which the surface of the serum is covered by a layer of oil, will give no uric acid precipitate. If the flask is not quite filled and the surface of the serum does not come up to the neck, then the precipitation of the excess of uric acid will take place in twenty four hours, even if the

surface is covered with oil. These phenomena are not observed for all sera, and the differences between them are not understood. Towards the explanation of the differences of behaviour of normal and inactivated serum, it is suggested that in the latter the higher hydroxyl ion content hinders the deposition of uric acid crystals. At 37° the solubility of uric acid in inactive ox-serum is found to be 1:1100 (overfilling) and 1:1925 (filling).

The solubility of monosodium urate in the same solvent and at the same temperature is 1:40,000. Monosodium urate is, therefore, less soluble in serum than uric acid, although it is more soluble than it is in water. Dilution with water and physiological saline inhibit the precipitation of these two substances from serum; OH-ions (NaOH) and H-ions (HCl) act similarly. So also do the salts of potassium, lithium, and magnesium, although sodium and ammonium salts usually act in the other direction.

Figures given indicate that the blood of gouty patients is supersaturated with urates and readily deposits them. In the treatment of gout, lithium salts are advised, but the amount present in "lithia waters" is much too small. Drinking spa waters, especially those containing potassium and magnesium, should be beneficial; waters containing sodium salts are not recommended. Similarly, a vegetable diet has, in spite of its potassium and magnesium salts and low purine content, the disadvantage that it gives rise to the elaboration of too much ammonium salts. Radium emanation interferes with the precipitation of uric acid from serum. Its influence on a solution of sodium urate cannot be definitely stated.

G. S. W.

Thyroidectomy and Carbohydrate Metabolism. FRANK P. UNDERHILL and WARREN W. HILDITCH (*Amer. J. Physiol.*, 1909, 25, 66—76).—In dogs the presence of at least two parathyroids maintains life in a healthy state. Complete removal of all the parathyroids and the thyroid itself lowers the power of the body to assimilate dextrose, and increases the urinary ammonia. If one thyroid and three parathyroids are removed, the sugar-assimilative power of the body is measurably lessened. The administration of adrenaline chloride subcutaneously causes glycosuria in dogs deprived of both thyroids, but retaining at least two parathyroids. No symptoms of myxœdema are observed in full grown dogs after removal of the thyroids and partial parathyroidectomy. Massaglia's positive results were obtained with young dogs.

W. D. H.

The Bleaching of Flour. WILLIAM D. HALLIBURTON (*J. Hygiene*, 1909, 9, 170—181).—The artificial bleaching of flour by nitrogen peroxide now so largely practised produces a diminution of its digestibility. Experiments *in vitro* show that minute amounts of nitrites retard the digestion of both starch and protein; this is partly due to their action on the enzyme, and partly (in the case of gluten and other proteins) to their action on the protein. In bread made from the flour, the lessening of digestibility is not so marked, and the amount of nitrite-reacting material present is reduced to one-half of that in the flour itself. Although the action is not pronounced, care will have to be exercised to see that millers do not exceed the limits of safety.

W. D. H.

The Resorption of Parenterally Administered Magnesium, and its Influence on Calcium Metabolism. KONRAD FROMHERZ (*Arch. exp. Path. Pharm.*, 1909, 61, 210—230).—Investigations were undertaken in view of the various employments of magnesium in surgical practice. Estimations were made of the amounts of magnesium and calcium ingested and excreted in both urine and faeces, and the influence of metallic magnesium (injected or sewn under the skin) and of magnesium oxide on the calcium-magnesium balance was determined. The nutrition is, however, of great influence on the division of the alkaline earths and phosphates between urine and faeces. With animal food, which is poor in lime and rich in phosphorus, the output is equally divided, or the excretion by the kidneys predominates. With excess of lime, the excretion by the gut predominates. The phosphoric acid content of the food also influences the mode of excretion. In a diet rich in phosphoric acid and lime, it was found that the replacement of calcium by magnesium is more difficult than in a diet poor in these substances. No definite conclusions as to the influence of magnesium on calcium metabolism can, however, be drawn without at the same time investigating the intake and output of phosphoric acid.

S. B. S.

Physiological Effect of Cobalt Carbonyl Vapour. HENRY W. ARMIT (*J. Hygiene*, 1909, 9, 249—251).—From the negative experiments on animals described, the conclusion is drawn that owing to its low vapour tension and ready dissociability, cobalt carbonyl contrasted with nickel- or iron-carbonyl is unlikely to produce acute poisoning.

W. D. H.

Oxidation of Borneolglucoside in a Bio-chemical Manner. HERMANN HILDEBRANDT (*Biochem. Zeitsch.*, 1909, 21, 1—4).—Borneolglucoside differs from many other glucosides (for instance, mentholglucoside) by its sparing solubility and in the difficulty with which borneol-glycuronic acid is prepared from it. If subcutaneously administered to rabbits, the urine contains a small amount of borneol-glycuronic acid, indicating that the warm-blooded animals are able to oxidise a small quantity of the material. This is not the case at all in frogs.

W. D. H.

The Behaviour of Betaine, Methylpyridinium Hydroxide, and Trigonelline in the Animal Organism. ARNT KOHLRAUSCH (*Chem. Zentr.*, 1909, ii, 465; from *Zentr. Physiol.*, 1909, 23, 143—147).—Betaine, after ingestion by cats and dogs, could be partly recovered unchanged in the urine. It was isolated by extracting the urine with methyl alcohol after evaporation to a syrup; the crude product was purified by means of the mercuric chloride double salt. Besides betaine, a product was isolated, of which the hydrochloride was more readily soluble than that of betaine, and yielded an aurichloride which was apparently identical with that of trimethylamine. Methylpyridinium hydroxide is unchanged in the organism. Trigonelline is not changed into methylpyridinium hydroxide after subcutaneous administration to cats and rabbits.

S. B. S.

The Biological Behaviour of Iodoproteins. HERMANN FREUND (*Biochem. Zeitsch.*, 1909, 20, 503—515).—The behaviour of iodoproteins as regards the formation of specific anti-substances was investigated, the biological reactions employed being the formation of precipitins, the deviation of the complements, and the production of anaphylaxis. It was found that immune sera which react strongly with normal proteins will not react with the corresponding iodoproteins. The anti-substances produced by injection of iodoproteins react with iodoproteins of different origins. Animals rendered over-sensitive to natural protein are not subject to anaphylactic shock on injection of the same protein after iodisation. The species specificity of a protein is considerably modified as regards its biological action by iodisation.. S. B. S.

Behaviour of Pyridine in the Hen's Organism. ZIN-NOSUKE HOSHIAI (*Zeitsch. physiol. Chem.*, 1909, 62, 118—119).—His and, later, Cohn stated that in the dog, pyridine unites with a methyl group from some unknown tissue constituent, and passes as methylpyridinium hydroxide into the urine. In rabbits, Abderhalden and his colleagues showed that this does not occur. The present experiments on the hen show that it acts like the dog. W. D. H.

Physiological Action of Tutin. FRANK FITCHETT and JOHN MALCOLM (*Quart. J. exp. Physiol.*, 1909, 2, 335—362).—The New Zealand tutu plant has been known to cause death in animals since the days of the early settlers. Tutin is a glucoside which is the active principle. The severity of its toxic effects in different classes of animals is proportional to the degree of differentiation of the nervous system, and the effects on the alimentary, respiratory, and other systems are the result of the excitation of nerve-cells. The heart is but little affected; the respiratory centre is strongly stimulated, and death is preceded by convulsions and coma, due to exhaustion of the nervous system; the cerebral grey matter is markedly congested. Tutin is readily absorbed, and excreted with difficulty; it is not found in appreciable amount in gastric juice, urine, or milk; it has no effect on nutrition as a whole. No remedy has been found, but alkalis will destroy unabsorbed tutin in the stomach. No immunity after repeated dosage occurs. W. D. H.

The Mechanism of the Action of Arsenic Derivatives in Trypanosomiasis. G. LEVADITI (*Ann. Inst. Pasteur*, 1909, 23, 604—643).—It has been found that the toxic action of atoxyl on trypanosomes *in vitro* is but slight. A trypanotoxyl can, however, be prepared by treating atoxyl with the extract of liver or other organs. This trypanotoxyl, which readily acts on trypanosomes *in vitro*, appears to be a protein derivative, and is rendered innocuous by heating it at 100°. It can be precipitated by alcohol. If the trypanosomes be treated with trypanotoxyl, they readily take up arsenic. The arsenic can also be taken up by other cells when they are treated by trypanotoxyl; spermatozoa can in this way be rendered immobile. For this reason, although trypanotoxyl kills trypanosomes *in vitro*, it is not more effective than atoxyl when injected into an infected animal,

unless it be mixed with the trypanosomes before injection. It is taken up by the cells of the body rather than by the parasites. The theory is advanced that the trypanotoxyl is prepared by the organs in the body and exerts its toxic action on trypanosomes *in statu nascendi*. The conception is also advanced that the protein in trypanotoxyl acts as an amboceptor, the arsenic acting as complement. S. B. S.

Mercury Poisoning with the Simultaneous Action of Hirudin. MARIE KOHAN (*Arch. expt. Path. Pharm.*, 1909, 61, 132—148).—It has been suggested that mercury poisoning is due to the production of thromboses. Investigations were carried out with the object of determining the truth of this hypothesis, hirudin being employed to prevent the normal clotting and to facilitate the detection of the thromboses in the post-mortem examinations. It was found that hirudin prevents the clotting of the blood, even in cases of mercury poisoning. In cases of acute mercury poisoning, the animals die and exhibit the same post-mortem symptoms whether hirudin be injected or not. The theory of thrombosis formation does not therefore appear to hold. The hirudin appears to accelerate the action of the mercury and to diminish the lethal dose. Rabbits were employed in the experiments. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Simple Ventilating Tube for Fermentations. A. P. BJERRE-GAARD (*J. Amer. Chem. Soc.*, 1909, 31, 1178).—A short piece of glass tubing constricted to a small opening at the lower end is packed fairly tightly with freshly ignited asbestos fibre, and inserted into the rubber stopper of the fermentation flask as soon as sterilisation is finished. This tube permits the escape of the gases produced during fermentation, but prevents the admission of foreign organisms.

E. G.

The Action of Salts on Bacteria. M. VON EISLER (*Centr. Bakt. Par.*, 1909, i, 51, 546—564).—The organisms used were *Vibrio El Tor V* and *B. subtilis*. They were differently affected by the different salts. Thus *N/10*-lithium chloride inhibited development of *B. subtilis*, but even at double the concentration had no effect on the growth of the vibrio. The inhibiting effect of lithium chloride on *B. subtilis* can be overcome by adding certain quantities of bivalent, but not of univalent, salts. The inhibiting effect of a bivalent salt, for example, manganese chloride, can, however, be overcome either by addition of univalent or of bivalent salts. Nothing was found to overcome the poisoning effect of mercuric chloride.

Addition of salts to the nutrient agar on which vibrio was developing led to a change in form of the organism, so that it became an

involute. The effect depends on the valency of the cation, bivalent salts being much more effective than univalent, whilst the anion seems only to play a subordinate part. Admixture with other salts gives the same results as before; the effect of a univalent salt is counteracted by addition of a bivalent, but not of another univalent, salt, whilst the potency of a bivalent salt is much reduced by addition of either a uni- or another bi-valent salt.

B. diphtheriae also assumes involution forms under the influence of neutral salts of the alkalis or alkaline earths, but larger quantities of salts are required. For this reason, addition of other salts has little or no effect in modifying the action. E. J. R.

Production of Indole by Bacteria. SELTER (*Centr. Bakt. Par.*, 1909, i, 51, 465—476).—The author detects indole by means of Salkowsky's reagent (1 c.c. of 1 in 5000 sodium nitrite; 1 c.c. of 25% sulphuric acid added to 10 c.c. of the culture solution to be tested), and concludes that the test is still valuable for discriminating between typhus, paratyphus, and dysenteric organisms, on the one hand, and *Bacillus coli communis* and pseudodysenteric organisms, on the other, in spite of newer tests that have been suggested.

The most suitable culture medium for indole production is a 10% peptone solution containing also 0.5% sodium phosphate and 0.1% magnesium sulphate. Bouillon to which 5% of peptone has been added generally proves a good medium, but the ordinary 1% peptone is not suitable, on account of the sugar sometimes present. It is no advantage to use putrefying meat for the preparation of the bouillon.

Paratyphus (enteritis), true dysenteric, and certain pseudodysenteric organisms never gave positive results. The typhus bacillus formed small quantities of indole, which, however, could only be detected in the distillate from large quantities of the culture solution. Most of the pseudodysenteric organisms behaved irregularly, and from the same solution, and under the same conditions, would sometimes produce indole and sometimes not. *B. coli communis* gives a good reaction.

E. J. R.

Poisonous Action of Cobalt Salts on *Aspergillus niger* in Cultures on Solid and Liquid Media. M. L. MORTENSEN (*Centr. Bakt. Par.*, 1909, ii, 24, 521—538).—In 1% solutions of cobalt chloride the production of spores took place fifty-seven days after inoculation. Addition of gelatin (10%) reduced the time to twenty-two days, whilst with agar (2%) and gum arabic (10%) the time was twelve and eleven days respectively. In presence of kaolin (50%) and sand (50%), the number of days were fifteen and eleven, whilst powdered asbestos (25%) and kieselguhr (15%) both reduced the time to five days.

In solid media the silicates had a still greater effect in overcoming the poisonous action of cobalt. Powdered clay, kieselguhr, and talc had the greatest effect, and pumice stone, quartz sand, and kaolin the least.

Powdered glass had itself a poisonous action on *Aspergillus*. In solutions to which 40% of glass was added, the production of spores was

delayed from two days (without glass and without cobalt chloride) to fifteen days. In presence of both glass and cobalt chloride (1%), the time was twelve days.

Precipitated calcium sulphate had only a slightly absorbing effect, whilst with gypsum plates there was a production of spores in eleven days in 3% solutions of cobalt chloride. N. H. J. M.

Chemistry of the Higher Fungi. IV. Maltases and Ferments which Decompose Glucosides. JULIUS ZELLNER (*Monatsh.*, 1909, 30, 655—662. Compare this vol., i, 543).—The sap of *Polyporus fomentarius* and *P. igniarius* have a vigorous hydrolysing action on maltose. Similar results were obtained with *Armillarius mellea*, *Hypholoma fasciculare*, *Daedalea quercina*, and *Trametes suaveolens*.

Aqueous extracts of *Trametes suaveolens* and *Polyporus igniarius* readily decompose salicin, amygdalin, coniferin, æsculin, and phloridzin. *Trametes* showed a selective action, salicin being much more readily decomposed than the other compounds. In the case of *Polyporus*, the powdered fungus was used, as the aqueous extract has little or no action, owing presumably to the insolubility of the enzyme.

Polyporus pinicola decomposes coniferin, amygdalin, salicin, and æsculin, but not phloridzin. N. H. J. M.

Polyporus rutilans. MAX BAMBERGER and ANTON LANDSIEDL (*Monatsh.*, 1909, 30, 673—674).—An acid having the properties of polyphoric acid was obtained from *Polyporus rutilans*, and several salts were prepared which were found to be similar to the derivatives obtained by Stahlschmidt (*Annalen*, 1877, 187, 177, and 195, 365). It is almost certain, therefore, that the fungus examined by Stahlschmidt was *Polyporus rutilans*, and not *P. igniarius*, as Klingemann suggested (*Abstr.*, 1893, i, 602). N. H. J. M.

Differences of Susceptibility of Plants to Stimulation. T. TAKEUCHI (*J. Coll. Agric. Tōkyō*, 1909, 1, 207—210).—Different plants were grown in the same soil in pots, both without and with manganous sulphate ($\text{MnSO}_4 \cdot 4\text{H}_2\text{O} = 0.2$ gram in 8 kilos. of soil). The increase due to manganese was, for each plant, as follows: Barley, 5.3; flax, 13.9; pea, 19.4, and spinach, 41.0%. N. H. J. M.

The Behaviour of Green Plants Towards Gaseous Formaldehyde. VIKTOR GRAFE and EMMY VIESER (*Ber. Deut. bot. Ges.*, 1909, 27, 431—446).—The authors grow seedlings of *Phaseolus vulgaris* under bell jars and arrange three series of experiments: (1) with ordinary air; (2) with air free from carbon dioxide; (3) with air free from carbon dioxide, but carrying formaldehyde. Whilst the present paper is only regarded as preliminary, it is shown that plants can assimilate formaldehyde under the conditions of the experiment, and that they make a greater growth than in normal air. E. J. R.

Starch Formation from Adonitol in the Leaves of *Adonis vernalis*. O. TREBOUX (*Ber. Deut. bot. Ges.*, 1909, 27, 428—430).—Adonitol, the alcohol of the ribose synthetically prepared by Fischer,

is the only pentitol known to occur in nature. It was first found in the leaves of *Adonis vernalis*, and is readily converted by them into starch.

The author picks leaves from the plant, keeps them in the dark long enough for all, or practically all, of the starch to disappear, and then floats them on a solution of adonitol. In a short time starch reappears in the leaf. No starch was formed when either galactose, milk sugar, mannitol, or dulcitol was substituted for adonitol; moreover, adonitol was more effective than the other sugars tried, for example, dextrose, lævulose, and sucrose. It appears that adonitol is the best source of starch for *Adonis vernalis*, but this rule does not hold for the other plants investigated. E. J. R.

Direct Assimilation of Ammonium Salts by Plants.

HENRY B. HUTCHINSON and NORMAN H. J. MILLER (*J. Agric. Sci.*, 1909, 3, 179—194. Compare Müntz, *Abstr.*, 1890, 79; Griffiths, *ibid.*, 1892, 229; Bréal, *ibid.*, 1893, ii, 590; Pitsch, *ibid.*, 1896, ii, 212; Mazé, *ibid.*, 1900, ii, 499; Kossowitsch, *ibid.*, 1902, ii, 684; Gerlach and Vogel, *ibid.*, 1905, ii, 346).—Three series of sand and water culture experiments are described, in which wheat and peas were grown under sterilised conditions with ammonium sulphate as source of nitrogen. The wheat plants in sand grew well when calcium carbonate was present, but were stunted in absence of carbonate. Sodium nitrate produced about the same amount as ammonium sulphate + calcium carbonate (sterilised), whilst ammonium sulphate inoculated with nitrifying organisms gave rather more dry matter. Wheat in water cultures gave similar results, although less dry matter was produced than in sand. The peas, which were grown in water cultures with calcium carbonate, showed no difference between the ammonium sulphate and the nitrate pots, all being equally healthy. The addition of dextrose to the ammonium sulphate pea cultures was without appreciable effect.

The results of all three series show that ammonium sulphate was directly assimilated, although in the case of wheat the plants showed a decided preference for nitrate. It is further shown that the plants which received ammonium sulphate contain a higher percentage of nitrogen than when supplied with nitrate. This accords with results furnished by the Rothamsted grass plots, the mixed herbage from the nitrate plot containing a lower percentage of nitrogen than that of the plots which have for a long time been manured with ammonium salts, and with results obtained by Pitsch and Mazé.

The seeds employed in the above experiments were sterilised by treating with warm mercuric chloride solution after removing any air bubbles with a vacuum pump. The apparatus employed for this purpose is described with sketch. The plants were grown in three-necked Woulffe's bottles, the middle neck being used for the plant, and the side necks for aeration and for adding water respectively.

N. H. J. M.

Phosphorus Metabolism in the Plant. W. STANISZKIS (*Bull. Acad. Sci. Cracow*, 1909, 95—123).—The analyses extend over the

whole vegetation period of millet. The seeds contain but little inorganic phosphorus; during development the phosphorus intake proceeds parallel with the increase in dry weight. Up to the formation of the panicles only small quantities of organic phosphorus compounds are formed, but afterwards, up to the ripening of the seeds, the amount of phosphoproteins and especially of phytin increases considerably; at the same time phosphorus passes from the stem to the leaves. The maximum lecithin content occurs in the early stages of formation of the panicles. While these are formed the protein-nitrogen decreases, although the total nitrogen increases; translocatory fission thus takes place. In ripe millet seeds, however, 97% of the nitrogen again occurs as protein. During the ripening of the seeds, the ratio protein-phosphorus: protein-nitrogen increases, showing that phosphorus-free proteins are being converted into phosphoproteins. G. B.

Erythrina. M. BETTING (*Pharm. Weekblad*, 1909, 46, 1089—1092).—One hundred grams of the crushed leaves of a variety of *Erythrina* were placed in a generating flask, gently heated on a water-bath, and by means of an aspirator a current of purified air was drawn through the flask; 0.03% of nitrous anhydride was found to be given off, but this, of course, does not represent the true amount generated. Acetone was also found to be given off; the nature of the active principle of the leaves will be investigated. L. DE K.

Development of Fat in the Black Walnut (*Juglans nigra*). F. M. M'CLENAHAN (*J. Amer. Chem. Soc.*, 1909, 31, 1093—1098).—Considerable uncertainty prevails with reference to the chemistry of the formation of fats in seeds. A study has therefore been made of the development of fat in the black walnut, and analyses have been made of the liquid kernel and of the solid kernel at various ages.

It has been found that the fat is not formed within the kernel from starch, sugar, or tannin, since these substances are absent from the interior of the kernel capsule at all stages of its development. The quantitative relations of the fats to the crude fibre, proteins, and pentosans indicate that the fats are not formed from the decomposition products of these substances. Magenta is not able to penetrate the interior of the kernel capsule, although it can penetrate the other parts of the nut, and it is therefore improbable that there is any direct circulatory connexion of the kernel with the outer parts. This is confirmed by the fact that, in the early stages, when the kernel is entirely liquid, there is a pronounced fluid pressure in the capsule. The walls of the capsule contain large quantities of tannin, and it seems possible that the fats may be formed from decomposition products of this substance, although these products do not reach the interior of the capsule by means of ordinary fluid circulation. The formation of the kernel commences by the deposition of a jelly-like substance on the interior surface of the capsule membrane. This gradually changes to a white solid, enclosing a further quantity of the jelly-like substance, which eventually is completely replaced by the solid kernel.

From a consideration of these facts, it is suggested that the inner-

most cells of the capsule membrane cause the decomposition of the tannin and effect metamorphic syntheses, the newly-formed substances entering the interior of the capsule by osmosis. E. G.

Fat from the Seed of *Erythrina hypaphorus subumbrans*. N. H. COHEN (*Chem. Weekblad*, 1909, 6, 777—784).—By saponification with alcoholic potash and extraction with ether, the fat of the seed of *Erythrina hypaphorus subumbrans* has been separated into acids and an unsaponifiable portion. The acids are formic, oleic, linoleic, palmitic, and behenolic acids. The unsaponifiable part contains sitosterol and two other cholesterols, either identical with stigmasterol and brassicasterol or closely related to them.

A. J. W.

Hydrogen Cyanide in Cassava Flour. L. VUAFLART (*Bull. Assoc. chim. Sucr. Dist.*, 1909, 27, 225—228).—The author has examined a sample of cassava flour intended for use as a food for animals, and found it to yield 0.0041% of hydrogen cyanide. Whilst this quantity is less than that which may be obtained from certain cyanogenetic seeds, haricot beans for instance, it should be remembered that haricot beans are generally cooked before use and most of the hydrogen cyanide is thus volatilised. Although no ill-effects resulted when pigs were fed on the cassava flour in question, it is considered advisable that farmers should obtain some information (by analysis) regarding the flour before using it as a fodder.

W. P. S.

Presence of Adenine in Bamboo Shoots. GINZABURO TOTANI (*Zeitsch. physiol. Chem.*, 1909, 62, 113—114. Compare Kozai, *Bull. Imperial College of Agriculture and Dendrology Komaba, Tōkyō*, 1890, 37).—The presence of adenine in the young shoots of bamboo has been established.

J. J. S.

Urease in Higher Plants. T. TAKEUCHI (*J. Coll. Agr. Tōkyō*, 1909, 1, 1—14).—The seeds and seedlings of the soy-bean (*Glycine hispida*) contain an easily separable enzyme, which rapidly liberates ammonia from urea; it has a slight action on biuret, but not on other amino-compounds examined.

G. B.

Photodynamic Action of Extracts of Etiolated Plants. WALTHER HAUSMANN and LEOPOLD VON PORTHEIM (*Biochem. Zeitsch.*, 1909, 21, 51—58).—Extracts in methyl alcohol of various etiolated plants invariably showed a distinct photodynamic action on suspensions of red-blood corpuscles.

N. H. J. M.

Influence of Salts on the Poisonous Action of Quinine on *Elodea canadensis*. M. VON EISLER and LEOPOLD VON PORTHEIM (*Biochem. Zeitsch.*, 1909, 21, 59—75).—In presence of calcium, manganese, and aluminium salts, the poisonous action of quinine was considerably retarded, whilst potassium, sodium, and ammonium salts produced very little effect. Magnesium salts have a greater effect than potassium, but less than calcium salts.

Immersion of leaves for half an hour to an hour and a-half in solutions of calcium nitrate or manganese chloride was without effect on a subsequent treatment with quinine. N. H. J. M.

The Nature of the Acid Soluble Phosphorus Compounds of Some Important Feeding Materials. EDWIN B. HART and W. E. TOTTINGHAM (*J. Biol. Chem.*, 1909, 6, 431—444).—Phytin is present not only in wheat, but also in maize, oats, and barley; it could not be isolated from rutabagas or alfalfa hay. In wheat it is largely localised in the outer layer of the grain, but in the other grains it is uniformly distributed; in those seeds the phytin phosphorus amounts to 38—48% of the total phosphorus.

In rutabagas hay, 64% of the total phosphorus is inorganic, but there is also an unknown organic phosphorus compound present. In alfalfa hay, 65% of the phosphorus is inorganic; here also an organic phosphorus compound occurs. The reducing substance separated by dilute acid from alfalfa hay is possibly dextrose. No pentose was found. W. D. H.

Is Potassium Sulphate Physiologically Acid? KEIJIRO ASŌ (*J. Coll. Agric. Tōkyō*, 1909, 1, 223—225).—Oats were grown in sand manured with calcium hydrogen phosphate, ammonium nitrate, ferric hydroxide, and magnesium hydrogen phosphate. In addition the three sets of pots received respectively (1) potassium sulphate, (2) potassium hydrogen sulphate, and (3) potassium sulphate + potassium carbonate. There was no great difference in the yields in the three sets; in (3), however, in which the least root was produced, the yield of grain was distinctly higher than in the others.

A second experiment was made in which rice grown in sand received (in addition to calcium hydrogen phosphate, ammonium nitrate, magnesium hydrogen phosphate, potassium sulphate, and ferric chloride) (1) disodium hydrogen phosphate, (2) sodium dihydrogen phosphate, and (3) trisodium phosphate. The results showed a decided depression in the yield in presence of weak acid manure. The conclusion is drawn that the physiological acidity of potassium sulphate is much less marked than that of ammonium sulphate. N. H. J. M.

Is Artificial Calcium Carbonate more Effective than Limestone Meal? H. YOKOYAMA (*J. Coll. Agric. Tōkyō*, 1909, 1, 181—182).—Sand culture experiments with oats showed that precipitated calcium carbonate is not essentially more effective than limestone meal. In accordance with previous observations, it was found that the yield of oats decreased as soon as the amount of magnesia exceeded that of the lime. N. H. J. M.

Lime Factor for Oats. J. N. SIRKER (*J. Coll. Agric. Tōkyō*, 1909, 1, 183—184).—The lime factor for oats in sand cultures was found to be 1, as shown by previous investigations. N. H. J. M.

Influence of Different Ratios of Lime to Magnesia on the Growth of Rice. KEIJIRO ASŌ (*J. Coll. Agric. Tōkyō*, 1909, 1, 171—173. Compare Abstr., 1904, ii, 765).—The former ex-

periment, in which the manure employed was of an alkaline nature, was repeated with acid manure, phosphoric acid being applied as double superphosphate, potassium as sulphate, and nitrogen as ammonium sulphate and sodium nitrate. One series received calcium and magnesium as sulphates, the other as carbonates.

The results, like the earlier ones, show that any change in the ratio $\text{CaO} : \text{MgO} = 1$ tends to reduce the yield. N. H. J. M.

Proteins of Rice Seeds. UMETARO SUZUKI, K. YOSHIMURA, and S. FUJI (*J. Coll. Agric. Tōkyō*, 1909, 1, 77—88).—The dry matter of rice freed from husks was found to contain: total N, 1.200%, and N as proteins, 1.165%; the husks contained 2.958% and 2.665% respectively.

The various cleavage products were isolated and the amounts estimated. The following results in (1) rice freed from husks, and (2) the husks, are given: alanine (1), 3.7; leucine (1) 14.3, (2) 8.6; proline (1), 3.3; phenylalanine (1), 2.0; aspartic acid (1), 0.4; glutamic acid (1) 14.5, (2) 4.7; tyrosine (1) 0.5, (2) 0.3; lysine (1), 0.86; histidine (1) 0.81, (2) 0.88; arginine (1) 1.60, (2) 3.40; ammonia (1) 2.33, (2) 1.13% of the dry matter. N. H. J. M.

Effect of Chemical Manures on the Composition of Meadow Hay. P. CHAVAN (*Bied. Zentr.*, 1909, 38, 593—594; from *Ann. Agric. Suisse*, 1908; and *J. d'agric. prat.*, 1908, ii, 711).—Potassium salts alone considerably increased the yield of dry produce, and superphosphate alone produced a much greater increase than potassium salts alone. The two manures used together increased the yield in three years from 2878 to 12453 kilos. per hectare. Phosphatic manure distinctly increased the percentage of proteins.

As regards botanical composition, potassium manure increased the gramineous and leguminous herbage from 40.8 and 8.76 to 44.09 and 15.73% respectively. With phosphate, the amounts were 34.38 and 45.12, and with potassium salts and superphosphate, 42.12 and 46.73%. N. H. J. M.

Yield of Leaves of Polygonum tinctorium with Abundant Nitrogenous Manure. T. TAKEUCHI (*J. Coll. Agric. Tōkyō*, 1909, 1, 189—191).—The plants were grown in plots of 12 square metres in a loamy humous soil. Application of sodium nitrate (300 and 360 grams) increased the yield of leaves by 16 and 41% respectively. Carbon disulphide (400 c.c.) gave an increase of 14%. N. H. J. M.

Application of Carbon Disulphide in Mulberry Culture. J. N. SIRKER (*J. Coll. Agric. Tōkyō*, 1909, 1, 185—187).—Application of carbon disulphide to the soil (450 c.c. to 16 square metres) increased the yield of mulberry leaves by 44%. N. H. J. M.

The Phosphoric Compounds in Wines. P. CARLES (*Bull. Soc. chim.*, 1909, [iv], 5, 962—969; *Bull. Assoc. chim. Sucr. Dist.*, 1909, 27, 217—223).—It is shown that most wines contain both mineral and organic phosphorus compounds, and that the organic

phosphorus is most probably present as potassium or calcium glyceryl-phosphate, and not in the form of lecithin. In Gironde wines the organic phosphorus constitutes about one-tenth of the total amount of phosphorus present. Red wines were found to contain from 0.235 to 0.590 gram of phosphoric acid in mineral combination, and from 0.005 to 0.130 gram of phosphoric acid as glyceryl phosphates. In white wines these quantities vary from 0.190 to 0.600 and 0.0 to 0.050 gram per litre respectively.

W. P. S.

The Chemical Composition of Tamari-Schoyu. K. YOSHIMURA (*J. Coll. Agric. Tōkyō*, 1909, 1, 89—96).—One litre of this beverage, obtained from soy beans, contains: putrescine 0.3 gram, ornithine 0.7 gram, ammonia 4.5 gram, and a base, $C_6H_9N_3$, 0.7 gram. The putrescine and ornithine are doubtless derived from arginine, of which the globulin of the soy beans contains about 5% (compare Osborne and Clapp, *Abstr.*, 1907, i, 990). The histidine of this globulin is perhaps the parent substance of the base $C_6H_9N_3$.

G. B.

The Carbohydrates of Shōyu. R. MITSUDA (*J. Coll. Agric. Tōkyō*, 1909, 1, 97—101).—There are present: glucose, a little galactose, traces of furfuraldehyde, and pentosans.

G. B.

Action of Sulphurous Acid on Soils. EMIL HASELHOFF (*Exper. Stat. Record*, 1909, 21, 219—220; from *Internat. Phytopath. Dienst. Beigabe Zeits. Pflanzenkrank.*, 1908, 1, 73—91).—Pot experiments in which beans and barley were grown in presence of sulphurous acid (14.96 grams to 8 kilos. of soil) showed that the effect depends largely on the amount and character of the soil bases. In acid soils, growth was retarded, whilst in soils containing sufficient base to neutralise the sulphurous acid, no injurious effect was observed.

N. H. J. M.

Catalase of Soils. DAVID W. MAY and P. L. GILE (*Exper. Stat. Record*, 1909, 21, 220; from *Porto Rico Stat. Circ.* No. 9, 3—13. Compare König, Hasenbäumer, and Coppenrath, *Abstr.*, 1906, ii, 303).—The rate of the reaction between soils and hydrogen peroxide depends on the amount of catalase present, on the amount and concentration of the peroxide, on the acidity or alkalinity of the solution, and on the amount of shaking. A method was adopted in which the number of minutes required by 5 grams of soil to liberate 100 c.c. of oxygen from 60 c.c. of neutral 0.92% hydrogen peroxide, was ascertained, the flask being shaken the whole time.

The catalytic action is materially inhibited by carbon disulphide; heating at a low temperature for a long time has more effect in destroying the catalase than higher temperatures for a short period.

N. H. J. M.

Improvements in Sand Culture. T. TAKEUCHI (*J. Coll. Agric. Tōkyō*, 1909, 1, 197—202).—The following amounts of mineral and nitrogenous manures are recommended: K_2HPO_4 , $KHPO_4$, K_2SO_4 , NaCl (each 0.3 gram); NH_4NO_3 , 1.2 gram (in two applications); $CaSO_4$,

0.6 gram ; $\text{Fe}(\text{OH})_3$, 0.8 gram ; magnesite, 6.7 grams, and limestone, 5.3 grams in 4 kilos. of sand. Kaolin (5%) may be added with advantage when the question does not relate to potassium compounds ; and the amount of limestone should be increased for plants other than *Gramineae* and flax. N. H. J. M.

Influence of the Ratio of Lime to Magnesia on the Yield in Sand Cultures. KEIJIRO ASŌ (*J. Coll. Agric. Tōkyō*, 1909, 1, 175—180. Compare Bernadini and Corso, this vol., ii, 606).—Results of sand culture experiments with different plants showed that the yields depend on ratio of lime to magnesia, whilst an absolute excess of either has no retarding effect when kept within certain limits. In experiments with oats manured with 2 grams of magnesia with 1, 2, 4, and 8 grams of lime, and with 10 grams of magnesia with 5, 10, 20, and 40 grams of lime, the highest yield was obtained in both cases when the ratio $\text{CaO} : \text{MgO} = 1 : 1$. N. H. J. M.

Manuring with Dicyanodiamide. KEIJIRO ASŌ (*J. Coll. Agric. Tōkyō*, 1909, 1, 211—222. Compare Abstr., 1906, ii, 890).—Water culture experiments with buckwheat showed that whilst 0.025% of dicyanodiamide killed the plants in about a month, 0.01% served as a nutrient. The same plants grown in soil (2 kilos.) containing 0.36 gram of dicyanodiamide were much injured. Oats in water cultures were not injured when the concentration was less than 0.025%.

Rice grown in paddy soil to which dicyanodiamide had been added three weeks before planting, produced nearly as much growth as with an equivalent amount of ammonium sulphate. N. H. J. M.

Manurial Experiments with Calcium Nitrate on Tobacco and Tomatoes. ALBERT STUTZER (*Bied. Zentr.*, 1909, 38, 638—639 ; from *Zeitsch. landw. Versuchswesen Oesterr.*, 1908, 531).—Calcium nitrate gave good results with tobacco. The experiments with tomatoes were inconclusive, owing to unfavourable weather.

N. H. J. M.

Preservation of Night-soil. KEIJIRO ASŌ and S. NISHIMURA (*J. Coll. Agric. Tōkyō*, 1909, 1, 145—151).—The following substances were employed as preservatives : (1) superphosphate, (2) gypsum, (3) monocalcium phosphate, (4) gypsum + monocalcium phosphate, and (5) kainite. It was found that gypsum and kainite had comparatively little effect. Monocalcium phosphate proved to be much the best preservative, and then superphosphate.

The amount of superphosphate employed was 0.5%, and the amounts of the other substances contained the same amount of sulphuric and phosphoric anhydrides respectively as were present in the superphosphate. N. H. J. M.

Application of Dicyanodiamide as a Nitrogenous Manure. R. INOUE (*J. Coll. Agric. Tōkyō*, 1909, 1, 193—196).—Rape and barley were grown in soil manured with the same amounts of nitrogen in the forms of ammonium sulphate and dicyanodiamide and

in both forms together. The results showed that dicyanodiamide applied at the rate of 1 gram of nitrogen to 8 kilos. of soil is injurious, whilst 0.35 gram of nitrogen as dicyanodiamide and 0.7 gram as ammonium sulphate gave better results than when the whole amount was applied as ammonium sulphate. N. H. J. M.

Vegetation Experiments with Precipitated Calcium Phosphate. HENRIK G. SÖDERBAUM (*Bied. Zentr.*, 1909, 38, 585—587; from *Experimentalfaltet. Stockholm*, Nos. 95, 98, and 99, and *Zeitsch. landw. Versuchswesen Oesterr.*, 1908, 506).—Electrolytically precipitated calcium phosphate, having the composition of a diphosphate, was found to be equal to superphosphate, and its availability, unlike that of tricalcium phosphate, is not essentially diminished by the presence of considerable amounts of calcium carbonate. N. H. J. M.

Secondary Calcium Phosphate as a Manure. T. TAKEUCHI (*J. Coll. Agric. Tōkyō*, 1909, 1, 203—206).—Experiments on rice grown in sand showed that the absorption of phosphoric acid, as secondary calcium phosphate, is depressed by an excess of calcium and magnesium to such an extent as to prevent the formation of ears. By increasing the amount of secondary calcium phosphate, the favourable ratio of lime to magnesia was altered somewhat; the gain due to phosphoric acid, however, much more than compensated for any depression due to an excess of calcium, and by altering the ratio $\text{CaO}, \text{MgO} : \text{P}_2\text{O}_5$ from 1 : 1 : 1 to 1 : 1 : 5 the yield of grain was increased by 65%.

As regards superphosphate, it is probable that only very large amounts of carbonate, will diminish its availability.

Other results will no doubt be obtained when calcium, magnesium, and phosphorus are present in forms soluble in water, or when the former are in other forms than carbonates. N. H. J. M.

Different Forms of Phosphoric Acid in Organic Manures. S.* TSUDA (*J. Coll. Agric. Tōkyō*, 1909, 1, 167—170).—The total phosphorus and the phosphorus soluble in ether and alcohol (lecithin), in 0.2% and in 5% hydrochloric acid, was determined in (1) soy bean cake, (2) rape cake, (3) red clover hay, (4) herring guano, (5) steamed bone dust, (6) cake from pupa of silkworms, and (7) crab shells. The amounts in percentages of dry matter are as follows:

	Total P_2O_5 .	As lecithin.	Soluble in 0.2% HCl.		Soluble in 5% HCl.		As nuclein.
			Inorganic.	As phytin.	Inorganic.	Organic.	
1.	1.311	0.114	0.050	0.640	0.040	0.120	0.236
2.	2.251	0.091	0.050	0.873	0.099	0.931	0.204
3.	0.554	0.050	trace	0.300	0.070	0.084	0.050
4.	4.670	0.310	1.894	0.860	0.372	0.648	0.583
5.	25.060	0.023	5.534	trace	18.859	0.530	0.112
6.	1.350	0.043	1.039	„	0.090	trace	0.169
7.	3.23	0.023	0.300	0.151	2.264	0.200	0.302

N. H. J. M.

Manurial Value of Various Organic Phosphorus Compounds. KEIJIRO ASŌ and Y. YOSHIDA (*J. Coll. Agric. Tōkyō*, 1909, 1, 153—161. Compare J. Stoklasa, *Abstr.*, 1896, ii, 266).—The results of pot experiments in which barley was manured with phosphorus ($P_2O_5 = 0.396$ gram in 2.5 kilos. of soil) in the form of sodium phosphate, lecithin, phytin, nuclein, and aluminium, iron, and tricalcium phosphates respectively, showed that lecithin is equal in value to tricalcium phosphate, whilst phytin and nuclein gave about the same amounts of dry produce as were obtained with aluminium phosphate.

The manurial effect of rice bran and rape cake is increased by extracting with ether, but their manurial value is lost by extracting with 0.2% hydrochloric acid, and the conclusion is drawn that most of the phosphorus present is in the form of phytin. N. H. J. M.

Availability of Phosphoric Acid in Various Forms in Herring Guano. R. MITSUTA (*J. Coll. Agric. Tōkyō*, 1909, 1, 163—165).—Pot experiments with barley grown in soil manured with herring guano, both in its original state and freed from its various phosphorus compounds. Extraction with ether and alcohol, which removed the oils and lecithin, reduced the yield of air-dried produce from 8.5 to 7 grams. Further, extraction with hot water, and with hot water followed by 0.2% hydrochloric acid, reduced the yield to 5 and 1.2 grams respectively. When the manure is so completely extracted that only nuclein remained, it has no immediate value as a source of phosphorus. N. H. J. M.

Analytical Chemistry.

Characterisation of Indicators. M. HANDA (*Ber.*, 1909, 42, 3179—3182).—The concentration of hydrogen or hydroxyl ions at which an indicator shows a change in colour can be determined as follows: To 50 c.c. of freshly boiled water are added four drops of a 0.2/*N*-barium hydroxide solution, and then two drops of the indicator. At a definite moment, 1 c.c. of freshly distilled methyl formate is added, and the time measured that is necessary for the colour change in the indicator to take place. In the case of phenolphthalein, litmus, and *p*-nitrophenol, the necessary hydrogen-ion concentrations have been determined by another method by Fels (*Abstr.*, 1904, ii, 320). If the logarithms of these concentrations are plotted as ordinates, and the times, measured as above, as abscissæ, the points so obtained lie on a straight line. If the times are then measured for any other indicators, the hydrogen-ion concentration necessary to bring about the colour change can be determined from the curve. In this way the following concentrations have been determined: With methyl-red the first change

in the alkali colour takes place when the hydrogen-ion concentration is $10^{-6.65}$, the characteristic intermediate colour being produced when the concentration is $10^{-6.4}$. Cyanin becomes decolorised when the hydrogen-ion concentration is $10^{-6.3}$. Methyl-red is thus slightly less delicate than litmus, and cyanin a little less delicate than methyl-red.

Accurate results could not be obtained with tropæolin, since the time to be measured is so short. Qualitatively the results confirm those of Fels, that is, the hydrogen-ion concentration which brings about a colour change is in the neighbourhood of $10^{-11.2}$. T. S. P.

The Accuracy of Volhard's Method for the Estimation of Chlorine. VICTOR ROTHMUND and A. BURGSTALLER (*Zeitsch. anorg. Chem.*, 1909, 63, 330—336).—It is necessary to the accuracy of the estimation of chlorine by Volhard's method that the precipitated silver chloride should not react to an appreciable extent with the soluble thiocyanate during the duration of the experiment. This condition is not usually fulfilled. When the quantity of chlorine is very small (under 5 millimols.), the results are inaccurate. A considerable excess of silver nitrate is of advantage, and inaccurate results are always obtained if an excess of thiocyanate is added and titrated back with silver. The tedious removal of the silver chloride by filtration, which ensures exact results, may be avoided by coagulating the chloride so as to reduce its surface. This may be done by adding sufficient ether to form two layers, shaking until clear, and then adding the ferric alum solution and titrating with thiocyanate. The sharpness of the end-point is increased by the presence of ether. This method is accurate, even when a very dilute solution is being titrated.

C. H. D.

The Gravimetric Estimation of Free Iodine by the Action of Metallic Silver. FRANK A. GOOCH and CLAUDE C. PERKINS (*Zeitsch. anorg. Chem.*, 1909, 63, 318—324; *Amer. J. Sci.*, 1909, [iv], 28, 33—39).—Free iodine may be estimated by shaking with reduced silver, the increase of weight of the latter being determined. Silver prepared by the action of zinc on the chloride, nitrate, or iodide, or by the action of hydrogen on the sulphide or oxide, should be treated before use with potassium iodide to convert any retained silver salts into iodide. An error is produced by the action of air on the potassium iodide, and this is greatest when the action of the silver is slow, as when the electrolytically deposited metal is used. The best results are obtained by working with electrolytic silver in a neutral or sodium hydrogen carbonate solution in an atmosphere of hydrogen, fifteen to twenty-five minutes being required for 0.65 gram of iodine, and the error being ± 0.0004 gram.

C. H. D.

New Method for the Estimation of Iodides and of Free Iodine. STEPHAN BUGARZKY and BÉLA HORVATH (*Zeitsch. anorg. Chem.*, 1909, 63, 184—196).—Iodine and bromine react in the presence of water reversibly: $I_2 + 5Br_2 + 6H_2O \rightleftharpoons 2HIO_3 + 10HBr$. The reaction is sufficiently rapid at 100° , and in presence of a large excess of bromine is practically complete in the sense of the upper arrow.

The excess of bromine may be rapidly boiled off without appreciable error, owing to the slowness of the reverse reaction.

The slightly acid solution, containing not more than 0.010—0.012 gram iodine, is placed in a narrow-necked 100 c.c. flask, and 50 c.c. of nearly saturated bromine water added, filling up with water. The flask is immersed in boiling water for an hour. The contents are transferred to a 250 c.c. conical flask, and boiled very briskly for four to five minutes to expel all the bromine. After cooling, 1—2 grams of potassium iodide are added, and, after acidification, the iodine is slowly titrated with thiosulphate, the quantity of iodine found being divided by six.

Ordinary bromine may be used, the iodine content being corrected for by a blank experiment, or the bromine may be purified by the following process, which completely removes iodine. The bromine is successively shaken with 20% potassium bromide solution, water, and concentrated sulphuric acid, and finally distilled over a little barium oxide in an apparatus entirely composed of glass, with ground joints.

The presence of an excess of bromides, chlorides, ammonium salts, nitrates, or nitrites in the solution to be analysed is without influence on the accuracy of the estimation. If the solution is sufficiently acid, the titration may even be performed in presence of iron or manganese salts, if the first disappearance of the blue colour be accepted as the end point.

The iodine content of the water from various iodine springs has been estimated by this method. Sea-water from Quarnero (Abbazia) contains 0.000075 gram of iodine per litre, being about one-millionth of the chlorine concentration.

C. H. D.

Apparatus for the Estimation of Fluorides in Foods. H. Rosser (*Ann. Chim. anal.*, 1909, 14, 365—366).—The apparatus, which is a modification of the one used by Blarez, consists essentially of a truncated leaden vessel, on to which is screwed a brass refrigerating vessel, through which cold water is circulating; this serves to press down a glass disk, and to prevent, by thorough cooling, an escape of hydrofluoric acid.

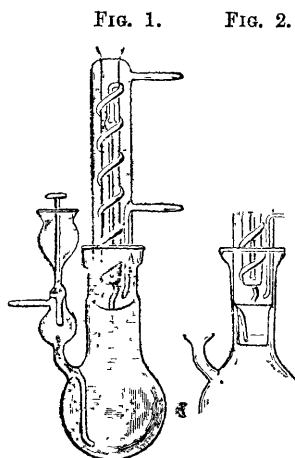
Into the leaden vessel is introduced the mixed barium fluoride and sulphate, obtained by adding to the solution some sodium sulphate and barium acetate, and also 5 to 10 c.c. of sulphuric acid. The vessel is then heated gently on a metallic plate for two hours. The effect of the etching on the glass disk is then noticed, and by a comparison with standards a fair idea may be got as to the amount of fluorine present.

L. DE K.

Apparatus for the Estimation of Sulphur in Iron and Steel. GEORG PREUSS (*Zeitsch. angew. Chem.*, 1909, 22, 2044—2045).—The flask (Fig. 1) is furnished with a side-tube for introducing the hydrochloric acid, and for the purpose of passing a current of carbon dioxide. By means of a ground-joint, the flask is attached to a condenser, inside which is the absorption vessel. The worm-tube serves to condense the acid vapours whilst the gases pass through the valve tube into the

absorption vessel. At the upper end of the tube a valve is attached in order to prevent any regurgitation of the absorption liquid.

Ten grams of steel, or 5 grams of pig-iron, are placed in the flask, and the condenser is fitted on and sealed with water. After introducing into the



absorption tube 40 c.c. of the usual cadmium solution, 75—150 c.c. of hydrochloric acid, D 1.12, are introduced, and the whole is heated until the iron has dissolved and the last traces of hydrogen sulphide are then removed by means of a current of carbon dioxide.

The condenser is then removed from the flask and the contents of the absorption vessel poured into a beaker; a few rinsings suffice to remove every trace of cadmium sulphide, which is then converted as usual into copper sulphide and weighed as such.

In the second form of apparatus (Fig 2) the gases evolved on heating with hydrochloric acid, D 1.19, are first passed through a little wash-bottle containing 50 c.c. of water so as to retain the greater part of the hydrochloric acid fumes. On removing the source of heat, this liquid runs back into the flask, whilst the recoil valve prevents a regurgitation of the cadmium solution.

L. DE K.

Detection of Sodium Sulphite in the Presence of Sodium Sulphate and Sodium Thiosulphate. FRANK E. WESTON (*Chem. News*, 1909, 100, 176).—A 5% solution of the mixture is prepared, and to 5 c.c. of this a solution of *N*/10-iodine is added, if decolorised (sulphite or thiosulphate, or both) the addition is continued until a faint coloration sets in. The liquid is now tested as to acidity, and if acid, a sulphite is probably present. To another 5 c.c. of the solution is added half the volume of iodine solution used in the first test, and sulphur dioxide is then recognised by its odour and also by its power of reducing potassium dichromate; the sulphur dioxide points to the presence of a sulphite. If no green coloration is noticed, thiosulphate is present.

Sodium sulphate is tested for with barium chloride as usual.

L. DE K.

Quantitative Precipitation of Tellurium Dioxide, and its Application to the Separation of Tellurium from Selenium. PHILIP E. BROWNING and WILLIAM R. FLINT (*Amer. J. Sci.*, 1909, [iv], 23, 112—118; *Zeitsch. anorg. Chem.*, 1909, 64, 104—111).—The basic nitrate is dissolved in a little hydrochloric acid and then diluted largely with hot water. The solution is made alkaline with ammonia, and then again slightly acidified with acetic acid. The tellurium dioxide is collected on an asbestos filter, washed with cold water, and dried at 105°. The nitrate may be also dissolved in aqueous

potassium hydroxide, and then acidified with hydrochloric acid, or the diluted solution may be simply acidified with acetic acid and then heated for some time to render the precipitate crystalline.

Attempts to effect the separation of tellurium from copper and bismuth by means of potassium hydroxide were, however, not very successful, but for the separation of tellurium from selenium the process answers very well.

L. DE K.

Estimation of Nitrogen. EILHARD ALFRED MITSCHERLICH (*Chem. Zeit.*, 1909, 33, 1058).—A reply to Schenke (this vol., ii, 669). The author prefers his own process (this vol., ii, 614), and further states that for the estimation of nitrous nitrogen Schenke's process is quite unsuitable.

L. DE K.

Estimation of Ammonia in Ammonium Chloride. OSWALD CLAASSEN (*Chem. Zeit.*, 1909, 33, 952).—A reversed condenser is inserted between the distilling flask and the Volhard's receiver in the distillation process. It is then unnecessary to cool the receiver, and there is no increase of volume of the contents. The same apparatus may be employed in the distillation of oxidising substances with hydrochloric acid.

C. H. D.

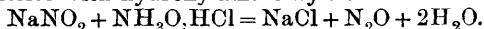
Cuvette Arrangement for the Estimation of Nitrates by Schloesing's Process. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1909, 27, 83—84).—The capillary gas delivery tube plunges into a layer of mercury, about 1 cm. high, contained in a small basin made of porcelain or earthenware, or even of wood weighted with lead. The mercury prevents the absorption of water into the apparatus.

L. DE K.

Influence of Chlorides on the Estimation of Nitrates in Waters by Grandval and Lajoux's Process. ANGEL SABATINI (*Ann. Chim. anal.*, 1909, 14, 366—367).—The author agrees with Perrier and Farcy (this vol., ii, 344) as to the influence of chlorides on the colorimetric determination of nitrates, and now proposes the following method: To 50—60 c.c. of the water to be tested are added 20 grams of silver oxide, and, after the lapse of two hours with occasional shaking, the liquid, now free from chlorides, is filtered and then examined colorimetrically for nitrates as usual.

L. DE K.

Estimation of Nitrite. A. SANIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 791—795).—The author's method for estimating nitrite is based on the change of acidity produced in a solution by the interaction of a nitrite with hydroxylamine hydrochloride:



The results are not affected by the presence of large or small proportions of nitrate. The solutions employed consist of *N*/20-sodium hydroxide and a solution of hydroxylamine hydrochloride (10 grams to 1 litre), the titre of which is measured against the sodium hydroxide solution, using phenolphthalein as indicator. The procedure is as follows:

Into a conical flask of capacity 150—200 c.c. are introduced 20 c.c.

of a solution of the nitrite containing 5 grams per litre and 20 c.c. of the hydroxylamine hydrochloride solution, the liquid being then heated for five to eight minutes on a gauze until bubbles of nitrous oxide are no longer evolved on shaking the flask; a temperature of 70—80° is sufficient for the completion of the reaction. After cooling, the solution is titrated with *N*/20-sodium hydroxide. The amount of nitrite is then calculated from the above equation. T. H. P.

Estimation of Phosphorus in Combustible Substances by the Bomb Calorimeter. PAUL LEMOULT (*Compt. rend.*, 1909, 149, 511—513. Compare Abstr., 1907, ii, 760).—Phosphorus and its gaseous compounds are burned without difficulty in the calorimetric bomb, using oxygen, and the phosphoric acids produced may be estimated as magnesium ammonium phosphate. Solid phosphorus compounds containing carbon give rise during combustion to some free phosphorus, which combines with the platinum capsule usually employed and escapes oxidation and estimation unless it is afterwards dissolved out by cold nitric acid.

Capsules of porcelain, glass, or quartz are invariably broken by the heat, allowing some of the substance to fall and escape combustion. If a porcelain capsule is supported in a platinum frame, there is no loss of material from this cause, but black stains containing unoxidised phosphorus always remain on the porcelain. Satisfactory analytical results are only obtained when a porcelain capsule in a platinum frame and coated with fused potassium nitrate is used. The phosphorus is completely converted into phosphoric acid, which is washed out of the bomb and weighed as ammonium magnesium salt. The author shows that the method is quite as accurate as Carius', but is quicker and less hazardous. R. J. C.

Estimation of Phosphoric Acid in Acid Solution by means of Alkaline Molybdate Solution and Gelatin. A. GRETE (*Ber.*, 1909, 42, 3106—3115).—In a previous paper (Abstr., 1888, 1341) the author has described the estimation of phosphoric acid in acid solution by means of acid molybdate solution and gelatin. The acid molybdate solution does not keep its titre, however, and the rubber tubing of the containing apparatus is attacked by the nitric acid. These difficulties have been overcome by the use of an ammoniacal molybdate solution; the acid which is necessary for the completion of the precipitation is added to the phosphate solution, which has been neutralised previously.

The method is a volumetric one and depends on the fact that in the presence of gelatin, the phosphomolybdate precipitate appears white, and is very voluminous, so that the presence of very small quantities of phosphoric acid can be detected. On boiling, the precipitate assumes the ordinary compact, yellow form and quickly settles, so that more molybdate solution may be added to see if any further precipitate is produced.

Very full details are given for the preparation and standardisation of the various solutions used, and also of the manner in which the determination must be carried out. The method can be used for the estimation of phosphorus in all ordinary cases, and only in the

presence of much iron is it necessary to modify it. It has been tested in more than 100,000 analyses. T. S. P.

Estimation of Graphite. FRANK BROWNE (*Chem. News*, 1909, 100, 162).—Satisfactory results have been obtained by the author in the assay of a sample of "Acheson Graphite" by means of the process published previously (Abstr., 1908, ii, 896), consisting in burning the sample with a fixed quantity of a specially prepared iron oxide.

L. DE K.

New "Boat" for Organic Analysis. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1909, [iv], 5, 876—877).—The boat consists of a piece of platinum foil measuring 15×1.4 cm., in which four oval depressions, each 2 cm. long, 0.7 cm. broad, and 0.3 cm. deep, are hammered in one line at intervals of 2 cm., beginning at 0.5 cm. from one end. Between the inner ends of the first and fourth depressions the platinum foil is cut away to the same diameter as the depressions, except at the centre, where for a short distance the original diameter (0.7 cm.) is retained to form a pair of central flanges. A boat of this size is used in the ordinary manner in a combustion tube of 1.7 cm. diameter in which it rests on the flanges at its ends and centre. The substance to be burned is distributed between the four depressions. It is claimed that by the use of this boat combustion takes place more uniformly and with less risk of loss due to "rushes" of carbon dioxide.

T. A. H.

Separation of Silica from Silicon and Carbon. ERHARD BRITZKE (*Chem. Zeit.*, 1909, 33, 1098—1099).—The author states that when heating a mixture containing silicon, carbon, and silica, at a sufficiently high temperature, in a current of hydrogen chloride, not only the silicon, but also the carbon, is ultimately volatilised, and only the silica remains.

Advantage of this reaction may be taken in the analysis of ferro-silicon and similar compounds. The iron also volatilises completely. The silica remaining should be examined for possible traces of non-volatile chlorides.

L. DE K.

Volumetric Estimation of Silver by Gay-Lussac's Method. ERNESTO PANNAIN (*Gazzetta*, 1909, 39, ii, 240—249).—The author has devised an apparatus for determining the end-point of the titration of a silver solution with standard sodium chloride solution. It consists of a glass tube 8—10 cm. long and about 3 cm. wide, open at the top and sealed at the bottom to a second tube 20—25 cm. long and 4—5 mm. in diameter, which passes through one hole of a doubly-bored stopper fitted to the titration vessel. At a short distance from the wide tube, the narrower one is enlarged, the enlarged part being packed with asbestos between two layers of glass wool. A side-tube, bent twice at right angles, enters the narrow tube just above and just below the enlargement, the vertical part of the side-tube being fitted with a tap. By this means, the liquid which has been forced up through the asbestos filter into the wide tube (by means of a filter-pump connected with this tube), and there tested to ascertain whether

silver or chlorine is in excess, can be returned, by opening the tap, into the titration vessel without passing again through the filter; the upper surface of the latter is thus kept free from precipitate, which would render turbid subsequent portions of liquid passed through the filter. This apparatus hence represents an improvement on the forms devised by Tarugi and Bianchi (*Abstr.*, 1906, ii, 627) and by Lang and Allen (*Trans.*, 1907, 91, 1370).

The maximum error of the method is 0.015%, and this may be diminished by careful working (compare Lang and Woodhouse, *Trans.*, 1908, 93, 1037).
T. H. P.

Iodometric Estimation of Silver based upon the Reducing Action of Potassium Arsenite. ROWLAND S. BOSWORTH (*Amer. J. Sci.*, 1909, [iv], 28, 287—290; *Zeitsch. anorg. Chem.*, 1909, 64, 189—192).—To the silver solution is added a definite volume of standard potassium arsenite and then an excess of a saturated solution of sodium hydrogen carbonate. The mixture is boiled to precipitate the silver as metal, and, after filtering (this is not strictly necessary), the liquid is acidified with hydrochloric acid and then again made alkaline with sodium hydrogen carbonate. The excess of arsenite is titrated with standard iodine. In the presence of other metals, the silver is precipitated first with hydrochloric acid, and the chloride is then dissolved in ammonia. After suitable dilution, standard arsenite is added, and, after boiling, the excess of this is determined in the manner described.

1 mol. of arsenious oxide = 4 ats. of silver.

L. DE K.

Micro-chemical Analysis. VIII. The Insoluble Substances. NICOLAAS SCHOORL (*Zeitsch. anal. Chem.*, 1909, 48, 678. Compare this vol., ii, 762, 831).—After heating moderately to obtain a sublimate of sulphur, if any, the substance is boiled with a drop of water and the solution is carefully decanted, mixed with a drop of acetic acid, and left to crystallise; the slide is then examined for calcium sulphate. Any undissolved residue is heated with a drop of strong sulphuric acid and then left to crystallise. Barium, strontium, and lead sulphates separate. The sulphuric acid is now completely expelled by heating, and from the residue any silver sulphate derived from silver halides may then be extracted with a drop of water. On treating the residue with hydrochloric or nitric acid, the oxides of tin, antimony, iron, aluminium, and chromium dissolve in quantity sufficient for recognition. Lead sulphate may be extracted previously with ammonium acetate.

Insoluble silicates are treated with hydrofluoric acid or a mixture of ammonium fluoride and sulphuric acid to expel the silica. The base may then be readily tested for by the processes already described. Fluorides are treated with hydrochloric acid and precipitated silica.

L. DE K.

Estimation of Calcium Carbonate in Soils. FRANCIS S. MARR (*J. Agric. Sci.*, 1909, 3, 155—160).—A soil freed from any trace of calcium carbonate originally present by treating with cold 5% hydro-

chloric acid and keeping for several hours in a vacuum over sodium hydroxide yielded 0.422, 0.224, and 0.211% of carbon dioxide when boiled for three successive periods of twenty minutes. Similar results, showing the production of carbon dioxide from organic matter by boiling with dilute hydrochloric acid, were obtained with a second soil.

The most satisfactory method for estimating carbonates was found to be the following: The soil is boiled with very dilute hydrochloric acid (5 c.c. of strong acid diluted with 100 c.c. of water) for about twenty minutes under reduced pressure, the carbon dioxide being absorbed by 4% sodium hydroxide in a Reiset tower and determined by the double titration method.

Carbonates may also be estimated by boiling the soil with a solution of an ammonium salt. A current of air free from carbon dioxide is passed through the distilling flask, then through an acid trap to retain the ammonia, and finally through a Reiset tower to absorb the carbon dioxide, which is determined by double titration.

This method is liable to give slightly high results, as it is shown that some soils contain organic matter which gives off carbon dioxide even when boiled with water alone.

N. H. J. M.

Estimation of Barium Sulphate in Presence of Interfering Substances. M. J. VAN'T KRUY'S (*Chem. Weekblad*, 1909, 6, 735—758).—The process is based on the fact that in presence of much calcium the barium sulphate obtained contains calcium sulphate, but is free from potassium, sodium, magnesium, iron, or cobalt. The co-precipitated calcium may be readily removed, and in this way a perfectly pure barium sulphate is left.

To the liquid, which should not contain too much acid, is added an amount of calcium chloride doubly sufficient for combining with the sulphuric acid present, and the boiling solution is then precipitated with a 10% solution of barium chloride; this should be added drop by drop until the amount used exceeds twice the quantity required. The solution is now boiled, and hydrochloric acid is added until the quantity amounts to about 20% of 38% acid, or a mixture of hydrochloric and nitric acid (3:1) is used in such quantity that the acidity amounts to 10%. The whole is now boiled gently for three hours with an occasional addition of a few c.c. of nitric acid if aqua regia has been used. After allowing the barium sulphate to deposit for a moment, the liquid is poured off as much as possible and evaporated in a glass basin to near dryness. Meanwhile, the precipitate is again boiled with 150 c.c. of 20% hydrochloric acid (or dilute nitrohydrochloric acid) and a few c.c. of barium chloride for three hours, and, after decanting, the operation is repeated once more. The acid liquids are all evaporated in the same dish. The residue is now taken up with boiling water, and the whole returned to the beaker containing the barium sulphate. In presence of iron, however, the residue should be heated first with about 0.5 c.c. of hydrochloric acid and a few drops of nitric acid in order to dissolve the basic iron salts.

After boiling for a few minutes, the barium sulphate is collected and washed as usual, and may be trusted to be pure enough for scientific

purposes. The results of sixty-eight experiments are given in a table.
L. DE K.

Solubility of Barium Sulphate in Ammonium Acetate Solutions. GIUSEPPE KERNOT (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], 15, 155—156).—In the analysis of galena, the usual method of separating the lead from the barium consists in treating the mixed sulphates, obtained by the action of nitric acid, with ammonium acetate solution, which dissolves the lead sulphate. The author finds, however, that the results yielded by this method vary with the concentration of the ammonium acetate solution employed, owing to variations in the amount of barium sulphate dissolved by this solvent. Measurements of the solubility of barium sulphate in ammonium acetate solutions of increasing concentrations at 25° show that the solubility reaches its maximum (0.133 gram per litre) with a solution containing about 300 grams of ammonium acetate per litre, and then again falls as the amount of the salt is increased.
T. H. P.

Estimation of Magnesium Chloride in Water. HERMANN EMDE and RICHARD SENST (*Zeitsch. angew. Chem.*, 1909, 22, 2038—2040).—A criticism of Pfeiffer's process (*ibid.*, 435). In this process the water, after being carefully neutralised with sulphuric acid, is evaporated to dryness, and the residue heated for an hour at 400—450°. In the meanwhile the chlorine is estimated as usual. The difference between the chlorine contained in the water and that left in the residue represents magnesium chloride.

The authors state that the process is untrustworthy for several reasons. First of all, magnesium chloride requires a higher temperature for decomposition (550—600°), and secondly, the process will always show the presence of magnesium chloride, although none may be present in the water, owing to the interaction of chlorides at a high temperature on magnesium sulphate, etc.
L. DE K.

Estimation of Magnesium Chloride in Water. PFEIFFER (*Zeitsch. angew. Chem.*, 1909, 22, 2040).—A reply to Emde and Senst (preceding abstract). The author upholds his process and states that the apparent loss in chlorine on heating magnesium sulphate with sodium chloride is due to a sparingly soluble compound of anhydrous magnesium sulphate with sodium chloride. This, however, dissolves completely on extracting repeatedly with hot water.
L. DE K.

Simplification of Mosander's Method for the Separation of Cerium from the other Ceritic Earths. OTTO HAUSER and F. WIRTH (*Zeitsch. anal. Chem.*, 1909, 48, 679—692).—Small quantities of cerium in ceritic earths may be estimated as follows: About 60 grams of the mixed nitrates are precipitated with ammonia and the excess is boiled off. After adding 40 c.c. of 3% hydrogen peroxide, a rapid current of chlorine is passed for half an hour. The precipitate is freed from other ceritic compounds by redissolving in nitric acid and reprecipitation as described. It is finally converted by ignition into cerium dioxide.

A special precipitating flask with stirrer is described, the object of which is to prevent the unpleasant effects of the chlorine.

L. DE K.

[Estimation of] Iron and Copper in Cheese Curds. A. SCHAEFFER (*Milchw. Zentr.*, 1909, 5, 425—430).—*Estimation of Inorganic Iron*.—Twenty grams of the curds are rubbed in a porcelain mortar with about twenty drops of ammonia, D 0·96, until the mass has become transparent. Five drops of yellow ammonium sulphide are next added, and, after trituring the mass, it is placed on a plate of porcelain or opaline glass. After ten minutes, the colour is compared with a colour scale showing amounts of iron varying from 0·0, 0·0003, 0·0007, 0·001, and 0·002%. Organically combined, or naturally occurring, iron is not indicated by this test.

Estimation of Copper.—A simple test for copper similar to the above has not yet been worked out. The curd must be burnt in presence of sodium carbonate and a little potassium nitrate, and the ash tested for copper in the usual manner.

L. DE K.

Sanchez's Process for the Separation of Nickel and Cobalt. HERMANN GROSSMANN (*Zeitsch. angew. Chem.*, 1909, 22, 2005—2006).—The author having tried Sanchez's process (this vol., ii, 621), states that, although based on an interesting reaction (behaviour of the complex cyanides with silver nitrate), it cannot be recommended for analytical purposes.

First of all the preliminary separation of cobalt and nickel sulphides from the other metals of the ammonium sulphide group by means of dilute hydrochloric acid is known to be inaccurate. Again, the final precipitation of the nickel by means of bromine and sodium hydroxide does not yield an oxide of a constant composition.

L. DE K.

Estimation of Molybdenum in Molybdenite. E. COLLETT and MORITZ ECKARDT (*Chem. Zeit.*, 1909, 33, 968—969).—The methods for the estimation of molybdenum are reviewed, and the loss of weight in igniting molybdic acid is recorded in the form of a curve. The following method is recommended.

The finely powdered molybdenite (0·3 gram) is digested with 25 c.c. of fuming nitric acid for two to three hours, the solution evaporated, and the residue heated with 1—2 c.c. of concentrated sulphuric acid, dissolved in 50 c.c. of water, and filtered while warm. The residue is washed on the filter with water, dilute ammonia, and again with water. Ammonia is added to the united filtrates until iron and alumina are precipitated, the filtrate is then concentrated to 150—200 c.c., and an excess of ammonium sulphide added. Copper sulphide is filtered off, the filtrate warmed with hydrochloric acid, and the molybdenum sulphide collected. The filtrate is evaporated, most of the ammonium salts expelled by heat, the residue dissolved, and ammonia and ammonium sulphide added. The two molybdenum sulphide precipitates are united, and weighed after ignition with sulphur in hydrogen as MoS_2 .

C. H. D.

Analysis of Molybdenite. WOLDEMAR TRAUTMANN (*Chem. Zeit.*, 1909, 33, 1106—1107).—The following process is recommended: 0.3 gram of the ore, which need not be very finely powdered, is mixed with a mixture of equal parts of sodium peroxide and sodium hydroxide and heated in a covered nickel crucible, gently at first, and then for five minutes at a bright red heat. When cold, the mass is dissolved in hot water, and the liquid filtered off from any undissolved matter. To the filtrate is added an excess of yellow ammonium sulphide, and, after warming on the water-bath, a slight excess of dilute sulphuric acid is cautiously added. After removing the excess of hydrogen sulphide by means of a current of air, the precipitate is collected and washed. When dry, it is detached from the filter, the filter-ash is added, and the whole converted into molybdenum trioxide by heating in a porcelain crucible over a very small flame. The precipitate may also be weighed as sulphide (preceding abstract). L. DE K.

Coloration in Peroxidised Titanium Solutions; Colorimetric Methods of Estimating Titanium and Fluorine. H. E. MERWIN (*Amer. J. Sci.*, 1909, [iv], 28, 119—125).—An investigation showing that in the colorimetric estimation of titanium, and the indirect colorimetric estimation of fluorine (which has a bleaching effect on the titanium solution oxidised with hydrogen peroxide), due notice should be taken of the amount of alkali sulphate present, and also of the temperature and free acidity. L. DE K.

Analysis of Sulphur Antimonii Auratum. FELIX JACOBSON (*Gummi Zeit.*, 1909, 23, 1075. Compare Abstr., 1908, ii, 540).—When antimony pentasulphide is distilled with concentrated hydrochloric acid, the estimation of the sulphur combined as hydrogen sulphide gives untrustworthy results, it being found that varying amounts of the free element combine to form an excess of hydrogen sulphide beyond that required by the formula $\text{Sb}_2\text{S}_5 + 6\text{HCl} = 2\text{SbCl}_3 + 3\text{H}_2\text{S} + \text{S}_2$. F. M. G. M.

Estimation of [Tantallic and Columbic] Acids. LUDWIG WEISS and MAX LANDECKER (*Zeitsch. anorg. Chem.*, 1909, 64, 65—103).—Columbic acid, precipitated by sulphuric acid, retains this acid, and the usual method of removal by igniting with ammonium carbonate is unsatisfactory. If the acid is neutralised with ammonia, the precipitate settles well, and is readily washed free from sulphate with dilute ammonia. It is, however, better to precipitate from the alkaline solution with acetic acid. Iron is best removed by dissolving the freshly precipitated acid in a mixture of oxalic and tartaric acids, adding ammonia, and passing a current of hydrogen sulphide, the iron alone being precipitated. The complex columbic or tantallic oxalates crystallise well from the filtrate, and yield the pure acids on ignition (see also Giles, this vol., ii, 352). Aluminium is not removed by this treatment.

For separation from all other elements except titanium, the sulphuric acid suspension is heated with sulphur dioxide; the precipitate then contains only columbic and tantallic acids, together with any insoluble sulphates. Any tin in the precipitate may be removed with ammonium

sulphide. To remove calcium sulphate, etc., warm sulphuric acid and hydrogen peroxide are added, when the earth acids dissolve completely.

In the alkaline fusion of mixtures containing titanium, a compound of titanium and columbium appears to be formed to some extent; this is hindered by the addition of an oxidising agent to the alkali. For the quantitative estimation, sodium nitrate is used. After dissolving in water and filtering, very little titanium remains in solution, and this is completely precipitated by hydrogen sulphide without carrying down the other earth acids. Sodium peroxide and borax gave incomplete separations. A mixture of six parts potassium cyanide and one part potassium hydroxide effects complete separation, the titanium becoming insoluble. Sodium carbonate and sulphite, and various acid mixtures, fail to give a complete separation.

Columbic and tantalic acids are best separated from one another by fusing with sodium carbonate and nitrate, dissolving in warm water, cooling, and precipitating tantalum with carbon dioxide. Slight variations in the conditions diminish the accuracy of the separation.

For the complete analysis of minerals, the material is fused with potassium hydrogen sulphate until clear, extracted with hot water containing sulphuric acid, and sulphurous acid is added to the boiling solution until the precipitate becomes flocculent. After twenty to thirty minutes' boiling, the precipitate is collected and washed with sulphurous acid. The residue, containing tantalum, columbium, titanium, and tin, is neutralised with ammonia, extracted with ammonium sulphide, heated in a platinum crucible, and fused with sodium carbonate and nitrate. The analysis is completed as above. Several complete analyses of tantalite are given.

The paper concludes with a list of the qualitative reactions of tantalum and columbium.

C. H. D.

Determination of the Degree of Pollution of Sea-water by the Estimation of the Organic Matters. C. LENORMAND (*Bull. Sci. Pharm.*, 1909, 16, 253—258).—To 100 c.c. of the clear but not filtered sample are added 1 gram of pure potassium carbonate and 10 c.c. of permanganate solution (made by dissolving 3.95 grams of the salt up to 1 litre of water and diluting this tenfold before use). The liquid is boiled for ten minutes, and then cooled rapidly and diluted to 100 c.c. It is then introduced into a suitable colorimeter, and compared with a standard made by diluting 10 c.c. of the dilute permanganate to 100 c.c. The loss in permanganate, which is then expressed in oxygen, is thus readily ascertained. The use of a suitable green glass in order to absorb the red colour is recommended. In some experiments made, the oxygen absorbed by the water agreed very well with the number of bacteria present, and the author thinks that in most cases the chemical test will suffice.

The self-purification of sea-water appears to take place with amazing rapidity.

L. DE K.

Detection of Nitronaphthalene in Mineral Oils. FERD. SCHULZ (*Chem. Zeit.*, 1909, 33, 1093).—Ten grams of the mineral oil, or

a mixture of mineral and vegetable oil, are mixed with 0.5 gram of American rosin and heated in a tube to 290—300°. After cooling to 80°, 4 grams of 10% sulphuric acid are added, and the whole is well shaken; the tube is then placed in a boiling-water bath, and, after some time, the acid layer is drawn off. On adding a few c.c. of cold saturated potassium dichromate, an azure-blue precipitate of aminonaphthol is obtained even with as little as 0.05% of nitronaphthalene. The precipitate may be washed with dilute alkali and then with water, and further identified by the fact that its alcoholic solution has a rose colour and its solution in benzene a cherry-red colour, or, if very dilute, a rose-red one. L. DE K.

Detection of Allyl Alcohol and its Derivatives. GEORGES DENIGÈS (*Bull. Soc. chim.*, 1909, [iv], 5, 878—879).—Two groups of colour reactions are described, depending on the formation from allyl alcohol of (1) glyceraldehyde and (2) dihydroxyacetone, and the condensation of these products with various reagents.

Bromine water (0.6 c.c. in 100 c.c. of water) is added to 0.1 c.c. of allyl alcohol until a slight permanent coloration is obtained, and the liquid is then boiled, allowed to cool, and divided into portions of 0.4 c.c. To each of these, 0.1 c.c. of a 5% solution of codeine, resorcinol, thymol, or β -naphthol is added, followed by 2 c.c. of sulphuric acid ($D=1.84$), and the mixture warmed during three or four minutes at 100°. Codeine and thymol give reddish-violet colorations, resorcinol wine-red, and β -naphthol yellow with a greenish fluorescence.

The second group of colour reactions is obtained by adding to the brominated liquid, obtained as described above, 5 c.c. of bromine water (0.6 c.c. in 100 c.c. of water), heating during twenty minutes at 100°, then boiling to remove excess of bromine, and cooling. This preparation gives the usual colour reactions of dihydroxyacetone (this vol., ii, 272, 273, 448). T. A. H.

Estimation of Essential Oil and Eugenol in Cloves. R. REICH (*Zeitsch. Nahr. Genussm.*, 1909, 18, 401—412).—The essential oil is separated by subjecting the cloves to steam distillation; for this purpose a weighed quantity of from 10 to 20 grams of the cloves is ground up with pumice-stone and placed in a brass cylinder provided with a perforated false bottom; a second cylinder fitting over the top of the first serves as a cover. This second cylinder contains a spiral spring attached to a disk, which presses on the mixture in the first cylinder. A tube leading from the bottom of the latter is connected with a steam-boiler, whilst a tube at the top of the second cylinder or cover is attached to an ordinary Liebig condenser. The cylinders are surrounded by a steam-jacket supplied with steam from the boiler. About 200 c.c. of distillate are collected and saturated with sodium chloride, the essential oil being then extracted with pentane. The pentane solution is evaporated in the manner described previously by the author (*Abstr.*, 1908, ii, 1075), and the residue of essential oil is weighed. The quantity of eugenol in the essential oil is ascertained by heating 1.5 grams of the oil with 20 c.c. of 5% sodium hydroxide solution on a water-bath and under a reflux apparatus.

After being heated for fifteen minutes, the mixture is cooled and the undissolved portion of the oil is removed by extraction with light petroleum. The alkaline solution is then diluted with 5% sodium hydroxide to a volume of 30 c.c., of which 15 c.c. are shaken with 5 c.c. of 25% sulphuric acid, 6 grams of sodium chloride, and 20 c.c. of pentane. When the pentane has separated, an aliquot part of it is transferred to a weighed vessel, the pentane is evaporated as described previously, and the residue of eugenol is weighed. The following percentage quantities of essential oil and eugenol were found in various samples of cloves:

	Essential oil.	Eugenol.
Amboyna cloves	21.3—22.1	17.0—17.6
Zanzibar „	18.4—20.1	15.4—16.6
Ground „ (commercial)	17.0—19.3	15.5—16.3
Clove stalks	5.8—6.7	5.4—5.7

W. P. S.

Presence of Inositol as a Characteristic of Natural Wines. G. MEILLÈRE (*J. Pharm. Chim.*, 1909, [vi], 30, 247—249).—Referring to Perrin's suggestion (this vol., ii, 624), that since inositol occurs in all natural wines, its detection serves to distinguish these from artificial wines, the author points out that he had already drawn attention to this method of identifying natural wines (*J. Pharm. Chim.*, 1908, [vi], 30, October). Perrin's method of isolating and characterising inositol is criticised in comparison with the author's own method (*Abstr.*, 1906, ii, 811).

T. A. H.

New Method of Working in the Estimation of Sugars by Bonnan's Process. P. MAILLARD (*Ann. Chim. anal.*, 1909, 14, 342—348, 370—374).—A table is given showing the factor to be used in the estimation of dextrose, which figure varies considerably with the time taken up in the titration with Bonnan's copper solution. For lactose, a special table has been constructed. The tables also give divisors by which the amount of dextrose or lactose per litre can be obtained. From the amount of dextrose found, the equivalent amount of inverted sugar is obtained by dividing by 0.96, and that of levulose by dividing by 0.923.

Actual Operation.—In the case of very weak solutions a definite amount of pure dextrose solution (8 grams per litre) may be added and allowed for; 10 c.c. of Bonnan's copper solution, 10 c.c. of tartrate solution, 5 c.c. of ferrocyanide solution, and 0.25—0.30 gram of pumice are placed in a short-necked, 100—150 c.c., flat-bottomed flask, and heated with a Bunsen burner in such a manner that boiling starts after two and a-quarter to two and a-half minutes. After two and a-half minutes, the liquid should be actively boiling, and the sugar solution may now be added from a burette with stopcock.

The nozzle of the burette is placed at a distance of 1 cm. above the neck of the flask, and the dextrose solution is run in at the rate of 2—6 c.c. per minute. The moment the first drop is added, the time is noted, and the instant the liquid turns yellow, the stopcock is regulated with the fingers, and turned off at once when a brown precipitate forms.

The exact time taken up by the titration is then recorded, and reference is made to the tables. If the amount of dextrose solution required exceeds 12 c.c., 0.1 c.c. should be deducted for every 1 c.c. used in excess.

In the case of lactose, the solution should not be added too rapidly to the copper solution. Maltose behaves like lactose, but the result expressed as lactose must be divided by 0.848.

Processes are also given for rendering the method applicable to urines and milks.

L. DE K.

Detection of Sucrose and Sugars in General. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1909, 27, 179—180).—The test described previously (Abstr., 1908, ii, 740) is rendered more sensitive if 1 c.c. of 5% ammonium molybdate solution is added to 2 c.c. of the sugar solution, and this mixture then poured on the surface of the sulphuric acid. A blue coloration is obtained at the junction of the liquids if as little as 0.0005 gram of sucrose is present, and 0.00002 gram may be detected if the aqueous layer is heated. The coloration is also given by other carbohydrates, but is not so intense as in the case of sucrose.

W. P. S.

Explanation of the Colour Reactions of Sugars. Reactions Due to the Formation of 2-Hydroxy-4-methylfurfuraldehyde. Reactions of Pettenkofer and Seliwanoff. JULES VILLE and EUGÈNE DERRIEN (*Bull. Soc. chim.*, 1909, [iv], 5, 895—901).—It has been shown already (Ville, Abstr., 1907, ii, 913, and Ville and Derrien, *Compt. rend. Soc. Biol.*, 1909, 66, 175) that Mylius' assumption (Abstr., 1887, 1149) that Pettenkofer's reaction is due to the formation of furfuraldehyde is inaccurate (compare Denigès, this vol., ii, 448). Kiermayer has observed (Abstr., 1896, i, 144) that by the action of oxalic acid on lævulose, 2-hydroxy-4-methylfurfuraldehyde is obtained. The authors now find that if the latter substance, or the anhydride into which it passes readily (*loc. cit.*), be substituted for lævulose or sucrose in Pettenkofer's reaction, the colour produced is identical spectroscopically with that obtained in the reaction as usually applied; whence they conclude that it is to the formation of this substance from the sugar and its condensation with bile acids that the coloration is due. Further, they show that this is also the mechanism of Seliwanoff's test for keto-sugars, the Boas reaction for hydrochloric acid in gastric juice, and of other similar tests. The fact that certain of the aldohexoses also give these reactions, although with difficulty, is explained by the suggestion that they may be converted into keto-hexoses by the action of the acid used.

T. A. H.

The Author's Method for the Estimation of Glycogen, and the Specificity of Substances of the Animal Body. EDUARD PFLÜGER (*Pflüger's Archiv*, 1909, 129, 362—378).—Further experiments have been carried out by Francke under the author's direction which show that glycogen is not altered by heating either with dilute or concentrated potassium hydroxide solutions. The errors obtained by heating organs with dilute alkali for the purpose of isolating

glycogen are due possibly to the fact that the protein is not entirely destroyed, and this carries down with it some glycogen. The glycogen may also undergo change during the process of isolation by the ferments of the organ. For these reasons, a stronger alkaline solution is advisable. The best concentration is 30%. The method of separating the glycogen from organs is given in detail by the author, who, in conclusion, calls attention to the fact that the same glycogen is obtained from all species of animals, contrasting this with the species differences in the proteins.

S. B. S.

Separation of Mixtures of Some Aliphatic Acids by means of Benzene and Toluene. THOMAS R. HODGSON (*Analyst*, 1909, 34, 435—436).—Lasserre (Abstr., 1907, ii, 991) having communicated a process for the separation of volatile fatty acids by shaking the aqueous solution with benzene, the author has investigated the method and found that the process cannot lay claim to accuracy, although by due observance of conditions it may be of some utility.

The best results are obtained when the acid solutions to be extracted are shaken with twice the volume of benzene; toluene has no advantage over benzene.

L. DE K.

Experiments on the Separation of Mixtures of Some Aliphatic Acids by means of Benzene. CHARLES A. KEANE and PERCIVAL NARRACOTT (*Analyst*, 1909, 34, 436—438).—An investigation of Lasserre's process (see preceding abstract). From experiments made with formic acid, acetic acid, propionic acid, *m*-butyric acid, *iso*-butyric acid, and *isovaleric* acid, it is shown that the separation of their aqueous mixtures by means of benzene is influenced by the proportions and concentrations of the acids, and that the method does not therefore rest on a satisfactory principle.

L. DE K.

Estimation of Fatty Matters in Fæces. A. CHAPUS (*J. Pharm. Chim.*, 1909, [vi], 30, 301—304).—Ten grams of the well mixed sample are triturated with 20 grams of anhydrous sodium sulphate, the dry mass is introduced into an extraction tube, and the mortar is rinsed with another 5 grams of sodium sulphate. In the case of very liquid fæces, the quantity of sodium sulphate should be increased.

The mass is extracted with anhydrous ether, which is then recovered by distillation. The residue is dissolved in 50 c.c. of hot alcohol, and titrated with *N*/10-potassium hydroxide. This gives the amount of free fatty acids calculated as stearic acid. Another 10 grams of the sample are then treated as before, after first adding a slight excess of hydrochloric acid to decompose any soapy matter. The ethereal extract is then evaporated in a weighed dish, and the residue, after drying in a vacuum over sulphuric acid, is weighed. It is then dissolved in alcohol and titrated with *N*/10-potassium hydroxide, using phenolphthalein as indicator. From the result obtained and after allowing for the free acids, the acids existing as soap and the neutral fat are readily calculated.

L. DE K.

Leucine Fraction of Proteins. PHÆBUS A. LEVENE and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1909, 6, 391—418, 419—430).—Leucine and *d*-isoleucine may be separated quantitatively from

d-valine as the normal lead salt. The relative proportion of the leucine isomerides may be determined polarimetrically in 10% hydrochloric acid solution; they may be separated from each other by Ehrlich's method of extracting their copper salts with methyl alcohol. The specific rotation of *isoleucine* is $+37.4^\circ$, instead of $+36.8^\circ$ as given by Ehrlich. A comparison of the percentage figures obtained by the new method with those given by Abderhalden is as follows:

	From caseinogen.		From edestin.	
	New method.	Abderhalden.	New method.	Abderhalden.
Leucine	7.92	} 10.5	8.1	20.9
<i>iso</i> Leucine	1.43			
Valine	6.69	1.0	5.6	0.45

No doubt all previously published estimations of leucine in proteins require revision. W. D. H.

Volumetric Estimation of Thiocyanic Acid and the Causes of the Low Results. K. SCHRÖDER (*Zeitsch. öffentl. Chem.*, 1909, 15, 321—336).—As the result of a large number of experiments, the author arrives at the following conclusions. The decrease in permanganate consumed increases with the time of the titration. If the manganese is precipitated with sodium carbonate and then again redissolved by adding hydrochloric acid, more permanganate will be required to complete the reaction. If the solutions are very dilute, the air should be excluded.

The best results are obtained by adding an excess of permanganate to the hot solution acidified with sulphuric and phosphoric acids. The free permanganate is then titrated in the usual way with oxalic acid or hydrogen peroxide. Probably good results may be also obtained by rapidly titrating with permanganate in a current of carbon dioxide.

L. DE K.

Jaffe's Colorimetric Method for the Estimation of Creatinine. A. CHASTON CHAPMAN (*Chem. News*, 1909, 100, 175*).—The author has shown that Jaffe's picric acid test being due to a somewhat complex reducing action, it is clear that the conditions under which the test is carried out must be fairly closely defined if accurate results are to be obtained. The temperature is of paramount importance, as also, but in a less degree, is the time. The presence of dextrose does not seem to interfere when working with cold solutions. Attention is also called to the necessity of working with solutions sufficiently diluted.

L. DE K.

[Estimation of Quinine and its Excretion in Urine.] PAUL GROSSER (*Arch. exp. Path. Pharm.*, 1909, 61, 274. Compare Nishi, this vol., ii, 710).—Nishi objected to the author's method of estimating quinine by extraction with ether in presence of charcoal. The author calls attention to the fact, however, that the extraction was made with dried substance and not in the presence of liquids.

S. B. S.

* and *Analyst*, 1909, 34, 475—483.

General and Physical Chemistry.

Indices of Refraction of Mixtures of Methyl Alcohol and Water. III. ANTONY G. DOROSCHEWSKY and S. V. DVORSCHANTSCHIK (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 951—958. Compare Abstr., 1908, ii, 241, 785).—For absolute methyl alcohol, D_{15}^{15} is 0.79047 and n_D^{15} 1.33057. For mixtures of methyl alcohol and water, the index of refraction increases to a maximum of n_D^{15} 1.34378 or $n_D^{17.5}$ 1.34308 for a 50% solution. The temperature-coefficient, dn/dt , of the index of refraction varies quite regularly from 0.00040 for methyl alcohol to 0.00009 for water. The values of α , β , and γ (compare this vol., ii, 841) are calculated for each 10% of the alcohol from 10% to 90%, the mean (and limiting) values being 0.982 (0.973—1.000), 0.895 (0.883—0.913), and 1.126 (1.110—1.138) respectively, so that for aqueous methyl alcohol, just as for aqueous ethyl alcohol, the mean value for α is approximately the arithmetic mean of those for β and γ . For these mixtures there exists, as Pulfrich assumed (*Zeitsch. physikal. Chem.*, 1889, 4, 561), a constant relation between the contraction of volume and the contraction of refractive capacity.

From the numbers calculated by means of the three general formulæ for the refraction: $(n-1)/d$, $(n^2-1)/(n^2+2)d$, and $(n^2-1)/d$, firstly, without correction, and secondly, with introduction of the Pulfrich-Hess correction (compare this vol., ii, 1), it is seen that the most satisfactory uncorrected results are yielded by Gladstone's formula; the other two formulæ, even when corrected, give results less concordant than those of the Gladstone formula. The best results of all are obtained by means of the Gladstone formula with Pulfrich's correction:

$$(n-1)(1-ac)/d(1-c)$$

(*Zeitsch. physikal. Chem.*, 1889, 4, 561).

T. H. P.

Determination of the Dispersion of Light in Non-Luminous Saturated Sodium Vapour at 385°. STANISŁAW LORIA (*Bull. Acad. Sci. Cracow*, 1909, 39—60).—The sodium vapour was contained in a transparent quartz tube, and the measurements of the dispersion were made by an interference method within the limits of the visible spectrum between $\lambda = 6.145 \times 10^{-5}$ cm. and $\lambda = 5.693 \times 10^{-5}$ cm. at 385°. The results are given in tables and curves, and it is shown that there is good agreement between the observed values and those calculated on the dispersion theory. An estimate is made of the ratio of the number of dispersion electrons to sodium atoms in equal volumes of the saturated vapour.

G. S.

Spectrum of Magnesium Hydride. A. FOWLER (*Phil. Trans.*, 1909, 4, 209, 447—478).—Photographs have been taken of the spectrum of an electric arc between magnesium rods in an atmosphere of hydrogen at a pressure of one to three inches of mercury. The wave-lengths of about two thousand lines composing the three principal flutings have been determined. The head lines in the

various groups of flutings correspond with the wave-lengths 5621·57, 5211·11, 4844·92, 4371·8, and approximately 2430. The identification of magnesium hydride in the sun-spot spectrum is confirmed. The presence of the magnesium hydride flutings accords with the view that spots are regions of reduced temperature, and that their darkness is partly due to absorption. The question as to whether lines of magnesium hydride are present in the ordinary solar spectrum is not definitely settled, but it is probable that very few, if any, of the thousands of lines tabulated by Rowland are to be accounted for by this substance.

H. M. D.

Chemical Reactions of Phosphorescence. WILDER D. BANCROFT (*Zeitsch. physikal. Chem.*, 1909, 69, 15—18).—Regarding phosphorescence as a chemical reaction, eight possible types of reactions are suggested which might give rise to phosphorescence, and methods for differentiating between most of these are given. The question is to be investigated experimentally on the lines laid down.

G. S.

Influence of Constitution on the Rotatory Power of Optically Active Substances. HANS RUPE (*Annalen*, 1909, 369, 311—369).—See this vol., i, 927.

Stereoisomerism of Internally Complex Salts. HEINRICH LEY and H. WINKLER (*Ber.*, 1909, 42, 3894—3902).—See this vol., i, 886.

Luminescence and Crystalline Form of Potassium Sodium Sulphate. B. A. LINDINER (*Bull. Acad. Sci. St. Pétersbourg*, 1909, 961—986).—The author has studied the various kinds of luminescence exhibited by, and the crystalline form of, the double sulphate of potassium and sodium.

When crystals of the double sulphate separate from the mother liquor containing the two sulphates, the separation is always accompanied by luminescence, which may be observed repeatedly with one and the same solution; but if the separated crystals are dissolved in water, luminescence is not, as a rule, produced on crystallisation of the solution thus obtained, owing to the readiness with which the double sulphate decomposes into its constituents. The intensity of the luminescence occurring when the double sulphate separates, either alone or mixed with sodium sulphate, varies with the concentration of the solution, and is considerably more intense with a dilute solution concentrated at the ordinary temperature than with a hot saturated solution. The relative proportions of the two alkali sulphates also influence the luminescence, which is very slight with pure solutions of the double salt, $3\text{K}_2\text{SO}_4, \text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$, and reaches its maximum intensity for a solution containing $2\cdot5 - 2\text{K}_2\text{SO}_4$ and $1\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$. The luminescence is also more marked on the separation of well-developed crystals, such as are deposited from a solution containing $2\text{K}_2\text{SO}_4$ to Na_2SO_4 , in a desiccator over phosphoric oxide, in which case it is apparent in daylight. Luminescence is observed only after the deposition of a certain amount of the crystals, the separation of

each crystal being then accompanied by a spark, this process being capable of continuing for three hours.

The luminescence produced by shaking the crystals (triboluminescence) may be observed for some days after crystallo-luminescence has ceased. Very intense triboluminescence occurs when a glass rod or other hard substance is drawn over the crystalline magma beneath the mother liquor. The more intense the luminescence observed during the formation of the crystals, the more intense is the triboluminescence exhibited by the latter. Further, the luminescence produced by friction is of equal intensity with the single and twinned crystals.

Sparks are also observed when the crystals of the double sulphate are either heated or cooled—a phenomenon to which the author gives the name *pyroluminescence*. The thermoluminescence exhibited by certain minerals may also be due to the change of temperature and not merely to the heating. A parallelism exists between the pyro-electrical properties and the pyroluminescence.

The optical properties, relations of symmetry, twinning, and the etched figures of the crystals are also discussed. T. H. P.

Spontaneous Luminosity of a Uranium Mineral.

ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1909, A, 83, 70—71).—It has been found that specimens of recently-raised autunite from Portugal are self-luminous. The mineral is easily perceived in a perfectly dark room by a well rested eye. It is more luminous than uranium nitrate, but less so than potassium uranyl sulphate. Old specimens of autunite from Cornwall and from Autun do not show the phenomenon. The loss of luminosity is connected with a loss of water of crystallisation, for when the active autunite was sealed up in an exhausted vessel with phosphoric oxide it was found that the self-luminosity disappeared after a few hours. H. M. D.

Photochemical After-Effect. LUDWICK BRUNER and Z.

ŁAHOCIŃSKI (*Bull. Acad. Sci. Cracow*, 1909, 265—267).—The photobromination of toluene is greatly retarded by the presence of oxygen. In order to remove the oxygen from a concentrated solution of bromine in toluene, the solution was submitted to the action of a strong light for a short time and then put in the dark until required. It was found, however, that the bromine was used up in a few minutes in the dark, because of a very pronounced photochemical after-effect. Investigation of this action has given the following results. When toluene is brominated in the dark in dilute solution, substitution takes place in the side-chain to the extent of 20% at 10° and 45% at 25°; bromination produced by the photochemical after-effect takes place exclusively in the side-chain. If the bromine (dissolved in carbon tetrachloride) and the toluene are separately exposed to the light and then mixed, there is no after-effect. Also, specially prepared mixtures of toluene, benzyl bromide, and hydrogen bromide do not show an abnormal bromination effect in the dark. The stronger the light in the photobromination the stronger is the after-effect; when the

former is very weak, the latter disappears. The greater the concentration of the solution on which the after-effect is to be studied, the less pronounced is the after-effect.

The after-effect may last for hours, according to the quantity of bromine used in the photobromination. If more than twenty-four hours elapse between the photobromination and the bromination in the dark, there is no longer an after-effect. Cooling a photobrominated mixture to the temperature of liquid air does not weaken the after-effect, whereas heating to 100° for two hours destroys it. T. S. P.

Experiments on Solarisation. G. A. PERLEY (*J. Physical Chem.*, 1909, 13, 630—658).—The theory of Abney, that oxidising agents facilitate reversal of the photographic image and reducing agents retard it, could not be confirmed in the cases of hypobromous acid and potassium permanganate. These oxidising agents have, however, a distinct clearing effect on the reversed image by retarding the formation of a second normal image. Such depolarisers as concentrated sodium nitrite applied to the plate before a long exposure give rise to very dense negatives of the metallic silver (doubly reversed) order, which mask the positive (reversed) image. With short exposures in a good light, a depolarised plate could be made to give a reversed (positive) image only, or a good negative of a dimly lit interior could be obtained by a short exposure of a "depolarised" plate which was developed immediately after exposure.

Exposure of a plate during development to greenish-blue light gave a good positive instead of a negative, particularly when potassium bromide and sodium carbonate were added to the stock developer. These positives were, however, too dense for lantern slides.

Sodium hypophosphate exerts a solvent action on the film, and gives rise to positive images after short exposures.

Thiocarbamide in Waterhouse's process for direct positives is found to produce its effect by increasing the sensitiveness of unexposed silver bromide so that it develops before the exposed bromide.

R. J. C.

Photoelectric Sensitiveness of Potassium as a Function of the Wave-length.—WILHELM HALLWACHS (*Ann. Physik*, 1909, [iv], 30, 593—597). It has been assumed that certain metals show a maximum photoelectric effect for a particular wave-length of incident radiation. The behaviour of potassium has been examined in this connexion for wave-lengths ranging from $578\mu\mu$ to $217\mu\mu$. For this purpose the potassium was enclosed in a special form of cell, closed by a quartz plate, and provided with electrodes, which were connected with an electrometer circuit. The observations show that the specific photoelectric sensitiveness of potassium increases continuously as the wave-length of the incident radiation diminishes. The rate of increase is, moreover, considerably greater in the ultra-violet region than it is in the region of the visible spectrum. H. M. D.

Multiple Atomic Disintegration. A Suggestion in Radioactive Theory. FREDERICK SODDY (*Phil. Mag.*, 1909, [vi], 18, 739—744).—The fact that the rate of disintegration of radioactive

substances is independent of all known conditions suggests that the cause of disintegration is something apart from the radioactive atoms. If this is the case, it is conceivable that more than one condition of instability can exist within the atom at the same time, and the author suggests that multiple modes of disintegration may be proceeding simultaneously and independently within the same atom. The law of probability will apply to each mode of disintegration exactly as if it were the only one in operation, and the quantity of any radioactive element which undergoes such multiple disintegration will diminish exponentially with the time as in a simple disintegration process. The quantities of the products formed in the various modes of disintegration will be always proportional.

The view put forward gives a satisfactory explanation of the known relations between uranium, actinium and radium. H. M. D.

Mobility of the Radioactive Ions and the Mass of Gaseous Ions. J. FRANCK (*Ber. Deut. physikal. Ges.*, 1909, 11, 397—405).—The question as to whether the ions of gases consist of simple charged molecules or of complex molecular aggregates has been examined. With this object the author determined the mobility of the radioactive ions of thorium-*D* in air, nitrogen, and hydrogen. The ions of thorium-*D* were obtained by the use of plates on which thorium -*A*, -*B*, and -*C* had been deposited by exposing the negatively-charged plates to the influence of the emanation of a radio-thorium preparation.

The experimental data show that the mobility of the positively-charged thorium-*D* atoms is approximately equal to the mobility of the positive gaseous ions in air, nitrogen, and hydrogen. This leads to the conclusion that the gas ions are complex molecular aggregates, a result which is opposed to the recently-expressed view of Wellisch, that the gas ions consist of single atoms or molecules. H. M. D.

The Radioactivity of the Gases of the Wiesbaden Hot Springs. FERDINAND HENRICH (*Zeitsch. Elektrochem.*, 1909, 15, 751—757).—The gases consist mainly of carbon dioxide and nitrogen with from 1.7 to 4.9% of argon, neon, and helium. The radioactivity is shown, by measurements of the rate of decay, to be due to radium emanation. The activity of the gases varies to a comparatively small extent from day to day, and the author attempts to find a connexion between these variations and variations of atmospheric pressure and other circumstances, but without success. T. E.

Attempt to Explain the Properties of Radium. NICOLAI N. BEKETOFF (*Bull. Acad. Sci. St. Pétersbourg*, 1909, 879—886).—In this paper the author develops his views, previously published (*Abstr.*, 1903, ii, 623), on the causes of the phenomena exhibited by radium. T. H. P.

Radium Content of Certain Igneous Rocks from the Sub-Antarctic Islands of New Zealand. C. COLERIDGE FARR and D. C. H. FLORANCE (*Phil. Mag.*, 1909, [vi], 18, 812—816).—As a result of the examination of various igneous rocks obtained from

islands to the south of New Zealand, it is found that the mean radium content approximates closely to that found for other igneous rocks by Strutt, and by Eve and McIntosh. A comparison of the relative values for the radioactivity shows that this corresponds roughly with the basicity and not with the age of the rocks.

H. M. D.

A Typical β -Radiation of Radium. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1909, 10, 741—745).—It is found that β -rays are not only emitted by radium-*B*, radium-*C*, and radium- E_2 , but also by radium itself. When a drop of a strong solution of a radium salt is evaporated to dryness on a strip of platinum foil, and the residue heated strongly in the blow-pipe in order to volatilise the disintegration products of radium, the β -ray activity is found to reach a lower limiting value. The soft β -rays which are emitted by the non-volatile product represent about 1.2% of the whole β -ray activity of radium in equilibrium with the disintegration products. The rays are half absorbed by a layer of aluminium 0.00222 cm. in thickness, which corresponds with an absorption coefficient $\gamma = 312 \text{ cm.}^{-1}$. On the assumption that every set of rays corresponds with a different substance, the authors conclude that what has been called radium previously is a complex substance. The observed facts seem to show that the newly-discovered β -rays are emitted by radium itself, whilst the α -rays are to be ascribed to its primary disintegration product, to which the name radium-*X* is given.

H. M. D.

Some Numerical Constants of Radium Emanation and their Relation to those of the Inactive Gases. GEORGE RUDOLF (*Zeitsch. Elektrochem.*, 1909, 15, 748—749).—From Ramsay and Gray's determinations (*Trans.*, 1909, 95, 1073), the author calculates the values of f for radium emanation in the equation $\log p_k - \log p = f(T_k/T - 1)$, where p and p_k are the vapour pressure and critical pressure at the temperature, T , and critical temperature, T_k . The mean value is 2.23; the value for argon is 2.25; krypton, 2.39, and xenon, 2.38. The values of a and b in van der Waals' equation are (for a gram-molecule and pressure in metres): argon, $a = 9.886 \times 10^5$, $b = 30.18$; krypton, $a = 17.63 \times 10^5$, $b = 39.79$; xenon, $a = 31.24 \times 10^5$, $b = 51.57$; radium emanation, $a = 49.3 \times 10^5$, $b = 62.1$.

The molecular heat of evaporation calculated by Nernst's modification of Trouton's rule is 4387 cal., whilst from the increase of vapour pressure with temperature, it is calculated to be 3960 cal. at the boiling point. The mean values calculated in the same way for the inactive gases are: argon, 1657 cal.; krypton, 2208 cal.; xenon, 3026 cal.

Radium emanation, therefore, has physical properties which are in harmony with those of the inactive gases.

T. E.

Spectrum of Radium Emanation. HERBERT EDMESTON WATSON (*Proc. Roy. Soc.*, 1909, A, 83, 50—61).—Photographs of the spectrum of carefully purified radium emanation have been taken with a prism spectrograph, and also with a grating. A new method of determining

the wave-lengths of the spectral lines without the usual comparison spectrum is described. The wave-lengths, intensities, and persistencies of the lines are compared with those of previous observers (Royds, this vol., ii, 206, 287; Rutherford and Royds, *Abstr.*, 1908, ii, 787; Cameron and Ramsay, *Abstr.*, 1908, ii, 786). The occurrence of xenon lines in the spectrum of the emanation obtained by Ramsay and Cameron is confirmed, but Royds's suggestion of accidental contamination with xenon is considered to be untenable. On the other hand, it is supposed that under the conditions obtaining in the experiments of Ramsay and Cameron, the emanation has undergone disintegration with the formation of xenon. Since copper electrodes were used in these experiments, it is suggested that copper may be the transforming agent, but the author considers that further evidence is required before such an assumption can be made. H. M. D.

Active Deposit from Actinium in Uniform Electric Fields. W. T. KENNEDY (*Phil. Mag.*, 1909, [vi], 18, 744—757).—Experiments have been made to determine the factors which influence the separation of the active deposit from actinium in a uniform electric field. Circular electrodes, furnished with guard plates, were employed, and these were exposed to the actinium emanation for two hours before being examined. In most experiments the difference of potential between the electrodes was 250 volts.

When the electrodes were separated, the active deposit on both plates steadily decreased. When the distance between the plates exceeded 3 mm., no deposit was obtained on the anode, but that on the cathode only fell to about one-half when the distance between the plates was increased from 1 to 8 mm.

With increasing distance between the actinium and the electrodes, the amount of the active deposit on both anode and cathode was found to undergo a steady diminution.

From experiments in air, carbon dioxide, and hydrogen at different pressures, it was found that the active deposits on both electrodes increased with falling pressure, and that in both cases maximum values were reached, the activities afterwards diminishing with further reduction in the pressure. At pressures of the order of 1 mm. of mercury, the anode and cathode were found to be equally active. A comparison of the pressures corresponding with the maximum cathode and anode deposits for the three gases examined indicates that diffusion is of paramount importance in connexion with the deposition of the active disintegration products. Although the pressures corresponding with the maximum cathode deposits are considerably higher than those corresponding with maximum anode activity, the pressure ratios for the three gases are approximately the same for both cathode and anode.

In the absence of an electric field, the total deposit was found to be practically the same as in a uniform field if the pressure exceeded a certain value. For pressures lower than this, the total deposits were greater when the electric field was applied. H. M. D.

Positive Charge of the Canal Rays. JOHANNES STARK (*Physikal. Zeitsch.*, 1909, 10, 752—756).—The observations which led

Wien to put forward the view that the line spectra are due to neutral atoms are adversely criticised. The fact that the canal rays show the Doppler effect has already led the author to the conclusion that the line spectra are to be attributed to positively charged ions, and to ascertain the cause of the discrepancy between these two views, experiments have been made by a method similar to that employed by Wien. It is shown that the canal ray discharge in mercury vapour under otherwise constant conditions varies with the material of which the receiver is constructed. The ratio of the canal ray discharge to that of the primary glow discharge is of the order 10^{-4} in mercury vapour, whereas the same ratio in hydrogen is of the order 10^{-2} . This observation is in accord with the author's theory. H. M. D.

Positive Rays of Mercury. WILHELM WIEN (*Physikal. Zeitsch.*, 1909, 10, 862. Compare Abstr., 1908, ii, 1006).—A reply to Stark (preceding abstract), in whose opinion the rays examined by the author were not canal rays, but a phenomenon resulting from the removal of positive and negative ions from the region of discharge by the stream of mercury vapour. It is pointed out, however, that the rays produce the characteristic fluorescence on the walls of the glass tube, and that no traces of mercury vapour could be detected in the region of observation. H. M. D.

Ultimate Product of the Uranium Disintegration Series. J. A. GRAY (*Phil. Mag.*, 1909, [vi], 18, 816—818).—The uranium minerals autunite and torbernite were examined spectroscopically by introducing them into a carbon arc with calcium chloride to serve as a flux. The only lines in the spectra of the minerals which did not belong to one or other of the chief constituents were those of iron, lead, barium, and strontium. Of these, lead is the only one which cannot be regarded as an accidental impurity, and its presence is considered to support the view that lead is the ultimate product of the disintegration of uranium.

An approximately quantitative comparison of the spectra obtained with calcium chloride containing determined quantities of autunite and lead respectively showed that the mineral examined contains about 0.0001 gram of lead per gram. The time required for the formation of this amount is about a million years. H. M. D.

Radioactivity of Preparations of Zirconium. ALBERT GÖCKEL (*Chem. Zeit.*, 1909, 33, 1121).—The examination of various preparations of zirconium has shown that the radioactivity diminishes with increasing purity. Natural zircon gives rise to induced activity, and the rate of decay of this indicates that the radioactive impurity is thorium. The measurement of the radioactivity is suggested as a means of determining the degree of purity of zirconium preparations. H. M. D.

Electronic Theory. PHILIP BLACKMAN (*J. Physical Chem.*, 1909, 13, 609—629. Compare this vol., ii, 291).—A summary of results already published, giving tables of molecular conductivities of salts, ionic conductivities, etc. R. J. C.

Electrical Conductivity of Liquid Ammonia Solutions.
III. EDWARD C. FRANKLIN (*Zeitsch. physikal. Chem.*, 1909, 69, 272—303. Compare Abstr., 1900, ii, 382; 1905, ii, 298).—The electrical conductivity of solutions of twenty-three compounds, including a number of salts and organic substances, in liquid ammonia has been measured. The apparatus used was a modified form of that already described, and the method of manipulation is discussed in detail. The results are given in tabular form, and are also represented graphically, the molecular conductivities being plotted as ordinates against the logarithms of the dilutions as abscissæ.

Franklin and Gibbs (Abstr., 1907, ii, 840) have recently shown that the molecular conductivity of certain compounds dissolved in methylamine increases at first with dilution of concentrated solutions, reaches a maximum, falls to a minimum, and then tends towards a second maximum in very dilute solutions. The present experiments were undertaken in order to find whether solutions in ammonia showed similar behaviour, and therefore measurements were made with as concentrated solutions as possible. The behaviour in question—two maxima and an intermediate minimum—was observed very distinctly for solutions of copper nitrate, zinc nitrate, potassium mercuric cyanide, and, much less distinctly, for potassamide. Many of the other solutions give curves, which, although they show no maxima or minima, rise rapidly with dilution from concentrated solutions, then more slowly through a moderate range of dilution, followed by a more rapid rise towards a maximum. The second rise towards a maximum is supposed to correspond with that observed for aqueous solution.

It was observed in the course of the experiments that silver iodide is extremely soluble in liquid ammonia; a solution was prepared, of which 16.76 c.c. contained about 28 grams of silver iodide. G. S.

Conductivity and Viscosity of Dilute Solutions of Lithium Nitrate and Cadmium Iodide in Binary and Ternary Mixtures of Acetone with Methyl Alcohol, Ethyl Alcohol, and Water. HARRY C. JONES and EDWARD G. MAHIN (*Zeitsch. physikal. Chem.*, 1909, 69, 389—418. Compare this vol., ii, 539).—The paper deals mainly with the electrical conductivity of solutions of lithium nitrate and of cadmium iodide in binary mixtures of acetone with methyl alcohol, ethyl alcohol, and water. Measurements have been made at 0° and 25° in dilutions up to 200,000 litres; the results are given in tabular form, and are also represented graphically.

As regards solutions containing lithium nitrate, the curves obtained by plotting the electrical conductivities as ordinates against the composition of the binary mixtures containing acetone as abscissæ vary considerably in form, and in some cases show minima. In the highest dilutions, ionisation appears to be practically complete in pure water and in pure acetone, and nearly so in the binary mixtures. The value of μ_{∞} for lithium nitrate in water at 25° is about 108, in acetone about 172. The product of viscosity and molecular conductivity, $\eta\mu$, (the highest value obtained for the latter being used), is about 0.70 for mixtures of acetone with methyl and ethyl alcohols, and is independent of temperature. The value of $\eta\mu$, for mixtures of

acetone and water varies from 0.60 in pure acetone to about 1.0 in pure water. The temperature-coefficients of conductivity are throughout of about the same value as the temperature-coefficients of viscosity. Ostwald's dilution law holds approximately for solutions of lithium nitrate in pure acetone beyond a dilution of $v=200$, but not for more concentrated solutions. It is shown by freezing-point determinations that lithium nitrate is associated in solutions of moderate concentration, an observation which explains the low conductivity values obtained for solutions of this salt in binary mixtures containing acetone.*

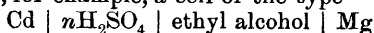
Corresponding measurements have been made for solutions of cadmium iodide, and the results are very similar to those obtained with lithium nitrate. Ostwald's dilution law applies to solutions of this salt in acetone from $v=5000$ to $v=50,000$, but not at higher or lower concentrations. The temperature-coefficient of the conductivity of solutions of cadmium iodide in acetone is negative when v exceeds 10,000. The value of $\eta\mu_v$ is not constant in binary mixtures containing the salt, probably owing to incomplete ionisation. G. S.

Supertensions in Organic Solvents. GIACOMO CARRARA (*Zeitsch. physikal. Chem.*, 1909, 69, 75—80).—The measurements were made by the usual method, the current passing through the solution being plotted against the difference of potential, which was progressively increased. The break in the curve, indicating the point at which gas begins to be given off, was either read off directly, or determined graphically, by extending the two parts of the curve in the usual way. The metals, in the form of wire, were used as cathode, the anode being of platinum, and as electrolytes, normal solutions of sulphuric acid (in one or two cases potassium hydroxide) in methyl and ethyl alcohol respectively were employed.

The degree of supertension for hydrogen varied with the nature of the metal, but the values in each case were approximately the same in the two alcohols. For iron, cobalt, nickel, gold, silver, copper, and lead, the supertension varied only between 0.20 to 0.26 volt in methyl alcohol, and between 0.23 and 0.28 volt in ethyl alcohol. For most metals, the supertension is smaller in the alcohols than in water, but in a few cases is about the same.

It is suggested that the proved dependence of the supertension on the nature of the solvent may account for the fact that the rate of dissolution of metals by acids depends greatly on the nature of the solvent (Kahlenberg). G. S.

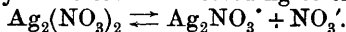
Galvanic Ennobling of Metals. CHARLES M. VAN DEVENTER and H. J. VAN LUMMEL (*Zeitsch. physikal. Chem.*, 1909, 69, 136—147. Compare Abstr., 1908, ii, 12, 558).—The greater part of the work described in this paper has already been published (compare Abstr., 1908, ii, 12, 558). Further experiments are described on the ennobling of one metal with reference to a second which in ordinary circumstances stands below the first in the potential series. In most cases, ethyl alcohol, containing a trace of acid, was used as insulator. When, for example, a cell of the type



is constructed, the current flows in the opposite direction to that observed under ordinary conditions when acid alone is used as electrolyte. G. S.

Electrochemical Potentials in Non-Aqueous Solvents. J. NEUSTADT and RICHARD ABEGG (*Zeitsch. physikal. Chem.*, 1909, 69, 486—498).—The *E.M.F.*'s of a number of cells in which methyl alcohol, ethyl alcohol, acetone and pyridine have been used as solvents for the electrolytes have been measured. In most cases one half-element consisted of silver/silver nitrate, the latter being dissolved in the organic solvent, but a few measurements of concentration cells were also made, for example, $\text{Cu} \mid \text{Cu}(\text{NO}_3)_2, 0.01N \mid \text{Cu}(\text{NO}_3)_2, 0.0025N \mid \text{Cu}$, in methyl alcohol. When possible, measurements were made with silver, lead, copper, mercury, cadmium, zinc, and their respective salts in all four solvents. For the absolute values, the original paper must be consulted.

In general, the potential differences in methyl alcohol, ethyl alcohol, and acetone are approximately the same as in water, a result which shows that the ratio of the solution tensions of the metals in these four solvents is approximately equal. The results in pyridine solution differ considerably from those for the other solvents; this is probably due to the small ionic concentrations of the metallic ions in this solvent. It has been found that NO_3^- migrates with silver towards the cathode in pyridine solutions, and it is suggested that the salt may be ionised in pyridine solution according to the equation :



The above results appear to indicate that in the other four solvents the ions are not associated with the solvent to a great extent.

A number of measurements have been made with compound cells containing a number of liquid junctions, in order to elucidate the question of contact differences of potential. In this case, also, pyridine solutions behave abnormally, as the contact differences between them and other solutions are very considerable. G. S.

The Oxidation Potential of Manganese Dioxide. WOLFRAM HAEHNEL (*Zeitsch. Elektrochem.*, 1909, 15, 834—842).—An attempt was made to measure the concentration of the iodine formed in the reaction : $\text{MnO}_2 + 4\text{H}^+ + 2\text{I}^- \rightleftharpoons \text{Mn}^{++} + 2\text{H}_2\text{O} + \text{I}_2$. The concentration of the iodon was kept at a constant small value by adding excess of silver iodide, and the hydrogen ions were added in the form of hydrochloric acid. The results were erratic, which is also true of the corresponding reaction with bromine in place of iodine. Two causes of disturbance were discovered : the solubility of iodine in a 1.1 molecular solution of manganous chloride is 6.23×10^{-3} , whilst its solubility in water is only 3.7×10^{-3} gram-mol. per litre, which indicates some combination ; secondly, iodide is oxidised to iodate by manganese dioxide under the conditions of the experiments, where the concentration of the iodine ions is small enough to permit of the existence of measurable quantities of iodate ion. It is also shown that equilibrium is reached extremely slowly, and that the rate varies in different experiments from unknown causes. From the incomplete

results, the author calculates the normal potential of manganese dioxide to be greater than 1.2 volts (compared with the hydrogen electrode). The potential which just deposits manganese dioxide from a solution of manganous sulphate is found to depend on the acidity of the solution. Calling e the observed potential, the normal potential, N , should be given by $N = e - 0.0295 \log. [H^+]^4/[Mn^{++}]$; this formula agrees well with the observations, and gives $N = 1.35$ volts.

When chlorine is passed into a neutral or faintly acid solution of manganese chloride, the dioxide is precipitated. It is found that in a 0.22*N* solution of manganous chloride, precipitation occurs when the concentration of the hydrogen ions is 0.0101, and does not occur when it is 0.013 gram-mol. per litre. This result leads to a value of about 1.57 volts for the normal potential of manganese dioxide, but in calculating this the formation of manganic chloride in the solution is neglected, the effect of which is to make the calculated value too large. T. E.

Solubility of Manganous Hydroxide and the Dissociation Pressure of Manganese Dioxide. OTTO SACKUR and E. FRITZMANN (*Zeitsch. Elektrochem.*, 1909, 15, 842—846).—The solubility of manganous hydroxide is measured by adding successive quantities of baryta solution to a solution of manganous sulphate and measuring the electrical conductivity of the solution after each addition. The whole operation is carried out in an atmosphere of hydrogen. The minimum conductivity is reached when the manganous sulphate is exactly precipitated, and the solution at this point is saturated with barium sulphate and manganous hydroxide. By subtracting the known conductivity of a saturated barium sulphate solution, that of a saturated solution of manganous hydroxide is obtained, and from this its solubility is found to be 2.15×10^{-5} gram-mol. per litre at 18°. From this determination (assuming that manganous oxide has the same solubility as the hydroxide), the *E.M.F.* of the galvanic cell oxygen at 1 atmosphere | saturated solution of MnO | MnO_2 | Pt, in which the reaction is $O_2 + 2MnO = 2MnO_2$, is calculated by means of this determination and Haehnel's determination of the normal potential of manganese dioxide (preceding abstract) to be 0.32 volt, from which the dissociation pressure of manganese dioxide at 18° is 6.3×10^{-23} atmosphere. Putting this value into Nernst's approximate formula: $\log p = -Q/2.3RT + 1.75 \log T + 3$, the heat of the above reaction is calculated to be 39,200 cals., which agrees moderately with Thomsen's value (for the hydrated oxides) of 43,000 cals. T. E.

Kinetics of Rapid Chemical and Ionic Reactions Investigated by the Oscillograph. D. REICHSTEIN (*Zeitsch. Elektrochem.*, 1909, 15, 734—740).—If silver, immersed in a solution containing cyanion, is polarised anodically, two reactions can occur: first, silver ions will be formed, and then they will react with cyanion, thus: $Ag^+ + 2CN^- = Ag(CN)_2^-$. The concentration of the silver ions at the surface of the electrode, therefore, will increase until the velocity of the second reaction is equal to that of the first. If a cell is built up of the polarised electrode and a silver plate immersed in a solution of silver

nitrate, its *E.M.F.* will be a known function of the concentration of the silver ions at the surface of the polarised electrode. Further, the rate at which the polarisation disappears when the current ceases to flow depends on the rate of reaction between silver ion and cyanion, supposing that the reaction is so fast that diffusion does not influence the change appreciably. The author has developed the mathematical expressions of these ideas, and has also photographed the curves of increase and decay of polarisation of copper and silver electrodes in cyanide solutions. The oscillograph used unfortunately required a rather large current, which made it impossible to compare the results quantitatively with the theoretical equations. The curves were, however, of the form expected. In similar circumstances, the polarisation of a copper electrode (in 4*N*-potassium cyanide) disappeared in 0.014 second, whilst with silver 0.005 second sufficed. T. E.

Absorption of Gases by the Anode in Glow Discharge. V. L. CHRISLER (*Physikal. Zeitsch.*, 1909, 10, 745—752).—The author has investigated the absorption of hydrogen, nitrogen, and helium by various metallic anodes during glow discharge. Hydrogen is absorbed by anodes of silver, sodium, potassium, sodium-potassium alloy, and mercury, and the relationship between the rate of absorption and the discharge current indicates that each atom of hydrogen is accompanied by an electron. Nitrogen behaves quantitatively the same towards anodes of sodium, potassium, and sodium-potassium alloy.

In the majority of the experiments with helium, no absorption was observed, but, in two experiments with a sodium anode and in two others with a mercury anode, helium was absorbed at a rate which indicated that each helium atom carried the same negative charge as the hydrogen and nitrogen atoms. H. M. D.

Electromotive Behaviour of Thallium as Anode. I. WOLF J. MÜLLER (*Zeitsch. physikal. Chem.*, 1909, 69, 460—481).—The phenomena occurring during the anodic polarisation of thallium electrodes in solutions of sodium hydroxide, sulphuric acid, and sodium sulphate have been examined. A cell was constructed with a platinum cathode, the external *E.M.F.* on the electrodes was progressively increased, and the strength of the current and the difference of potential between the anode and the solution observed for each value of the applied *E.M.F.* The results are given in tabular form, and are also represented graphically. The values of the *E.M.F.* are referred to the *N*/10-calomel electrode throughout.

In *N*/10-sodium hydroxide, the current increases regularly with the polarisation, and thallium dissolves in the univalent form up to an applied *E.M.F.* of 10 volts. The behaviour of the anode in *N*-sodium hydroxide is much more complicated. There are three points on the polarisation-strength of current curve at which the polarisation remains practically constant with increased current, the first, at -0.7 volt, represents the dissolution of thallium in the univalent form; the second, at ± 0 volt, probably represents the dissolution in the bivalent form; the third, at $+1.1$ volt, has not been fully

investigated. When the polarised oxidised electrode is allowed to discharge, halts are observed at -0.3 and -0.6 volt.

When the applied *E.M.F.* in *N*/10-sulphuric acid is gradually raised, a point is reached at which the current remains practically constant on further increasing the *E.M.F.*, and pulsations occur. The current in these circumstances is proportional to the surface of the electrode, and stirring increases it considerably. The explanation advanced is that thalious sulphate forms on the anode, and give rise to a considerable resistance, but as it diffuses away, it allows the current to pass. Stirring naturally accelerates the diffusion of the salt, and thus increases the current. In both *N*- and *N*/10-sulphuric acid with larger applied *E.M.F.*, abnormal polarisation occurs. In the former solution, yellow crystals are formed on the anode, which probably represent a mixture of thalious and thallic sulphate. Complicated phenomena also occur when sodium sulphate is used as electrolyte.

The phenomena at the higher values of polarisation are discussed from the point of view of passivity, and, on the basis of the electron theory of passivity, the law is deduced that the influence of an anion in rendering an anode passive is inversely proportional to the solubility of the resulting compound in the surface layer.

G. S.

Electromotive Behaviour of Oxygen. FRITZ FOERSTER (*Zeitsch. physikal. Chem.*, 1909, 69, 236—271).—When a platinised platinum electrode is anodically polarised with oxygen up to a high potential, and is then removed from the polarising solution and placed in fresh sulphuric acid through which a stream of oxygen is passed, the potential falls steadily, in the course of some days, to 1.08 volts (measured against a hydrogen electrode in the same electrolyte) and shows no noticeable halts at intermediate points. When a platinum electrode covered with finely-divided iridium is subjected to the same treatment, the potential falls steadily, and more rapidly than when platinised platinum is used, to 0.86 volt; there is no halt at 1.06 volts, the potential of the hydrogen-oxygen cell with iridium electrodes. In explanation of this behaviour, it is suggested that labile peroxides are formed on charging the electrodes, these peroxides forming solid solutions with the finely-divided metals. The peroxides gradually decompose, giving up oxygen and forming more stable lower oxides, and it is this slow decomposition which determines the steady fall of potential. The platinum peroxide is more stable than the iridium peroxide, corresponding with the more gradual fall of potential in the former case.

The formation and decomposition of these oxides also explains the behaviour of anodes towards hydrogen peroxide and ozone. When hydrogen peroxide is added to a solution containing an electrode polarised with oxygen, the potential falls rapidly, owing to the interaction of the platinum peroxide with hydrogen peroxide with production of free oxygen and a consequent diminution in the platinum peroxide concentration. If, on the other hand, the electrode is only slightly polarised, hydrogen peroxide increases the platinum peroxide concentration and raises the potential. A similar explanation holds for the action of ozone. The observed potentials are therefore not

true equilibria, but depend on the rate at which the platinum peroxide is formed and decomposed.

It is well known that oxygen is given off at a platinised platinum anode at a lower potential than at a smooth platinum surface. It is now shown, however, that with small currents at high temperature the oxygen is given off at a smooth platinum electrode at the low potential observed for the platinised platinum electrode, but the potential soon rises to the higher value. A similar behaviour is observed with smooth iridium electrodes, except that in this case the oxygen continues to come off at the low potential. This phenomenon is also accounted for on the theory of a peroxide formation; it is suggested that the anodes which have reached the high potential are saturated with the peroxide, and superficially covered with it. The fact that the low potential is more persistent in the case of iridium is due to the greater instability of the iridium peroxide. G. S.

Liberation of Oxygen during the Electrolysis of Hydrochloric Acid with a Platinum Anode. GEORG PFLEIDERER (*Zeitsch. physikal. Chem.*, 1909, 68, 49—82).—When a dilute solution of hydrochloric acid is electrolysed with a fresh platinum anode, and the current is kept constant, the potential rises gradually from about 1.4 to about 1.9 volts, and it is only at the last-mentioned potential that oxygen is given off freely. This phenomenon is doubtless connected with the gradual formation of a layer of platinum oxide on the anode (compare Foerster, preceding abstract). The oxidation of the platinum may be due to the influence of hypochlorous acid, formed by the action of chlorine on water.

Both oxygen and chlorine are formed when a dilute solution of hydrochloric acid is electrolysed, and the relative amounts of these gases liberated under varying conditions have been measured. With constant condition of the electrode and electrolyte, the relationship between the proportion of current, i_2 , employed in liberating oxygen and that used up for other purposes is represented by the equation: $\log i_2 = a \log i_1 + b$, where a and b are constants depending on the condition of the electrode and the nature of the electrolyte. Further, the dependence of the oxygen given off on the concentration of hydrochloric acid is represented, between 0.10 and 1.5*N* by the equation: $b = b_0 + 2 \log c$, where c represents the concentration. A theoretical explanation of these results is given, depending on the occurrence of supertension at the electrode.

The formation of oxygen in the electrolysis of hydrochloric acid might be looked upon as a secondary phenomenon due to the action of chlorine on water, represented by the equation: $2\text{Cl}_2 + 2\text{H}_2\text{O} = 4\text{HCl} + \text{O}_2$ (the "Deacon process"), this reaction being accelerated at the anode as the result of a chemical or electrochemical catalysis. The fact that a change in the rate of stirring has little influence on the proportion of oxygen formed, appears to show that the catalysis is not purely chemical. In any case, the proportion of oxygen given off is smaller than corresponds with the equilibrium of the Deacon process, but there is evidence that immediately after the discharge the concentration of oxygen is not less, and may be greater, than that corresponding

with the equilibrium. The alteration in the relative proportions in the gas given off is due to the very different velocity with which the two discharge products change to the ordinary gaseous condition.

G. S.

Phenomena of the Electrolytic Decomposition of Hydrochloric Acid. FRANK A. GOOCH and F. L. GATES (*Amer. J. Sci.*, 1909, [iv], 28, 435—446; *Zeitsch. anorg. Chem.*, 1909, 64, 273—286).

—Doumer (Abstr., 1908, ii, 252, 349, 458) has claimed that the ratio of the volumes of oxygen and hydrogen evolved in the electrolysis of hydrochloric acid is constant and independent of the strength of the current and concentration of the solution, and uses his results to show that the velocities of the hydrions and chloridions are equal. In order to test Doumer's results, the authors have further studied the electrolysis of hydrochloric acid under various conditions. The apparatus used was on the principle of a Hofmann voltameter; it was provided with a leveller, so that gas measurements could be made directly under atmospheric pressure. In every case the cathode was of platinum, but the material of the anode varied.

In the first set of experiments the anodes were of silver, and their area varied from 1 to 21.4 sq. cm.; the hydrochloric acid was either *N*/50 or *N*/100, and the current strength varied from 0.05 to 0.085 ampere. Oxygen was liberated only when the silver surface open to attack was small, and in no case attained the proportion (0.332 of the hydrogen) noted by Doumer. As long as the anode exposes a large silver surface, both oxygen and chlorine attack it. Silver chloride once attached may remain fixed on the anode, but silver oxide is subject to the action of the hydrochloric acid as well as to that of the liberated chlorine; colloidal silver chloride may be formed during these latter reactions (compare Noyes and Sammet, Abstr., 1903, ii, 126).

In the next set of experiments, the anode was made by dipping a piece of silver wire of 2.27 mm. diameter and 4 cm. long in fused silver chloride, and then using it as anode in a preliminary electrolysis of fairly concentrated hydrochloric acid until chlorine was freely evolved. In the actual experiments, the currents used were 0.05, 0.10, and 0.15 ampere, and the concentrations of hydrochloric acid were 0.43, 0.86, and 4.3 parts per 1000. The ratio of oxygen to hydrogen was found to increase markedly as the concentration of the solution decreased, although it was not materially affected by variations in the current strength or in the potential across the electrodes. Doumer's ratio was only attained with the lowest concentration of acid. When the protected silver anode was replaced by a spiral of platinum wire (area, 1.25 sq. cm.), the ratios of the volumes of oxygen to hydrogen were very little less for the two lower concentrations of acid, but much lower for the higher concentration.

In another series of experiments, the concentration of the acid was 0.043 part per 1000, and the anode (platinum) area 1.25 sq. cm.; the current varied from 0.07 to 1.0 ampere. The ratio of oxygen to hydrogen was fairly constant (= 0.44) throughout the entire period of electrolysis, and higher by about 30% than Doumer's ratio. Other

experiments with platinum anodes of varying area and with acids of different concentrations confirmed the result that the proportion of oxygen liberated increases as the concentration of the solution decreases. The highest ratio (0.477) of oxygen to hydrogen was found at a concentration of 0.0086 part per 1000 and at a high current density (3.12 amperes per sq. dm.), and is within 5% of what it would be were water the primary and sole electrolyte.

The observed phenomena afford no criterion for deciding how much of the oxygen liberated in the electrolysis of hydrochloric acid is transferred through the liquid and how much is evolved by the action of transferred chlorine at the anode. T. S. P.

Theoretical Considerations on the Electrolytic Dissociation of Dissolved Electrolytes. JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1909, 69, 433—435).—Reference is made to the author's views on solution (*Archives Teylser*, 1908, ii, 235). G. S.

Molecular-theoretical Considerations regarding Electrolytic Dissociation. GIACOMO L. CIAMICIAN (*Zeitsch. physikal. Chem.*, 1909, 69, 96—101).—The author shows that the view first suggested by him (*Abstr.*, 1891, 390), that association between solvent and solute precedes electrolytic dissociation, is now meeting with wide acceptance. G. S.

Hydrolytic and Electrolytic Dissociation of Aluminium Bromide in Aqueous Solution. IWAN KABLUKOFF and AL. SACHANOFF (*Zeitsch. physikal. Chem.*, 1909, 69, 419—432).—Solutions of aluminium bromide have a relatively high electrical conductivity; the values at 25° are somewhat greater than those for sodium bromide under equivalent conditions. As later measurements showed that the salt is not greatly hydrolysed in moderate dilution, the high conductivity must depend on electrolytic dissociation. This is confirmed by determinations of the Br'-ion concentration by measurements of the *E.M.F.* of concentration cells; when the dilution is about 20 litres per gram-equivalent, two-thirds of the bromine is electrolytically dissociated. The main ionic equilibrium in solution is probably represented by the equation: $\text{AlBr}_3 \rightleftharpoons \text{AlBr}^{++} + 2\text{Br}'$.

The degree of hydrolysis of solutions of aluminium bromide has been determined by measuring the H'-ion concentration from the results of *E.M.F.* measurements. Between $v=0.5$ and $v=5$ litres the degree of hydrolysis is almost independent of dilution; above $v=5$ it increases regularly with dilution. When $v=1000$ litres, the degree of hydrolysis is only about 4%. The main hydrolytic equilibrium is probably represented by the equation: $\text{AlBr}^{++} + \text{HOH} \rightleftharpoons \text{AlOH}^{++} + \text{H}' + \text{Br}'$. Neutral salts diminish the degree of hydrolysis slightly, and potassium bromide and nitrate exert about the same effect under equivalent conditions. G. S.

Anomaly of Strong Electrolytes and the Limits within which the Dilution Law is Valid. RUDOLF WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1909, 69, 603—629).—The fact that the

dilution law does not hold for strong electrolytes is connected with the high concentrations of ions in concentrated solutions of such electrolytes. The author has calculated in detail for the different groups of electrolytes, namely, organic acids and bases, inorganic acids and salts, the limits within which the dilution law is applicable, and draws the conclusion that, in the absence of complex formation, etc., the law in question is approximately valid for all binary electrolytes with univalent ions up to an ionic concentration of about 0.03 mol. per litre; in stronger solutions deviations from the simple law occur. In arriving at this conclusion, however, some rather uncertain assumptions are made, more particularly with reference to the values of μ_{∞} for inorganic salts. G. S.

Theory of the Direct Method of Determining Transport Numbers. W. LASH MILLER (*Zeitsch. physikal. Chem.*, 1909, 69, 436—441).—It is shown theoretically, by a method involving no assumptions as to rates, mobilities, currents, or constitution of the ions, that transport numbers calculated from observations of the motion of the meniscus must be identical with those obtained by the ordinary analytical method of Hittorf. G. S.

Thermal Conductivity of Air and other Gases. GEORGE W. TODD (*Proc. Roy. Soc.*, 1909, A, 83, 19—39).—An improved method of measuring the thermal conductivity of gases is described. The gas is enclosed between two parallel metal plates, the upper one of which forms the base of a steam chamber, and the lower one the top of a chamber through which cold water is circulated. To ensure thorough circulation, the interior of the cold chamber is divided up by means of a series of partitions parallel to the plate forming the roof of the chamber. The space between the hot and cold plates is cut off from the exterior by means of a ring of insulating material, and for comparative observations with gases other than air, the chamber is sealed by painting round the edges of the plates and ring with shellac varnish.

The rate at which heat passes through the lower plate is measured by observation of the rise in temperature of water, which is made to flow at a uniform and measured rate through the cold calorimeter chamber. In the case of air, observations were made with the hot and cold plates separated by distances varying from about 0.1 to 0.7 cm., and from the series thus obtained the radiation effect can be eliminated.

The values obtained for the thermal conductivity at the mean temperature of 55° are: air 0.0000571, carbon dioxide 0.0000411, oxygen 0.0000593, nitrogen 0.0000569, nitric oxide 0.0000539, nitrogen peroxide 0.0000888. H. M. D.

Specific Heats of Silicates and of Platinum. WALTER P. WHITE (*Amer. J. Sci.*, 1909, [iv], 28, 334—346).—For determining the specific heats of silicates up to 1500° the method of mixtures was used, in which the heated substance and containing crucible are dropped from a furnace into a calorimeter at room temperature. A special

form of electric furnace was used in order to diminish the lack of uniformity in the furnace temperature, this ordinarily being one of the chief sources of error, and an electrical method of releasing the crucible was devised to reduce the time required in transferring it from the furnace to the calorimeter. All temperatures, including that of the calorimeter, were read by thermo-elements. The calorimeter was completely enclosed by a water-jacket, except just at the moment when the crucible was dropped in, and an unusually large temperature rise (sometimes 23°) was employed to increase the accuracy.

A table of mean specific heats, from zero, of eight substances, including quartz, is given, and also the following table of true specific heats.

Temp.	Platinum.	Wolla- stonite.	Pseudo- wollastonite.	Ortho- clase.	Diopside.	Orthoclase glass.	Soft tubing glass.
500°	0.0356	0.251	0.250	0.257	0.262	0.264	0.298
700	0.0368	0.263	—	—	0.272	—	0.324
800	—	—	—	0.272	—	0.282	—
900	0.0380	0.262	—	—	0.281	—	0.340
1100	0.0390	0.261	0.259	0.279	0.286	0.297	0.335
1300	0.0400	—	0.257	—	0.278	—	0.333
1500	0.0407	—	—	—	—	—	0.332

The mean specific heats are accurate to less than 0.5% at most temperatures; the true specific heats are not so accurate. The specific heats of silicates show a considerable increase with temperature up to 700° , followed by a tendency to diminish at higher temperatures.

The mean specific heats of platinum and of diopside are expressed by the following formulæ: Platinum, $0.03198 + 3.4 \times 10^{-6}t$; diopside, $0.1779 + 1.516 \times 10^{-4}t - 1.047 \times 10^{-7}t^2 + 2.81 \times 10^{-11}t^3$, where t is the temperature.
T. S. P.

Specific Heats of Mixtures of Saturated Alcohols and Water. II. ANTONY G. DOROSCHESKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 958—977).—Measurements of the specific heats of aqueous solutions of methyl, propyl, *isopropyl*, and *isobutyl* alcohols, of various concentrations and at different temperatures, show that these mixtures exhibit the peculiarity observed with mixtures of ethyl alcohol and water (Abstr., 1908, ii, 807; compare also Bose, Abstr., 1907, ii, 332, 333), the specific heats of all the solutions being greater than the values calculated from their compositions, and those of dilute solutions greater than the specific heat of water. The specific heats of these mixtures for the temperature-interval 18 — 100° exhibit maxima for 10% solutions in the case of methyl and propyl alcohols, and for 20% solutions with ethyl and *isopropyl* alcohols. A maximum specific heat is evidently exhibited by all solutions for which a great difference exists between the composition of the vapour and that of the boiling (at 760 mm.) liquid.

Aqueous solutions of *isobutyl* alcohol containing from 100% to 83.63% or from 0% to 4.66% of the alcohol, that is, those solutions which remain homogeneous when heated from 18° to 100° , have specific heats greater than the calculated values, but less than that of

water; a maximum specific heat was not observed with these solutions. Solutions containing 7—8% of the alcohol, which separate into layers and subsequently mix again when heated from 18° to 100°, show a marked rise in specific heat. Such rise is observed also with a solution containing 6.76% of isobutyl alcohol, although no separation into layers and re-dissolution occur; here, too, the cause of this phenomenon lies doubtless in a certain, although not an evident, separation of the two liquids. An analogy probably exists between the separation into layers and the specific heat of isobutyl alcohol solutions, on the one hand, and the vaporisation and specific heat of the lower alcohols, on the other. T. H. P.

Specific Heats of Solutions of Salts in Water and Alcohol. ANTONY G. DOROSCHEWSKY and ADAM W. RAKOWSKI (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1110—1116).—For the calculation of the specific heats of solutions, the following two formulæ, both representing straight lines, have been employed: (1) $S_1 = S_0 - (S_0 - \sigma)m/100$, and (2) the more simple form, $S_1 = S_0 - S_0m/100$, where S_1 , S_0 , and σ are the specific heats of solution, solvent, and solute respectively, and m is the weight of solute per 100 grams of solution. The authors have investigated the following cases:

(1) Aqueous solutions of cadmium iodide.—Here the specific heat follows the above formulæ neither quantitatively nor qualitatively, the curve connecting percentage of salt present and specific heat being not a straight line, but a complex curve exhibiting a bend. For solutions containing up to about 20% of cadmium iodide, the curve lies below, and for more concentrated solutions above, the straight line represented by formula (2). So that here, as in many other cases, the specific heat of the solutions is less than that of the water they contain; the solutions behave, indeed, like the solvent does under great pressure.

(2) Solutions of cadmium iodide in absolute ethyl alcohol.—For these solutions, the specific heats lie on a straight line, but are, in all cases, greater than the calculated values.

(3) Five per cent. solutions of mercuric chloride in aqueous alcoholic mixtures, varying in concentration from 0 to 100%.—When the solvent contains less than about 15% of alcohol, the curve connecting specific heats of the solutions with the percentages of salt present approximates to the typical curve for aqueous solutions, whilst for solvents containing more than 15% of alcohol, the curve is similar to those for alcoholic solutions. T. H. P.

Forms of the Partial and Total Vapour Pressure Curves of Binary Mixtures. JAN VAN ZAWIDZKI (*Zeitsch. physikal. Chem.*, 1909, **69**, 630—662).—A theoretical paper. The possible forms of the partial and total vapour pressure curves of binary mixtures are deduced from the integrals of the well-known Duhem-Margules equation. The partial pressures are expressed as fractions of the pressures of the pure components, the so-called "reduced" partial pressures, and it is then shown that the reduced partial pressure curves can be divided into symmetrical and unsymmetrical, and each

of these again into a number of forms. The total pressure curves are dealt with in a similar way.

These conclusions are illustrated by choosing different relative values of the factors in the integrals, and determining the influence on the forms of the curves; the results are also illustrated graphically. It is probable that alterations of temperature have only a slight influence on the forms of the reduced partial pressure curves. G. S.

Vacuum Distillation and the Effect of Gravity on the Boiling Point. FRIEDRICH KRAFFT (*J. pr. Chem.*, 1909, [ii], 80, 242—261).—Polemical against von Rechenberg (this vol., ii, 544). The author points out that von Rechenberg has overlooked much of his work on distillation in the cathode light vacuum, and shows that the criticisms of the latter chemist are not justified. The influence of the weight of the column of vapour on the boiling point in a vacuum has already been discussed, and it has been shown that in these circumstances the boiling point is a function of the molecular weight (*Abstr.*, 1908, i, 1). G. S.

Effect of Gravity on the Boiling Point. Determination of the Boiling Point under the Ordinary Pressure. FRIEDRICH KRAFFT (*J. pr. Chem.*, 1909, [ii], 80, 469—472. Compare preceding abstract).—Gravity is shown to exert a measurable influence on the boiling point of a liquid. The b. p. of *p*-xylene under a pressure of 757 mm. is found to be about 0.038° higher at Gothenberg (58° *N. Lat.*) and about 0.015° higher at Bremen (53° *N. Lat.*) than at Heidelberg (49.5° *N. Lat.*), whilst ethylene bromide under constant pressure boils about 0.016° higher at Bremen than at Heidelberg. W. H. G.

A Source of Error but little Considered in the Determination of Boiling Points under Diminished Pressure. CHRISTIAN JOHANNES HANSEN (*J. pr. Chem.*, 1909, [ii], 80, 449—455).—Polemical against von Rechenberg (compare this vol., ii, 544). W. H. G.

Certain Relations between Boiling Points. JOHN C. EARL (*Chem. News*, 1909, 100, 245).—The replacement of one atom of chlorine by one atom of bromine in a large number of organic substances raises the boiling point by about 23 — 24° . The difference in boiling point between XBr_2 and XCl_2 is about 48° ($= 2 \times 24^{\circ}$), and between YBr_3 and YCl_3 about 72° ($= 3 \times 24^{\circ}$). Iodine and bromine show similar relations.

The difference between the boiling points of chlorine and bromine, 92.4° ($= 4 \times 23.1^{\circ}$), suggests that these elements at their boiling points are Cl_4 and Br_4 . R. J. C.

Efficiency of Fractional Distillation by Heat Generated Electrically. THEODORE W. RICHARDS and J. HOWARD MATHEWS (*J. Amer. Chem. Soc.*, 1909, 31, 1200—1202).—In the previous paper (*Abstr.*, 1908, ii, 828) a method was described for use in fractionating organic liquids depending on the use of a coil of platinum wire heated by an electric current.

Further experiments have now been carried out, and have shown that, whilst a somewhat better separation is effected by the electrical heating than by the ordinary method, and much less superheating is produced, the gain in the efficiency of separation is not in all cases as great as was at first supposed. E. G.

Determination of Melting Points. WALTER P. WHITE (*Amer. J. Sci.*, 1909, [iv], 28, 453—473).—The author discusses the principal causes of oblique melting curves, giving a mathematical treatment of the same. Actual melting and freezing-point curves are nearly always oblique. The prime cause of obliquity in melting curves is the obliquity of the melting itself, due to impurity. The true melting point is the high end of the oblique melting interval. The melting hysteresis of some very viscous substances (mostly compounds of boron and silicon) is also an occasional (and then serious) cause of obliquity.

The determination of a melting curve necessarily involves two factors: temperature rise and heat supply. The latter depends on the temperature difference between the furnace and the charge being melted; if this varies, the curve is considerably distorted, but corrections are easily applied. The most common example is where the furnace temperature is allowed to rise or fall continuously, whilst that of the substance remains nearly stationary during the process of melting or freezing.

The freezing point is easier to observe than the melting point, since it occurs at the beginning of the interval where temperature distribution in the charge is relatively uniform; it is, however, inadmissible in substances where undercooling is marked. The melting point, coming at the end (in time) of the interval, is liable, where stirring is not practiced, to obliquities resulting from uneven temperature distribution: (1) Due to the inevitable temperature difference between the inside and outside of the charge; this is troublesome with large charges, but negligible with small. (2) Due to various irregularities in heat flow; these are least with narrow charges and small thermo-elements. (3) Due to the conduction of heat down the thermo-element; this is usually negligible for narrow charges and small thermo-elements, but it may amount to several degrees with enclosed elements.

Electrical conductivity in the fusion produces an error in the reading of bare thermo-elements; this is negligible for small charges. Contaminated elements, besides reading false, read so as to increase obliquity. The obliquity is also increased by differentiation and diathermancy of the charge.

Melting points have been determined above 800° agreeing with each other to 0.05° . In most cases an experimental obliquity remains of 0.5 — 1.5° (at high temperatures), the cause of which is still to be definitely determined.

The following melting points are given: sodium chloride, $801^{\circ} \pm 1^{\circ}$; sodium sulphate, $885^{\circ} \pm 1^{\circ}$. T. S. P.

Melting-Point Methods at High Temperatures. WALTER P. WHITE (*Amer. J. Sci.*, 1909, [iv], 28, 474—489).—The author discusses

the apparatus and procedure necessary to determine melting curves, according as the main object is the accurate location of heat absorptions, their quantitative measurement, or their mere detection when obscure.

Platinum-resistance furnaces of simple construction provide complete control of the temperature for melting-point work up to 1600°. Where uniformity of temperature throughout the working-chamber is important, special modifications are necessary. Small charges (2.5 grams) give very sharp melting points, are economical of material, and permit of convenient manipulation.

A number of advantages result from the use of a second thermo-element, which records the furnace temperature about the charge. The measurement and regulation of the heat supply from the furnace is a factor of great importance in accurate melting-point determinations.

Methods of treating and insulating thermo-elements and of avoiding the effects of contamination are described.

The melting points of very viscous substances, showing hysteresis, can be determined easily and effectively by very slow heating and occasional examination outside the furnace.

The approximate determination of latent heats of fusion directly from melting curves is possible by measurement of the furnace temperature, but there are several hitherto undetermined sources of error. The attainment of an accuracy greater than 10% (about 10 calories in many silicates) accordingly requires special apparatus and procedure. The smaller latent heats of inversion can usually be determined to one or two calories with no other apparatus than the two thermo-elements.

For determining faint or sluggish thermal effects, rapid rates of heating and the utmost precision in furnace regulation and temperature measurement is needed.

The accurate location of eutectics by thermal means requires the detection of small residues of the component in excess. This can be accomplished by a special method involving the use of a neutral substance.

T. S. P.

Retrogressive Melting-point Lines. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 227—230).—From an examination of van der Waals' equation for melting-point curves, the author draws the conclusion that if a hydrate loses much water at its transition point, a retrograde solubility curve may be expected, for it is probable that the change in the heat of melting is less than that in the heat of mixing.

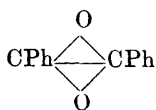
To explain the retrograde solubility curve of rhombic sodium sulphate, it seems necessary to assume a retrogression of the hydration in solution with rising temperature. The strongly retrogressive character of the solubility curve of monoclinic sodium sulphate as compared with that of the curve for the rhombic salt indicates that the latent heat of liquefaction of the former is much smaller than that of the latter.

H. M. D.

Melting-point Curves of Endothermic Compounds. A. H. W. ATEN (*Zeitsch. physikal. Chem.*, 1909, 68, 39—42).—As bismuth trichloride and pentachloride unite to form the endothermic

compound SbCl_4 , it seemed possible that antimony trichloride and pentachloride might combine to form the compound SbCl_4 . The melting-point curve of the latter system shows a eutectic point about 2.5° (m. p. of antimony pentachloride, 4°), the eutectic mixture containing about 3% of antimony pentachloride, and from this point rises fairly steeply to the melting point of antimony trichloride, although between 30 and 80 mol. % of the trichloride the curve is rather less steep. This form of curve does not correspond definitely with any of the three possible forms of curve for a binary system in which an endothermic compound is formed, and therefore the melting-point curve affords no evidence of the existence of the compound SbCl_4 . G. S.

cycloHexane as a Cryoscopic Solvent: Cryoscopic and Ebullioscopic Behaviour of Ketones Dissolved in cycloHexane. LUIGI MASCARELLI and I. MUSATTY (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 195—202. Compare this vol., ii, 790).—The authors have examined the cryoscopic and ebullioscopic behaviour of solutions in cyclohexane of a number of ketonic compounds (compare this vol., ii, 19), all of which have molecular weights higher than the theoretical values in the freezing solvent. Benzil is not soluble in the cold, but



in boiling cyclohexane it has the normal molecular weight, being probably transformed, owing to the proximity of the two ketonic groups, into the form represented by the annexed formula (*loc. cit.*). The results indicate that where a ketone is able to form an enolic modification, the latter is produced and undergoes association in cyclohexane solutions. T. H. P.

cycloHexane as a Cryoscopic Solvent. Behaviour of cycloHexanone Dissolved in cycloHexane. LUIGI MASCARELLI and I. MUSATTY (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 253—258).—Fresh results have been obtained which, in conjunction with those already published (preceding abstract), indicate that the anomalous cryoscopic behaviour of cyclohexanone in cyclohexane is due to three causes: (1) association occasioned by the presence of the carbonyl group; (2) association owing to the formation of a hydroxy-compound by tautomeric change; (3) formation of solid solutions between solvent and solute. T. H. P.

Cryoscopy of Neutralisation of Certain Acids. E. CORNEC (*Compt. rend.*, 1909, 149, 676—678).—The curves representing the variation of freezing-point lowering with composition in mixtures in all proportions of equivalent solutions of acids and bases show sharp minima where sharply defined salts are produced, and bends where partly stable compounds are present.

Thus, on successively adding quantities of 0.5*M*-sodium hydroxide to 0.5*M*-hydrogen chloride, the freezing-point lowering falls regularly from 1.885° to 0.890° when equivalent proportions are present, and then rises regularly to 1.705° , the value given by the pure sodium hydroxide solution. The graph consists of two practically straight lines, showing that only one compound, sodium chloride, is produced.

Sodium sulphate gives a well-defined minimum, but there is no evidence of the existence in solution of NaHSO_4 , which appears to be resolved into a mixture of free acid and normal salt.

Arsenic acid gives a minimum for Na_3AsO_4 , and two folds representing the partial formation of NaH_2AsO_4 and Na_2HASO_4 .

Acetic acid behaves like hydrochloric acid; citric and phosphoric acids resemble arsenic acid; also, with oxalic acid a fold represents the acid salt, whereas the normal salt gives a sharp minimum.

Phosphorous acid, H_3PO_3 , behaves like the dibasic oxalic acid, giving a minimum at Na_2HPO_3 . There is no indication of a normal phosphite, Na_3PO_3 . Hypophosphorous acid, H_3PO_2 , behaves as a monobasic acid. These facts are in accordance with what is known of the solid phosphites and hypophosphites.

When ammonia is used instead of sodium hydroxide, the results obtained with all the above-mentioned acids are the same, except that the normal phosphates and arsenates of ammonia are not formed, minima being observed at the compositions: $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{HASO}_4$ instead.

The indications of the electrical conductivity method are often at variance with the author's conclusions. It is pointed out that conductivity is a complicated function of the number of ions and their mobility, whereas the freezing point, which depends only on the number of molecular units, is preferable, and affords evidence in agreement with chemical evidence.

R. J. C.

Condition of Substances in Absolute Sulphuric Acid.

ARTHUR HANTZSCH (*Zeitsch. physikal. Chem.*, 1909, 68, 204—213).—A reply to Oddo and Scandola (this vol., ii, 377), in which the author maintains the accuracy of his freezing-point measurements. In support of this it is shown that when molecular weight values are calculated for solutions containing the hydrogen sulphates of potassium, sodium, ammonium, pyridine, quinoline, and acridine from the successive freezing-point differences, the numbers obtained from the author's data are much more nearly constant than those obtained from the data of Oddo and Scandola. On account of the discrepancies inherent in the determinations of these observers, the data obtained by them cannot be used as an argument against the author's hydronium theory.

H. M. D.

New Thermo-regulator for Use with Gas. PAUL POETSCHKE (*J. Amer. Chem. Soc.*, 1909, 31, 1218—1219).—The apparatus consists of a large cylindrical bulb filled with air, which is placed in the incubator or oven required to be kept at a constant temperature, and is connected to the side-arm of a U-tube containing nearly sufficient mercury to reach the opening of the tube by which the gas is admitted; the latter tube is provided with a small hole in the side. The regulator operates in the same manner as the usual well-known forms. It has the advantage of great sensitiveness, and is easily manipulated and readily cleaned. It can be used in air-baths at temperatures even above the boiling point of mercury, but its sensi-

tiveness to changes of atmospheric pressure preclude its use in cases in which differences of a few hundredths of a degree are of importance.
E. G.

Simple Method for Determining Vapour Densities and for Analysing Binary Mixtures. PHILIP BLACKMAN (*Chem. News*, 1909, 100, 174—175).—A summary of work already published (this vol., ii, 21, 298, 643).
G. S.

Easy Method for Determining Vapour Densities. PHILIP BLACKMAN (*J. Physical Chem.*, 1909, 13, 606—608. Compare this vol., ii, 867).—An improved form of capillary tube and a filler for it are described.
R. J. C.

Critical Volumes and Density Curves of Solutions. MIECZYSLAW CENTNERSZWER (*Zeitsch. physikal. Chem.*, 1909, 69, 81—89. Compare Abstr., 1908, ii, 13).—When a series of sealed tubes containing different amounts of a pure liquid in contact with its vapour are heated, it is observed that the temperature at which the boundary between the two phases disappears (the “limiting temperature”) increases at first as the fraction of the tube filled with liquid is increased, reaches a maximum, and with further increase in the proportion of liquid, gradually falls. Thus, if the average density of the contents of the tube is plotted against the temperature at which the meniscus disappears, a parabolic curve is obtained, the maximum point of which corresponds with the critical temperature.

Corresponding observations have now been made for solutions of phenanthrene in methyl chloride, naphthalene in ethyl ether, and potassium iodide in methyl alcohol. For the first system, the curves obtained by plotting the densities as abscissæ against the limiting temperature as ordinates show no maxima; the maximum for the pure liquid has become a point of inflexion for solutions. It may, however, be expected that a maximum will be obtained for solutions when the two components do not differ greatly in volatility, and this is shown to be the case for solutions of naphthalene in ether. The density curve for this system shows a critical point at 196°, and a maximum at a rather higher temperature (the temperature of maximum condensation). On the other hand, the density-temperature curve for solutions of potassium iodide in methyl alcohol is extremely steep in the neighbourhood of the critical point for the pure liquid, corresponding with the great difference in the volatility of the components.

It was incidentally observed that potassium iodide is less soluble in methyl alcohol in the neighbourhood of the critical temperature than at ordinary temperatures, and as the temperature-coefficient in the neighbourhood of 25° is positive, there must be a maximum on the temperature-solubility curve.
G. S.

Propagation of “Shocks” in Fluids. PIERRE DUHEM (*Zeitsch. physikal. Chem.*, 1909, 69, 169—186).—A mathematical paper. The main conclusions are as follows. When a “shock” is propagated in a perfect gas, the speed of the wave, referred to the fluid behind, always

exceeds in absolute value the speed of sound in the fluid in front; the speed of the shock, referred to the fluid in front, is inferior in absolute value to the speed of sound in the fluid in front as long as the density of the fluid in front is inferior to the product of the density of the fluid behind by $2C_v/(C_p - C_v)$; when the density of the fluid in front surpasses this limit, the speed of the shock referred to the fluid in front exceeds, in absolute value, the speed of sound in the fluid behind.

As the ratio of C_p , the specific heat of a gas at constant pressure, to C_v , the specific heat at constant volume, is about 1.4 for a perfect diatomic gas, the expression $2C_v/(C_p - C_v)$ above referred to is about 5.

G. S.

Internal Friction in the Critical Zone. DEMETRIUS E TSAKALOTOS (*Zeitsch. physikal. Chem.*, 1909, 68, 32—38).—The viscosities of certain binary systems have been measured at temperatures very near the respective critical solution temperatures, but such that the systems were still homogeneous. With the system isobutyric acid and water (completely miscible above 23.5°), measurements were made at 26° and for certain mixtures at 22°. At both temperatures the viscosity curve shows a distinct maximum at 65% of the acid, and the viscosities are greater than that calculated by the mixture rule. The viscosity curve of mixtures of amylene and aniline (completely miscible above 14.4°) was determined at 20°; it is hyperbolic, and the viscosities are less than those calculated by the mixture rule.

The viscosity curve of the system triethylamine and water (completely miscible below 18.7°), measured at 15°, shows a distinct maximum, corresponding with a composition of about 48% by weight of triethylamine. The corresponding measurements with nicotine and water have already been published (compare this vol., i, 412).

The general course of the viscosity curves is therefore independent of the existence of the critical zone. The maxima on the curves appear to indicate combination between the two components of the binary mixture.

G. S.

Viscosity of Binary Mixtures at their Boiling Points. ALEXANDER FINDLAY (*Zeitsch. physikal. Chem.*, 1909, 69, 202—217).—The viscosities of the following six binary mixtures, benzene and carbon tetrachloride, benzene and ethyl alcohol, acetone and chloroform, benzene and methyl alcohol, chloroform and ethyl alcohol, and carbon tetrachloride and ethyl alcohol, containing the components in varying proportions have been determined at temperatures just below those of the boiling points of the respective mixtures instead of at a single temperature, as has hitherto been usual. A slightly modified form of the Ostwald viscosimeter was used; it was adjusted to a temperature exactly 1° below the boiling point of the particular mixture under investigation, these boiling points being known from the work of previous observers. The densities of the mixtures were also determined at the temperatures in question.

The observed values of the viscosity are compared with those

calculated according to the mixture law by means of the formula $1/\eta = v_1/\eta_1 + v_2/\eta_2$, where η_1 and η_2 refer to the viscosities of the components at the temperature of the experiment, and v_1 and v_2 are calculated from the density determinations. The results are given in tabular form, and the observed viscosity curves and those calculated according to the mixture law are represented graphically in order to show the deviations. Except in the cases of benzene and carbon tetrachloride and of chloroform and acetone, the observed values of the viscosity are lower than the calculated. The nature and even the extent of the deviations from the mixture law are approximately the same as when the viscosities are determined at a single temperature in those cases where comparison is possible. The author regards the position of maximum deviation between observed and calculated values of the viscosity as of more importance than the position of the points of maximum or minimum viscosity which are sometimes met with in viscosity curves of binary systems. G. S.

Surface Tension and Adsorption. EDGARD ZUNZ (*Bull. Soc. chim. Belg.*, 1909, 23, 374—378).—Solute which lower the surface tension of their solvent tend to accumulate at the surface, and the greater this surface tension effect the more easily the solute is adsorbed by an adjacent solid or liquid surface. When adsorption occurs, the increase of the surface tension is often a rough index of the amount of solute transferred from the solution, and the absence of adsorption is in many cases indicated when the surface tension remains unchanged.

The author has investigated the adsorption of diphtheric toxin and antitoxin, cobra venom, pepsin, enterokinase, and active and inactive pancreatic fluid by animal charcoal, kaolin, clay, talc, barium sulphate, and kieselguhr. There appears to be no relation between the adsorption of these substances and the comparatively insignificant changes in density, freezing point, and refractive index. The surface-tension phenomena are quite clear, although surface tension is apparently not the only factor in adsorption.

Animal charcoal adsorbs diphtheric toxin and antitoxin, but not the combination, toxin-antitoxin. Barium sulphate, talc, clay, kaolin, and wood-charcoal adsorb neither toxin, antitoxin, nor their combination.

Animal-charcoal, clay, kaolin, barium sulphate, and, to a slight extent, talc and wood-charcoal absorb the tetanic lysin and cobra venom, whereas kieselguhr is without effect. Antilysin and the combination, lysin-antilysin, are not adsorbed by any of the above substances.

The adsorptive power of a substance does not only depend on the area of surface it exposes, as Freundlich supposed, but also on its specific relation to the substance adsorbed. Of the two kinds of adsorption distinguished by Michaelis and Rona, namely, mechanical and electrochemical, the cases studied by the author are probably electrochemical.

It is suggested that when a toxin or a lysin is neutralised by its anti-substance, the latter is adsorbed by the serum proteins, and the toxin or lysin is subsequently adsorbed. When brought together in

the same protein molecule, the toxin and antitoxin slowly combine together and forsake the protein molecule, the neutralisation becoming then an irreversible one.

R. J. C.

Adsorption of Certain Bases by Soluble Starch. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1909, 23, 378—383. Compare Fouard, this vol., i, 699).—The experiments of Fouard on the precipitation of alkalis along with soluble starch by means of alcohol led him to the conclusion that no chemical combination of the alkali had occurred. The author shows, however, that Fouard's values are best explained on the hypothesis that compounds of alkali and starch are formed which are easily dissociated by water in accordance with the mass action law. It must be assumed that each equivalent of $C_6H_{10}O_5$ in the starch molecule exercises an equal attraction for the molecules of alkali: $C_6H_9O_4(OH) + KOH \rightleftharpoons H_2O + C_6H_9O_4(OK)$. Hence, if a , x , and 3.184 are the concentrations of total alkali, combined alkali, and $C_6H_{10}O_5$ expressed in milligram-molecules per litre, the concentration of the water being practically constant,

$$x/(a-x)(3.184-x)$$

should be a constant.

A fair constant is actually obtained when a few of the experimental results, which do not fall on the experimental curves, are omitted. The mean constants are KOH 0.29, NH_4OH 0.014, and piperidine 0.0034.

Imperfectly solubilised starch has less affinity for alkalis, but obeys the same law, giving a constant 0.16 for KOH.

The chemical actions in question are not necessarily of the above type, but may be of the types $R=O + KOH \rightleftharpoons R(OK)(OH)$ or $R=O + NH_3 \rightleftharpoons H_2O + RNH$, the last recalling the formation of osamines from dextrose, maltose, etc. (Lobry de Bruyn, *Abstr.*, 1895, i, 640).

R. J. C.

Dissociation of Hydrogen Sulphide. GERHARD PREUNER and W. SCHUPP (*Zeitsch. physikal. Chem.*, 1909, 68, 157—168. Compare *Abstr.*, 1907, ii, 861)—In the previous investigation of the dissociation of hydrogen sulphide, the results obtained were only in moderate agreement with the requirements of Nernst's equation connecting equilibrium constants and temperature. On this account new measurements have been made, partly by Loewenstein's method (*Abstr.*, 1906, ii, 272), and partly by the use of a quartz spiral manometer of the type described by Abegg and Johnson (*Abstr.*, 1908, ii, 157). The time required for the measurements according to the former method was greatly reduced by the use of a null manometer. By this means the equilibrium pressure could be obtained by observations on the rate of change of the pressure resulting from the diffusion of the hydrogen through the platinum diaphragm.

The results obtained by the two methods of investigation are in satisfactory agreement. The values of the dissociation constant $k = 2p^3/760(2A - 3p)^2$, where A is the total gas pressure, and p the partial pressure of the dissociated hydrogen, are as follows:

750°	830°	945°	1065	1132°
0.89	3.8	24.5	118	260×10^{-4}

The mean value obtained for the heat of formation of hydrogen sulphide from the variation of the equilibrium constant with the temperature is 40,000 cal. (instead of 39,400 cal.); this, of course, refers to the formation from sulphur vapour. The new values of the dissociation constants agree fairly well with Nernst's equation.

H. M. D.

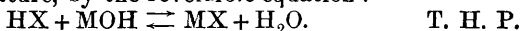
Hydrolysis of Sodium Borates. JOHN LUNDBERG (*Zeitsch. physikal. Chem.*, 1909, 69, 442—448).—The OH' -ion concentration in solutions of borax and in other solutions prepared by adding to borax varying proportions of sodium hydroxide has been measured at 25° by observations of the rate at which ethyl acetate is hydrolysed in the solutions. All the solutions behave as if they represented mixtures of NaBO_2 and HBO_2 in varying proportions. The former is partly hydrolysed according to the equation $\text{NaBO}_2 + \text{HOH} \rightleftharpoons \text{NaOH} + \text{HBO}_2$, and in $N/10$ solution at 25° the salt is hydrolysed to the extent of 1.38%. The equilibrium constant $k = [\text{OH}'][\text{HBO}_2]/[\text{BO}_2'] = 1.90 \times 10^{-5}$, and it can easily be shown that the OH' -ion in a solution of borax is independent of the borax concentration. In a $N/10$ -solution of borax, 0.019% of the salt is hydrolysed. From the above value of k , it is calculated that the dissociation constant of boric acid at 25° is 6.4×10^{-10} , which is only in moderate agreement with the value obtained directly by Walker, $k_1 = 17 \times 10^{-10}$ at 18° .

G. S.

Diffusion of Electrolytes in Aqueous Solutions. B. LINO VANZETTI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 229—234).—The author has made experiments, according to the method previously described (compare Abstr., 1908, ii, 20, 88), with the object of testing Nernst's theoretical formula for the coefficient of diffusibility of an electrolyte as a function of the osmotic pressure and of the velocities of migration of the single ions, $D = 2UV.RT/(U + V)$, U and V being proportional to the electrolytic mobilities of the component ions. Solutions of various concentrations of the chlorides, bromides, and iodides of hydrogen, sodium, potassium, rubidium, caesium, and lithium were made to diffuse along the capillary tube of the apparatus towards solutions of silver nitrate of corresponding densities, the distances traversed by the alkali salts before precipitates were deposited in the tube being expressed as percentages of the total length of the tube.

The results obtained show that with increase of dilution of the solutions, the velocities of diffusion of the halogen salts and acids increase in comparison with that of the silver salt; this increase causes the values for the halogen hydracids to approach, and those for the salts to recede from, the values calculated by means of Nernst's formula. More especially with hydrogen chloride, the value for which surpasses the theoretical number, and with the chlorides, this behaviour is partly attributable to supersaturation phenomena; but the latter do not explain those cases in which, for the higher concentrations, the precipitate is formed nearer to the alkali salt solution than to the silver nitrate solution. It is hence necessary to suppose that some influence is exerted by the concentration, and the

author suggests that the salts undergo hydrolysis, yielding small quantities of the corresponding acids, which outstrip the salts, the positions of the precipitates being those corresponding with the acids; this phenomena would become appreciable only at excessive dilutions. This hydrolytic dissociation, which probably takes place before the electrolytic dissociation is completed, is regarded as expressed, at the ordinary temperature, by the reversible equation :



Size of the Pores in Porcelain and Osmotic Effects. S. LAWRENCE BIGELOW and F. E. BARTELL (*J. Amer. Chem. Soc.*, 1909, 31, 1194—1199).—Bigelow (Abstr., 1908, ii, 88) has shown that the passage of water through collodion, gold-beaters' skin, parchment paper, and unglazed porcelain conforms to the laws regulating the passage of liquids through capillary tubes, and it has therefore been considered probable that these membranes consist of networks of capillaries.

In order to determine the diameter of such capillary tubes, measurements have been made of the pressure required to force the water out of a porcelain membrane previously saturated with it, and from the data so obtained, the diameter of the pores has been calculated by the application of Jurin's law. Experiments have also been made to ascertain the conditions under which such membranes show osmotic effects. The method and apparatus employed are described with the aid of diagrams.

The results indicate that the maximum pore diameter for a distinct osmotic effect with porcelain is 0.37 micron, with porcelain clogged with barium sulphate, 0.59 micron, and with porcelain clogged with sulphur, 0.49 micron. These figures must only be regarded as approximations, and, from the fact that they are so nearly the same, it seems probable that the diameter of the capillary is the chief factor in determining the appearance of osmotic phenomena. E. G.

Capillary Ascension of Colouring Matters. LOUIS PELET-JOLIVET (*Arch. Sci. phys. Nat.*, 1909, [iv], 28, 333—347; *Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 238—243).—The capillary ascension of a dye in a strip of a textile fabric suspended in contact with the dye solution varies strictly inversely as the adsorption of the colour by the fabric. Positive and negative ions influence the amount of capillary ascension differently with different dyes. In general, any electrolyte which tends to diminish the electric charge on the colloidal particles of the dye coagulates the colour, increasing the adsorption and decreasing the ascension. R. J. C.

The Influence of Electrolytes in Different Concentrations on the Dyeing Process. LOUIS PELET-JOLIVET and HANS SIEGRIST (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 235—237).—Continuation of earlier work with the view of examining Justin-Mueller's hypothesis, that the influence of electrolytes in the dyeing process is a function of their effect in diminishing the solubility of the dye.

The dyeing process in the presence of electrolytes is related to the contact electrification produced. G. S. W.

Solubility Influences. III. VICTOR ROTHMUND (*Zeitsch. physikal. Chem.*, 1909, 69, 523—546. Compare Abstr., 1900, ii, 467; 1902, ii, 447).—In the first part of the paper, a rather complicated general equation representing the mutual influence of substances on their respective solubilities is deduced. From this equation, by means of certain simplifying assumptions, the equation $1/C \log_e(\eta_1/\eta'_1) = \alpha/RT = \beta$ (1), representing the influence of a non-electrolyte on the solubility of an electrolyte, is deduced; in this equation, c represents the concentration of the non-electrolyte, η_1/η'_1 the ratio of the amounts of dissolved electrolyte before and after the addition of the non-electrolyte, and β is a constant. A corresponding equation for the influence of a salt on the solubility of a non-electrolyte is also deduced.

The influence of twenty-three non-electrolytes (organic compounds) on the solubility in water of lithium carbonate, silver sulphate, potassium bromate, potassium perchlorate, and strontium hydroxide (all slightly soluble salts) has been determined at 25°. For lithium carbonate, the non-electrolytes were employed in $N/8$, $N/4$, $N/2$, and N solution; for the other salts, only $N/2$ -solutions were used. The solubilities are throughout referred to equal volumes of solution, and not to equal amounts of water.

The solubility of lithium carbonate in water at 25° amounts to 0.1687 mol. per litre; it is increased by mannitol, dextrose, sucrose, and mercuric cyanide, and is diminished by the other electrolytes; the effect of the three sugars is ascribed to salt formation. From the observations of different concentrations of non-electrolytes on the solubility of this salt, it is shown that equation (1) represents the results satisfactorily, and the results of all the experiments are therefore calculated according to this equation and given in terms of 100β . The solubilities of the other salts in water in mols. per litre are as follows; silver sulphate, 0.0267; potassium bromate, 0.478; potassium perchlorate 0.1475, and strontium hydroxide, 0.0835. The solubility of silver sulphate is increased by the addition of acetonitrile, carbamide, mannitol, phenol, and other substances; that of potassium bromate by glycine only, and that of potassium perchlorate by formamide and carbamide. The solubility of strontium hydroxide is increased by glycerol, ethylene glycol, and mannitol. In all other cases non-electrolytes diminish the solubility.

The validity of a deduction previously made by the author (*loc. cit.*), that the diminution of solubility of a salt caused by a non-electrolyte is so much the greater the more effective the salt itself is in diminishing the solubility of non-electrolytes, appears to be confirmed by the results.

The observations are also discussed from the point of view of hydration in solution. Philip's method of calculating the hydration of salts from their effect in diminishing the solubility of non-electrolytes (*Trans.*, 1907, 91, 711) is regarded as untenable, and the views of Abegg (*Zeitsch. Elektrochem.*, 1901, 7, 677) and of Hudson (this vol., ii, 131) on hydration in solution are also adversely criticised.

G. S.

Piezochemical Studies. IV. Electrical Determination of the Influence of Pressure on the Solubility. ERNST COHEN and L. R. SINNIGE (*Zeitsch. physikal. Chem.*, 1909, 69, 102—109. Compare this vol., ii, 291, 641, 796, 857).—The solubility of cadmium sulphate and of zinc sulphate, under different pressures has been determined by an indirect method depending on measurements of *E.M.F.* Different cells of the Weston type containing (1) a saturated solution of the salt in question, in contact with the solid; (2) a saturated solution, not in contact with solid; (3) an unsaturated solution of the salt of known concentration, were used, and the measurements were made at 25° in the compression apparatus already described. The solubility of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$, at 25°, expressed in grams of the anhydrous salt to 100 grams of water, is as follows: 76·80 at 1 atmos., 77·53 at 250 atmos., 78·02 at 500 atmos., 78·60 at 750 atmos., and 78·96 at 1000 atmos. For $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, at 25°, 57·95 grams anhydrous salt at 1 atmos., 57·84 grams at 250 atmos., 57·84 grams at 500 atmos., 57·67 at 750 atmos., and 57·74 at 1000 atmos. The results are in all cases in excellent agreement with those obtained by the direct method.

The electromotive method cannot be employed when the solubility diminishes with increase of pressure unless supersaturation occurs, as in the case of zinc sulphate. G. S.

Influence of Pressure on the Miscibility of Two Liquids. J. TIMMERMANS and PHILIPP KOHNSTAMM (*Proc. K. Acad. Wetensch. Amsterdam*, 1909, 12, 234—244).—Measurements have been made of the influence of pressure on the critical solution temperature of a large number of pairs of substances. The results are discussed in reference to the general theory of plait-point curves, and the various systems are classified according to the nature of the observed pressure influence.

H. M. D.

Theory of Concentrated Solutions. HANS G. MÖLLER (*Zeitsch. physikal. Chem.*, 1909, 69, 449—459).—Dolezalek (compare this vol., ii, 22) has proposed a theory of concentrated solutions, based on the assumption that the partial pressure of each form of substance is proportional to the molar proportion of it present in the mixture, and has tested it by application to the experimental data for the vapour pressures of binary mixtures due to Zawidzki (*Abstr.*, 1901, ii, 6). The author points out that a crucial proof of the value of the theory can be obtained by calculating the partial pressures of the components of a binary mixture *AB* from the experimental data for the systems *AC* and *BD*, and comparing them with the observed values.

The two systems chosen are carbon tetrachloride-benzene and ethyl acetate-ethyl iodide, and from the results the partial pressures of the components in the system carbon tetrachloride-ethyl acetate have been calculated; the agreement between observed and calculated values is excellent. In the course of the investigation, it is shown that ethyl iodide contains single and triple molecules, about two-thirds of it being present in the latter form under the experimental conditions, and ethyl acetate contains about 28% of double molecules. G. S.

Solid Solutions of the Elements. W. GUERTLER (*Zeitsch. physikal. Chem.*, 1909, 68, 177—203).—From a critical consideration of observations relating to the formation of mixed crystals by elementary substances, the author arrives at the conclusion that the factors which determine the formation of these solid solutions are similar to those which are operative in the case of liquid solutions, and that the part played by isomorphism is not of essential importance. In support of the analogy between liquid and solid solutions, attention is drawn to the occurrence of diffusion in mixed crystals, to the fact that thermal changes accompany their formation, and further, to the influence of temperature on the formation of mixed crystals. It seems probable that all pairs of elements are capable of forming mixed crystals, if only to a very limited extent, and this is again analogous to the universal miscibility of pairs of liquids. On the other hand, the influence of the crystalline form of the component elements on the ability to yield mixed crystals appears to be very limited. Many pairs of elements which crystallise in the same form only yield mixed crystals to a very slight extent, although both components form a complete series of mixed crystals with a third isomorphous element. Similarly, it is found that many elements give rise to extensive series of mixed crystals, although the elements crystallise in forms belonging to different systems.

The frequent occurrence of mixed crystal aggregates containing compounds of two elements and one or other of the components is also discussed.
H. M. D.

Solubility in the Solid State between Aromatic Compounds and the Corresponding Hexahydrogenated [Completely Hydrogenated] Compounds. LUIGI MASCARELLI and V. BABINI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 222—228).—The authors have studied cryoscopically the mutual solubility of various aromatic compounds and the corresponding completely hydrogenated compounds (compare Mascarelli and Pestalozza, *Abstr.*, 1908, i, 527). The following are the mean molecular depressions of freezing point for certain of these compounds, which have not been previously used as cryoscopic solvents: benzanilide, 96·5; benzoylcyclohexylamine, $C_6H_{11} \cdot NHBz$, 142; hexachlorocyclohexane, 165; hexachlorobenzene, 207·5, a value higher than that for any other cryoscopic solvent.

Dicyclohexyl has the normal molecular weight in diphenyl. With dicyclohexylethane, $C_6H_{11} \cdot CH_2 \cdot CH_2 \cdot C_6H_{11}$, dissolved in dibenzil, somewhat discordant cryoscopic results are obtained, but these are not such as to indicate abnormal behaviour. Decahydronaphthalene dissolved in naphthalene behaves normally. With decahydro- β -naphthol in β -naphthol solution, the molecular weights obtained are in all cases lower than the calculated value, and vary from 124 to 152, owing to the fact that the solvent does not readily exhibit its true freezing point; the results show, however, that these two compounds do not form solid solutions. Benzoylcyclohexylamine has the normal molecular weight in freezing benzanilide, but the latter gives molecular weights varying from 300 to 306, instead of 197, in benzoylcyclohexylamine solutions. Similarly, hexachlorocyclohexane exhibits

normal cryoscopic behaviour in hexachlorobenzene, whilst the latter gives molecular weights varying from 310 to 337, instead of 285, in freezing hexachlorocyclohexane (compare Mascarelli and Pestalozza, Abstr., 1907, ii, 936). T. H. P.

Ultramicroscopical Investigations. J. AMANN (*Chem. Zentr.*, 1909, ii, 1031; from *Schweiz. Woch. Chem. Pharm.*, 1909, 47, 439—443).—(1) Ultramicroscopes.—One of the most practical systems is Wenham's paraboloid. (2) Many pharmaceutical preparations have been found to be pseudo-solutions, and it was found that the therapeutic activity of these drugs depends on the condition of the pseudo-solution. (3) Some substances insoluble in water are rendered soluble by colloids. The colloidal solution of egg-albumin in the course of a few days dissolves trioxymethylene, and the pseudo-solution keeps for an unlimited time without change, but mineral acids give a precipitate. (4) A freshly prepared ammoniacal copper sulphate solution gives under the ultramicroscope the impression of a pseudo-solution of copper hydroxide in a true solution. On adding alcohol, and observing certain conditions, a colourless filtrate is obtained which proves to be a pseudo-solution. L. DE K.

Crystallisation from Aqueous Solutions. III. ROBERT MARC and WALTHER WENK (*Zeitsch. physikal. Chem.*, 1909, 68, 104—114. Compare Abstr., 1908, ii, 160; this vol., ii, 798).—The velocity of crystallisation of potassium sulphate is considerably accelerated by certain inorganic salts which are not markedly absorbed by the potassium sulphate crystals formed. The influence of colouring matters on the velocity of crystallisation of potassium sulphate has also been investigated; those which do not colour the salt have practically no influence (for example, methylene-blue), those which colour the salt slightly exert a retarding effect (for example, patent-blue), and those which colour the salt strongly almost completely inhibit the crystallisation of supersaturated solutions of potassium sulphate (for example, Bismarck-brown). That the latter phenomenon is not due to the coating of the crystals or nuclei with the colouring matter is shown by the fact that the colouring matters do not retard the dissolution of potassium sulphate by water. These results support the view already advanced (*loc. cit.*), that crystallisation is preceded by adsorption. G. S.

Crystals which are Absolutely Stable only at High Pressures. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1909, 69, 569—584).—Crystalline substances which are unstable (pseudo-stable) at atmospheric pressure may have a field of absolute stability at higher pressures, provided that the modification unstable at lower pressures has a greater density than the stable modification. This possibility is in accordance with van't Hoff's rule connecting displacement of equilibrium with pressure. Whether the transition takes place on increasing the pressure depends on two factors: (1) the power of spontaneous transition; (2) the velocity of the transition, and these factors are discussed in detail for the transition curve of phenol I to phenol II (compare Tammann, *Schmelzen und Krystallisieren*, Leipzig, 1903).

If the form stable at atmospheric pressure is transformed to the other modification by applying very high pressures, and the new modification is then rapidly cooled, it should be possible to obtain it in a pseudo-stable form at low pressures if the spontaneous transition and the velocity of transition are sufficiently small. This has actually been done for the forms of phenol and of ice known as phenol II and ice III. At 10° , phenol begins to change to phenol II at a pressure of about 2200 kg./cm.² The pressure was raised to 3200 kg. in order to ensure that the transition was complete, then the phenol II was cooled to -80° in solid carbon dioxide, and the pressure slowly released. Phenol II remained stable when the pressure had fallen to 300 atmos. at -80° , and even between 0° and 10° under a pressure of 400 kg. Under suitable conditions it might be possible to obtain this form of phenol in open vessels. Similar experiments were made in order to obtain the dense unstable form of ice, ice III, at low pressures, but in this case the transition to the ordinary form took place between -60° and -40° under a pressure of 180–400 kg. There is some evidence that this transition takes place in two stages.

The relationship between diamond and graphite is similar to that between phenol II and the ordinary form, and the transformation of graphite to diamond can theoretically be accomplished by the method described above.

Very little is known as to the possibility of obtaining the two forms from solution. G. S.

Formation of Solid Surfaces on Colloidal Liquids and their Photo-electric Behaviour. F. PLOGMEIER (*Ber. Deut. physikal. Ges.*, 1909, 382–396).—The development of photo-electric properties of solutions of colouring matters and inorganic colloids has been found to be due to the formation of a solid layer at the free surface of the solutions. Aqueous solutions of magenta, methyl-violet, Hofmann's violet, rhodamine, eosin, and naphthol-yellow were examined. Freshly formed surfaces of these solutions show little or no photo-electric effect, but as the age of the surface increases, the photo-electric qualities are developed. The sensitiveness increases rapidly at first, then more slowly, and approaches a constant limiting value. This limiting value is almost independent of the concentration of the solution, but the time required for the attainment of this value diminishes as the concentration increases.

Experiments with solutions of magenta in contact with air, carbon dioxide, and hydrogen show that the formation of the solid surface layer which conditions the photo-electric sensitiveness is independent of the nature of the gas in contact with the solution. The phenomenon is therefore not due to the formation of an insoluble substance as the result of oxidation. On the other hand, it is shown that conditions which favour evaporation of the solvent are also favourable to the formation of the surface layer.

This is also found to be accelerated when electrolytes are added to the solution; the addition of non-electrolytes is without any appreciable effect.

Similar results were obtained when colloidal solutions of gold,

silver, and palladium were examined. On the other hand, photo-electric sensitiveness was not always developed in the case of colloidal solutions of arsenious and antimony sulphides, although surface layers could be detected. This is supposed to be due to the circumstance that the surface layers in these cases are discontinuous, and are therefore wetted by the solution.

The author expresses the view that the phenomenon investigated is essentially dependent on the colloidal character of the solution. When the colloidal particles come within the range of the "dead space" at the surface of the solution, their mobility is lowered to such an extent that they cannot escape to the interior, and a process of segregation results.

H. M. D.

Heterogeneous Equilibria of Dissociating Compounds. F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 257—265).—The six types of equilibrium curves are discussed in which intersection of the plait-point curve and the three-phase line of a dissociating binary compound occurs. With ammonia, hydrogen chloride, hydrogen sulphide, and carbon dioxide form systems which belong to the same type; a different type is furnished, however, by ammonia and sulphur dioxide.

Quantitative data for the system ammonia-hydrogen sulphide are recorded.

H. M. D.

The System Water-Sodium Sulphate. ANDREAS SMITS and J. P. WUITE (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 244—257).—The vapour pressures corresponding with the various three-phase systems built up from water and sodium sulphate have been determined for a series of temperatures. At 32.4°, when the decahydrate is transformed into the anhydrous salt, the vapour pressure of the system is 30.8 mm. of mercury. At 24.4°, when the heptahydrate is converted into the anhydrous salt, the pressure amounts to 18.9 mm. The vapour pressures of the saturated solution of the anhydrous salt are recorded for temperatures between 50° and 260°. When these pressures are compared with the vapour pressures of pure water a maximum difference is found at about 234°, which is the temperature at which rhombic sodium sulphate is converted into a monoclinic form.

The composition of the saturated solution of sodium sulphate has also been determined for temperatures between 62° and 319°. The curve representing the solubility of the rhombic form is of retrograde character, the solubility falling to a minimum and then increasing. From 240° to 319°, when the solid phase in contact with the solution is the monoclinic form of sodium sulphate, the solubility decreases rapidly. At 365° the critical phenomenon is observed, and since this temperature is practically identical with the critical temperature of pure water, the authors conclude that the saturated solution at this temperature contains very little sodium sulphate.

H. M. D.

The Impassable Line in Systems of Three Components and its Relation to the Law of Combining Weights. RUDOLF RUER (*Zeitsch. physikal. Chem.*, 1909, 68, 1—31).—A theoretical paper. Ostwald (*Lehrbuch* II, 2, 991) has shown

that when a two-phase system of three components is represented in the usual way by an equilateral triangle, and there is a special point D on the line AB (representing, for example, a maximum or minimum point on the freezing-point or boiling-point curve), the line CD divides the triangle into two sections in such a way that the points representing the composition of the ternary system in one of these sections differ from those in the other section with reference to the components from which they are built up, and in this sense it is not possible to cross the line CD from one section to the other. Schreinemakers (Abstr., 1901, ii, 57, 146) has pointed out certain objections to Ostwald's views.

The author shows that the line CD can, in general, be crossed when D represents a binary mixture of A and B , but not when D represents a chemical compound. The general relations which must hold in order that it may not be possible to cross the line CD from one triangle to the other are worked out mathematically. G. S.

Equilibria in Quaternary Systems. The System: Sodium Oxide, Barium Oxide, Hydrochloric Acid, and Water. FRANZ A. H. SCHREINEMAKERS (*Zeitsch. physikal. Chem.*, 1909, 68, 83—103).—The various points in the equilibrium figure have been determined by solubility measurements at 30° in the usual way, and the results confirmed by the "residue" method. The measurements and figures are complicated by the occurrence of a large number of salts and hydrates, including the compound $\text{BaCl}(\text{OH}) \cdot 2\text{H}_2\text{O}$, already described by Beckmann. G. S.

Isomorphous Mixtures. The Systems *o*-, *m*-, and *p*-Chloronitrobenzene and *o*-, *m*-, and *p*-Bromonitrobenzene. ROBERT KREMANN (*Jahrb. K. K. Geol. Reichsanstalt*, 1908, 58, 659—672).—The isomorphous mixtures formed by the three corresponding chloro- and bromo-nitrobenzenes have been examined. Temperature-concentration curves are given, showing the relationships between the co-existing liquid and solid phases. In the case of the ortho-compounds, the melting point of each component is lowered to a small extent on addition of the second component. On the other hand, the melting points of *m*- and *p*-chloronitrobenzenes are raised on addition of the corresponding bromo-compounds. The melting-point curves in these two cases show a distinct break, indicating the existence of two series of isomorphous mixtures.

The crystals which separate on cooling from liquid mixtures of the ortho-compounds contain a smaller proportion of the bromo-compound than that which is present in the salt. The reverse holds for mixtures of the meta- and para-compounds. The observed differences in respect of the formation of isomorphous mixtures are attributed to the action of forces of the same nature as those which give rise to the phenomenon of steric hindrance. In view of the possibility that the differences might be due to the formation of double molecules in the case of the ortho-compounds, the temperature-coefficients of the molecular surface energy were determined for equimolecular mixtures of the three series of compounds, but in all cases these coefficients were found to have a normal value. H. M. D.

P, T, X-Spacial Representation of the System Ether-Anthraquinone. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 231—233).—Since the usual method of representing the pressure, temperature, concentration relationships in space is not well adapted to systems in which the two components are physically very different, an alternative method of spacial representation is described and illustrated for the case of ether and anthraquinone.
H. M. D.

Chemical Dynamics of the Alkyl Iodides. KATHARINE A. BURKE and FREDERICK G. DONNAN (*Zeitsch. physikal. Chem.*, 1909, 69, 148—168. Compare *Trans.*, 1904, 85, 555).—The paper contains an account of further experiments undertaken with the object of elucidating the nature of the reaction between silver nitrate and alkyl iodides in alcoholic solution.

The main products of the reaction, nitric acid, alkyl nitrate, and ether, have practically no effect on the velocity of the reaction. The rate of the reaction between ethyl iodide and silver nitrate is accelerated by calcium nitrate, and to a still greater extent by ammonium nitrate. This result is probably due to the effect of the NO_3^- ions in diminishing the ionisation of the silver nitrate, as the authors consider that it is the non-ionised silver nitrate which reacts with the alkyl iodide. If the view as to the accelerating influence of NO_3^- ions is correct, nitric acid, which does not accelerate the reaction, must be much less ionised in alcoholic solution than ammonium nitrate under corresponding conditions, a deduction which has been confirmed by electrical conductivity measurements.

Under varying conditions, about 70% of the total silver nitrate used up always appears as nitric acid, the remainder as ethyl nitrate, a result which proves that these products are formed in simultaneous reactions.

The reaction between methyl iodide and silver nitrate has been measured at 24.5° in mixtures of ethyl alcohol and water in varying proportions, and the corresponding reaction with ethyl iodide in mixtures containing up to 60% of water. The initial concentrations both of alkyl iodide and silver nitrate were $n/40$ in each case. With methyl iodide the velocity attains a maximum in mixtures containing 5% of water, and falls off regularly as the proportion of water is further increased. With ethyl alcohol there is also a maximum at 5% of water, but the velocity reaches a minimum at about 35° of water, and increases slowly up to 60% of water, beyond which point the experiments could not be carried out, owing to the insolubility of ethyl iodide in the mixed solvent. The proportion of acid formed in the mixed solvent appears to be greater than in either of the pure solvents.

As regards the mechanism of these reactions, the authors agree with Wegscheider (*Abstr.*, 1907, i, 373) that it is probably the non-ionised silver nitrate which reacts, but some points still remain unexplained.

The fact that the order of the reactivity of the alkyl iodides as measured by silver nitrate is different from that obtained in

other ways may be connected with the fact that in the former case the solvent plays a part in the reaction. G. S.

Correction. (Formation of Esters.) HEINRICH GOLDSCHMIDT (*Zeitsch Elektrochem.*, 1909, 740—742).—A claim of priority against Kailan (this vol., ii, 723). T. E.

Relation between the Structure of the Aliphatic Alcohols and their Rate of Esterification. BORIS N. MENSCHUTKIN (*Ber.*, 1909, 42, 4020—4021).—It is pointed out that Michael and Wolgast (this vol., ii, 873) have not referred to some of the later work of N. Menschutkin (*Abstr.*, 1893, i, 158). J. J. S.

Synthetic Ferment Action. JACOBUS H. VAN'T HOFF (*Sitzungsber. K. Akad. Berlin*, 1909, 42, 1065—1074).—If an enzyme is an ideal catalyst it should have no effect on the actual equilibrium attained. In most cases, especially those which are of biological importance, it is impossible to determine the equilibrium constant in the absence of an enzyme, so that it is difficult to submit the above statement to direct experimental proof. The following method is suggested by the author, and is worked out in the case of the equilibrium in the system: benzoic acid, phenol, phenyl benzoate, and water, which is typical of the hydrolytic decomposition and synthetic formation of a fat. The method is based on the following principle: In the case of optical antipodes in equilibrium there is no heat of reaction and no tendency for the solids to change one into the other. When mixed in equal quantities they will be in equilibrium with the fused mass, the vapour, or the saturated solution, and the whole system is inactive; from thermodynamic principles it follows that the equilibrium constant is $1(\log k = 0)$. In equilibria where the heat of reaction is zero or approximately so, as is the case in enzymatic processes which depend on the addition of water and the subsequent splitting of the molecule, the position of equilibrium will thus be characterised by that existing in the condensed system, that is, when ester and ice are in equilibrium with the solid mixture of alcohol and acid. The saturated vapour, fusion, or saturated solution in contact with this condensed system will also have the same equilibrium when thermoneutrality exists. Thus, from the compositions of the saturated solutions or vapour, the equilibrium can be determined.

The mixture of phenol, benzoic acid, phenyl benzoate, and water gives two cryohydric mixtures at -1.2° and -10° , the compositions of which, in parts by weight, were found to be:

	Water.	Ester.	Acid.	Phenol.
At -1.2°	938	0.02	1.57	60
At -10°	58	263	74	605
Vapour at 0°	0.0049	0.0415	0.0915	0.0022

The last line represents the composition of the saturated vapour. This was not determined directly, but calculated by making use either of the rule of corresponding conditions or of Trouton's rule.

The equilibrium constant, $[\text{water}][\text{ester}]/[\text{acid}][\text{phenol}] = K$, cal-

culated from these results has the values: Calculated (*a*) from the solutions, 0.64–1.1; (*b*) by rule of corresponding conditions, 0.7–1.9; (*c*) from Trouton's rule, 0.43–1.8, that is, it lies in the neighbourhood of 1. It is therefore very probable that $\log k = 0$.

Assuming that the relation $\log k = 0$ holds for a system, the author draws certain conclusions with respect to isomerism and molecular symmetry. He also deduces, by making use of Trouton's rule, that when four substances are in equilibrium, and thermoneutrality exists, the sum of the boiling points, taking those of the reciprocal system as negative, is zero. This corresponds with Kopp's additive rule with respect to boiling points, which can therefore only hold when thermoneutrality exists.

It is pointed out that Menshutkin's work on esterification can be used to indicate the equilibrium point in hydrolytic decompositions or the reverse syntheses, assuming that enzymes act as ideal catalysts.

T. S. P.

Fundamental Stoichiometric Laws and the Atomic Theory. WILHELM OSTWALD (*Zeitsch. physikal. Chem.*, 1909, 69, 506–511)—A short recapitulation of the author's Faraday lecture (Trans., 1904, 85, 506).

G. S.

Importance of Physical Chemistry for the Determination of Atomic Weights. PHILIPPE A. GUYE (*Zeitsch. physikal. Chem.*, 1909, 69, 315–336).—The author shows how the principles of physical chemistry have contributed to increased accuracy in atomic weight determinations, and indicates the lines along which further advances may be made.

G. S.

Vacuum Correction of Weighings Applied to Atomic Weight Determinations. PHILIPPE A. GUYE and N. ZACHARIADES (*Compt. rend.*, 1909, 149, 593–594).—The usual correction for reducing a weighing to the vacuum value, based on the density of the substance weighed, is always too high, because a counter correction should be made for the weight of gases or vapours condensed on the surface of the substance. The authors have determined the magnitude of this error in the case of a number of powdered chlorides, bromides, sulphates, etc., by direct weighings in a vacuum.

The error on 100 grams varies from 1 mg. in the case of cupric oxide to 33 mg. in the case of potassium nitrate. It depends on the physical condition of the substance, being 5 mg. for fused potassium chloride, 20 mg. for crystals, and 32 mg. for fine powder. It is altogether fallacious to weigh more accurately than to 1 part in 10,000 in air, or to calculate atomic weights with any greater precision than this, when they are founded on weighings in air corrected for displacement by calculation (compare Scott, Proc., 1909, 25, 286).

R. J. C.

Influence of Mass Distribution in the Molecule on the Magnitude of the Molecular Forces. EMIL BOSE and MARGRETE BOSE (*Zeitsch. physikal. Chem.*, 1909, 69, 52–68).—A theoretical paper. Certain considerations lead to the conclusion that the mole-

cular forces may advantageously be regarded as localised in different parts of the molecule, and not, as is usually assumed, at the centre of the molecule. The consequences of this assumption are tested, mainly by reference to the attraction constant, a , of van der Waals' equation, the values of a for substances of approximately equal molecular weight being compared, as well as cases in which, for approximately equal values of a , the molecular weights are different. The hypothesis also throws some light on certain regularities in the boiling points of organic compounds. G. S.

Theoretical Basis of Structural Formulæ for Inorganic Substances. ALFRED WERNER (*Arch. Sci. phys. nat.*, 1909, [iv], 28, 317—332).—Theoretical. An account of the author's well-known theory on this subject. R. J. C.

A Simple Mechanical Shaker. DOUGLAS H. B. COUMAN (*Chem. News*, 1909, 100, 209).—Steam, generated in a copper bottle of one-litre capacity, is directed by means of a glass outlet tube, provided with a jet, against a series of metallic vanes inserted round a cork. The latter is placed on the top of a stirring rod, which rotates in a glass collar in which it is supported by an enlargement of the rod. The glass collar is held in position by two lateral brass supports, placed one above the other at a suitable angle, and soldered to the boiler. The apparatus is figured in the original. T. A. H.

Laboratory Methods. ERNEST MURMANN (*Oesterr. Chem. Zeit.*, 1909, 12, 145—146).—The author describes the following apparatus and processes: (1) a convenient form of Kipp's apparatus; (2) a method for fastening down crucible lids with carborundum; (3) a convenient "tube" crucible; (4) a form of tripod; (5) a distillation apparatus; (6) an easily fusible alloy (m. p. 95—100°) containing cadmium 2.248, tin 3.570, thallium 4.082, and bismuth 12.510 parts; (7) a rapid method of preparing a perchlorate; (8) a colorimetric method of estimating manganese; (9) the collection and washing of magnesium ammonium phosphate. F. M. G. M.

Inorganic Chemistry.

[Catalytic Action of Colloidal Palladium on the Union of Hydrogen and Oxygen.] CARL PAAL and WILHELM HARTMANN (*J. pr. Chem.*, 1909, [ii], 80, 337—348).—The rate of combination of hydrogen and oxygen under the catalytic influence of colloidal palladium in presence of sodium protalbinat as protective colloid has been investigated. When excess of hydrogen is present in the gas mixture, the velocity of the reaction is greater than when the hydrogen and oxygen are present in the volume ratio 2:1. On the other hand, excess of oxygen lowers the reaction velocity. In the former case a

maximum velocity is reached when the effect of the excess of hydrogen is counter-balanced by the diminishing concentration of the oxygen in the reaction mixture.

The observations show that palladium behaves differently from platinum in its catalytic influence on the union of hydrogen and oxygen. In the case of platinum, a maximum velocity is found when the two gases have the volume ratio 2:1. It is suggested that the large adsorptive power of palladium for hydrogen is the cause of the observed velocity differences.

H. M. D.

Density of Hydrogen Chloride; Atomic Weight of Chlorine.

OTTO SCHEUER (*Compt. rend.*, 1909, 149, 599—601. Compare Gray and Burt, *Trans.*, 1909, 95, 1633).—The density of hydrogen chloride prepared from sodium chloride and sulphuric acid, dried by phosphoric oxide, and purified by fractional distillation, was determined by direct weighing of a number of bulbs filled simultaneously. The values obtained in seven series of observations comprising twenty-eight determinations in all are strikingly concordant, and give as final value (arithmetic mean) 1.6394 grams as the weight of one litre of the gas.

Combining with this determination the critical constants of hydrogen chloride determined by Leduc or by Briner, or the coefficient of compressibility determined by Leduc and Sacerdote, the author calculates that the atomic weight of chlorine is certainly very near 35.45.

R. J. C.

Oxidation of Iodine by Ozone. FR. FICHTER and FRANZ

ROHNER (*Ber.*, 1909, 42, 4093—4100. Compare Muir, *Trans.*, 1909, 95, 656).—When a saturated solution of iodine in chloroform is treated with ozone (8%), an amorphous, yellowish-white precipitate is obtained, which consists of a compound of iodine and oxygen. It is very sensitive to moisture, deliquescing to an almost black syrup. If the deliquescent mass is exposed to the air for some days, vapours of iodine are gradually evolved, and a residue of crystals of iodic acid left, the water which was formerly absorbed gradually evaporating. The same product can be obtained, but not so conveniently, by treating powdered and dry iodine with ozone at a temperature of 40—50°. Analysis points to the formula I_4O_9 , rather than to I_2O_4 or I_3O_7 . Its properties do not agree with those of Millon's oxide, I_2O_4 (*J. pr. Chem.*, 1845, 34, 321).

On being heated, iodine vapours begin to be evolved at 75°, and between 120—130° there is a vigorous decomposition, the whole mass swelling up. It reacts violently with phenol, iodine being evolved. Concentrated sulphuric acid dissolves it in the cold, and the solution deposits crystals of Millon's sulphate, which are possibly a mixture of $I_2O_3 \cdot SO_3 \cdot \frac{1}{2}H_2O$ with iodine pentoxide (Chrétien, *Abstr.*, 1897, ii, 138).

The compound I_4O_9 is considered to be the iodate of tervalent iodine. With water it reacts, giving iodic acid and iodine trihydroxide: $I(IO_3)_3 + 3H_2O = I(OH)_3 + 3HIO_3$. The iodine hydroxide then decomposes, thus: $3I(OH)_3 = 2HIO_3 + HI + 3H_2O$, and iodine is formed from the interaction of the iodic acid and hydrogen iodide,

Millon's compound of the composition I_2O_4 is to be considered as a basic iodate of iodine, namely, $O:I(IO_3)$. T. S. P.

Preparation of Hydrogen Iodide from Barium Peroxide, Iodine, and Sulphur Dioxide. GEORG KASSNER (*Chem. Zentr.*, 1909, ii, 1304; from *Apoth. Zeit.*, 1909, 24, 562—563. Compare Bodroux, *Abstr.*, 1906, ii, 156).—Finely-powdered iodine is mixed with the calculated quantity of barium peroxide, which has been ground up with water; oxygen is evolved, and a solution of barium iodide formed. To this solution, after filtration from barium carbonate and the excess of barium peroxide, is added a further quantity of iodine equal to that originally taken, and then sulphur dioxide passed in; barium sulphate is precipitated, and the solution gradually becomes colourless. On distillation, a solution of constant composition (55% hydrogen iodide) distils over at 127° . At the same time, iodine vapours are formed in large quantity, there is an odour of hydrogen sulphide, and amorphous sulphur is deposited in the condenser. The latter is probably formed from the hydrogen sulphide and iodine, whereas the hydrogen sulphide is formed as a decomposition product of the barium sulphate. If sodium sulphite is heated with 55% hydrogen iodide, sulphur and iodine are formed in large quantities, and there is an odour of hydrogen sulphide. Thus, a solution of hydrogen iodide which is not very concentrated is a strong reducing agent.

It is impossible to prepare a pure dilute solution of hydrogen iodide from barium peroxide, iodine, and sulphur dioxide unless distillation is finally resorted to. T. S. P.

Aqueous Solutions of Hypoiodous Acid. ANTON SKRABAL and F. BUCHTA (*Chem. Zeit.*, 1909, 33, 1184—1185, 1193—1195. Compare this vol., ii, 224).—The anomalous behaviour of iodine when oxidised by chlorine in aqueous solution is discussed in the light of previous researches. It is best explained by regarding the compound HIO , not as hypoiodous acid, but as a base, iodine hydroxide (compare Hartmann and Meyer, *Abstr.*, 1894, i, 242, 461). In presence of an excess of hydrochloric acid, ICl is formed, and this is very stable. Solutions in sulphuric acid are unstable, owing to extensive hydrolysis. Sulphuric acid solutions are more stable in the presence of an excess of halogen, owing to the formation of the compounds I_3OH and ICl_2OH .

Tri-iodine hydroxide, I_3OH , is prepared in solution by oxidising a solution of potassium iodide and sulphuric acid with potassium permanganate and manganous sulphate, and reducing the excess with oxalic acid. For analysis, a definite volume of the solution is titrated with thiosulphate after adding potassium iodide: $5I_3OH + 5I' + 5H' = 5H_2O + 10I_2$. An equal volume is shaken with chloroform: $5I_3OH = 2H_2O + 7I_2 + H' + IO_3'$, and the aqueous solution titrated after addition of potassium iodide: $IO_3' + 5I' + 6H' = 3H_2O + 3I_2$. In a solution of the correct composition, the two quantities of iodine found are in the ratio 10 : 3.

Iodine trichloride is to be regarded as $ICl:Cl_2$. It is decomposed by water according to the equation: $2ICl_3 + 3H_2O = 5HCl + ICl + HIO_3$.

The solution in hydrochloric acid is stable, that in sulphuric acid undergoes hydrolysis: $\text{ICl}_3 + \text{H}_2\text{O} = \text{ICl}_2\text{OH} + \text{HCl}$. C. H. D.

Basicity of Acids and the Constitution of Certain Anomalous Acid Salts. GIUSEPPE BRUNI (*Zeitsch. physikal. Chem.*, 1909, 69, 69—74).—Mainly a discussion of results already published (Abstr., 1908, ii, 935, 1012). The attempt was made to throw light on the nature of the so-called "ultra-acid" salts, for example, KF , HF and KIO_3 , HIO_3 , by measuring the change of electrical conductivity when the acid is progressively neutralised by addition of a base. Although the results are not conclusive as far as the main object of the investigation is concerned, the theory of the change of conductivity on neutralisation has been worked out, and is fully confirmed by experiment. G. S.

Apparatus for the Preparation of Pure Oxygen. GUSTAV MOSSLER (*Chem. Zentr.*, 1909, ii, 785—786; from *Zeitsch. Allg. Oesterr. Apoth. Ver.*, 1909, 43, 301—302).—Large quantities of pure oxygen can be made by the interaction of 10% hydrogen peroxide and a concentrated solution of potassium permanganate acidified with sulphuric acid. T. S. P.

Demonstration of the Presence of Ozone in Flames. WILHELM MANCHOT (*Ber.*, 1909, 42, 3948—3951).—The presence of ozone in the flame of burning hydrogen (compare Fischer, Abstr., 1906, ii, 224) is readily proved by the action of the flame on silver (compare this vol., ii, 1003). A strip of clean silver is heated by immersing one end in a sand- or oil-bath at 260° . The flame used is a long one produced by burning a vigorous current of hydrogen at a narrow jet, and only the point of the flame is used to touch the silver. A black stain is rapidly produced, which is most intense where touched by the hottest part of the flame, as demanded by the theory of ozone formation. To produce an equal effect without a flame, oxygen containing 2 or 3% of ozone is necessary. The absence of ozone from the outside of a flame is due to its breaking down in passing through the zones of lower temperature. Blow-pipe and oxy-hydrogen flames give the ozone reaction. The reaction is not due to either oxides of nitrogen or hydrogen peroxide. The latter reacts with silver at 155° , but not at higher temperatures. Silver is a more sensitive reagent than tetramethyldi-*p*-aminophenylmethane.

The presence of hydrogen peroxide in the oxy-hydrogen flame is proved by allowing the flame to play on to the surface of a concentrated solution of a titanium salt, when an intense yellow coloration is produced in half a minute. Hydrogen peroxide is also present in the flame of moist carbon monoxide burning in moist oxygen. Neither ozone nor hydrogen peroxide is an agent in the process of combustion, their production being merely an effect of the high temperature of the flame. C. H. D.

Formation of Ozone in a Flame. OSCAR LOEW (*Ber.*, 1909, 42, 4218—4219. Compare preceding abstract).—The author points out

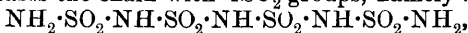
that as far back as 1870 (*Zeitsch. Chem.*, [ii], 6, 65, 269) he proved the formation of ozone in a flame. A strong current of air was blown through a tube into the flame of a Bunsen burner, and the gases collected; in a few seconds enough ozone had been collected to readily identify it by its intense odour and the common tests. T. S. P.

Structural Classification of Oxides, Oxygen Acids, and their Salts. RICHARD ABEGG (*Zeitsch. physikal. Chem.*, 1909, 69, 1—14. Compare Abstr., 1904, ii, 475).—The author revives the suggestion of Berzelius that the oxy-salts are to be regarded as double oxides (K_2SO_4 , for example, is represented as $K_2O \cdot SO_3$), and discusses the nature of oxides, oxygen acids, and their salts from this point of view.

The mutual combining capacity of oxides, leading to the formation of hydrates (in which case one of the oxides is water) and other poly-oxides and salts, is discussed, and from the available data it is shown that the driving force influencing the combination of oxides is the power of the resulting complex to split up into two parts of contrary electrical character; the more readily this polar differentiation can take place, the more stable is the complex molecule.

The different types of polyoxides are considered, and the general rule is provisionally laid down that the weaker the basic oxide so much the greater is the tendency of one mol. of the acidic oxide to combine with several mols. of the basic oxide, and, conversely, the weaker the basic oxide, the more readily are compounds of the type of acid salts formed. G. S.

The Reaction between Sulphuryl Chloride and Ammonia. FRITZ EPHRAIM and FRANZ MICHEL (*Ber.*, 1909, 42, 3833—3849. Compare Abstr., 1902, ii, 14; 1905, ii, 312; *Trans.*, 1900, 77, 324).—In previous work on the interaction between sulphuryl chloride and ammonia, the experiments have been so carried out that at first the sulphuryl chloride was in excess. The authors proceed in the opposite manner, a solution of sulphuryl chloride in light petroleum being added to a concentrated solution of ammonia in the same solvent, and a rapid current of ammonia being passed through the latter solution during the time the sulphuryl chloride is being added, so as to keep the ammonia in excess. The products of reaction with the second method are different from those obtained with the first method. Sulphamide and trisulphimide (or sulphomelide) are formed only to a very slight extent, the chief products being long-chain compounds which give sulphamide only by a secondary action. If ammonia is always present in excess, imidosulphamide is the chief product formed, but in other cases the chain with $4SO_2$ -groups, namely:



seems to be favoured.

The substances were isolated in the form of their silver salts. The product of reaction in the light petroleum was dissolved in water, and the solution digested with freshly precipitated lead hydroxide to remove the ammonium chloride. After cooling and filtering, the filtrate was acidified with nitric acid, and the remaining chlorine precipitated

with silver nitrate. After collecting the silver chloride, the filtrate was fractionally precipitated by ammonia. The first fraction was obtained by adding ammonia until the white, flocculent precipitate began to ball together, and then stirring for some minutes. The filtrate from this reacted acid; excess of ammonia was added, and the second and chief fraction was obtained. The filtrate was again acid, and gave a further precipitate of an impure product (not further investigated) on neutralising with ammonia. The silver salts were all amorphous, and contained irregularly varying amounts of water; they were very difficult to purify.

Second fraction.—White powder, only slightly affected by light. Analysis gave $(\text{SO}_2)_4\text{N}_5\text{Ag}_6\text{H} + 11\text{H}_2\text{O}$. Dissolves in hot silver nitrate, and could be fractionally recrystallised from the hot mother liquor. The fractions were unchanged in composition, except that the amount of water present was $1\frac{1}{2}\text{H}_2\text{O}$. The formula may be either $\text{Ag}_2\text{N}\cdot\text{SO}_2\cdot\text{NAg}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{SO}_2\cdot\text{NAg}\cdot\text{SO}_2\cdot\text{NAg}_2$ or $\text{N}(\text{SO}_2\cdot\text{NAg}_2)_2\cdot\text{SO}_2\cdot\text{NH}\cdot\text{SO}_2\cdot\text{NAg}_2$; the latter is favoured.

First fraction.—This was not pure. After treatment with dilute ammonium hydroxide and then acetic acid, a product was obtained, which could not be recrystallised, and answered to the formula $(\text{SO}_2)_3\text{N}_5\text{Ag}_3\text{H}_6 + 5\frac{1}{2}\text{H}_2\text{O}$; it is considered to be an equimolecular mixture of silver sulphamide, $\text{SO}_2(\text{NHAg})_2$, and silver imidosulphamide, $\text{NAg}(\text{NH}_2\cdot\text{SO}_2)_2$. On dissolving in a concentrated solution of pyridine nitrate and keeping, rhombic crystals of an additive product, $\text{NAg}(\text{SO}_2\cdot\text{NH}_2)_2\cdot\text{C}_5\text{H}_5\text{N}$, were obtained.

In one experiment the fractionation with ammonia was carried out in four operations. The second fraction gave $(\text{SO}_2)_4\text{N}_5\text{Ag}_6\text{H}, 28(?)\text{H}_2\text{O}$, and the third, $(\text{SO}_2)_4\text{N}_5\text{Ag}_7 + 8\text{H}_2\text{O}$.

In one experiment the reaction mixture was submitted to the prolonged action of ammonia, and the silver salt obtained in 9 fractions. Silver imidosulphamide, $(\text{SO}_2)_2\text{N}_3\text{Ag}_3\text{H}_2$, was obtained in each case, but the amount of water varied.

The silver salt, $(\text{SO}_2)_4\text{N}_5\text{Ag}_6\text{H}$, was treated with alkyl iodides and with potassium iodide, but with no very definite results.

In the preparation of sulphamide according to the method of Hantzsch and Holl (Abstr., 1902, ii, 14), a salt was obtained having the composition $(\text{SO}_2)_4\text{N}_7\text{Ag}_5\text{H}_8, 4\text{H}_2\text{O}$; this is considered to be either $\text{NH}_4\cdot\text{NAg}\cdot\text{SO}_2\cdot\text{NAg}\cdot\text{SO}_2\cdot\text{NAg}\cdot\text{SO}_2\cdot\text{NAg}\cdot\text{SO}_2\cdot\text{NAg}\cdot\text{NH}_4$ or else a mixture of $2\text{SO}_2(\text{NHAg})_2$ and $\text{NAg}(\text{SO}_2\text{NH}_2)_2$. T. S. P.

Transformations of Selenium. MAURICE COSTE (*Compt. rend.*, 1909, 149, 674—675).—Sticks of fused selenium have D 4·302. On conversion into metallic selenium, cavities are formed, and although the product appears to have D 4·356, after repeatedly crushing and boiling the metallic selenium in toluene, it is found to have D 4·80. Metallic selenium is slightly soluble in potassium hydroxide, carbon disulphide, toluene, nitrobenzene, quinoline, and aniline. When crystallised by slowly cooling from 230° a solution in concentrated potassium hydroxide, metallic selenium is obtained in long needles of D 4·82 and m. p. 219°.

Rapid cooling of selenium solutions gives red selenium, which in presence of quinoline, aniline, or carbon disulphide, is converted into red crystals of D 4·455. Metallic selenium is not produced under these conditions, as supposed by Saunders, and although selenium precipitated by sulphur dioxide often turns black, it is owing to traces of the solvent, and the substance obtained does not melt below 250°. Crystalline red selenium is converted into metallic selenium by heating for some hours at 105—107·5°, or by raising the red selenium to its melting point (144°), when it is rapidly converted into the metallic variety, which solidifies.

The time required for the transformation of vitreous into metallic selenium in presence of toluene at 100°, as measured by the dilatometer, is one hour. The product contains cavities which render its density low. In presence of silver selenate, the rate of transformation is doubled, and the product, being without blow holes, has the full density. Arsenic, on the other hand, retards the transformation.

R. J. C.

Molecular Weight of Selenium in Solution. F. OLIVARI (*Atti. R. Accad. Lincei*, 1909, [v], 18, ii, 264—268. Compare this vol., ii, 805).—Further cryoscopic measurements confirm the existence of selenium in iodine solution in the form of Se_2 (compare this vol., ii, 39), but the molecular weight corresponding with the diatomic molecule is attained only in solutions of greater concentration than 5%; in more dilute solutions, lower molecular weights are observed. The selenium which crystallises from solution in iodine is insoluble in carbon disulphide, and seems to be the metallic modification. The change of colour occurring in the violet solutions of iodine in carbon disulphide on shaking with amorphous selenium (compare Beckmann, this vol., ii, 642) is not necessarily to be attributed to a combination taking place between the two elements, but may be explained by the superposition of the two absorption spectra: (1) of the violet solution of iodine, and (2) of the yellow solution of selenium in carbon disulphide.

T. H. P.

Complexity of Tellurium. PHILIP E. BROWNING and WILLIAM R. FLINT (*Amer. J. Sci.*, 1909, 28, 347—352; *Zeitsch. anorg. Chem.*, 1909, 64, 112—118. Compare Abstr., 1908, ii, 33; *Trans.*, 1907, 91, 1849).—When water is added in large amount to a solution of tellurium tetrachloride, this compound is hydrolysed, and the greater part of the tellurous acid is precipitated, whilst some of the tellurium remains in solution, however, large the amount of water present. The tellurium remaining in solution may be completely precipitated as the dioxide by heating to boiling, and treating first with ammonia and then with acetic acid in faint excess (this vol., ii, 934).

These observations suggested a possible method for decomposing tellurium, on the assumption that it is a complex substance. Ninety-two grams of purified tellurium were submitted to repeated fractionation, being first converted into the tetrachloride and precipitated as above, the two end-fractions being denoted as the water fraction (a) and the ammonia-acetic acid fraction (β). These two fractions were

converted into the basic nitrate, $2\text{TeO}_2 \cdot \text{HNO}_3$, and analysed according to three different methods, namely: 1. The basic nitrate method (Norris, *J. Amer. Chem. Soc.*, 1906, **28**, 1675). 2. Gooch and Danner's modification of Brauner's permanganate method (Abstr., 1893, ii, 15). 3. The ammonia-acetic acid method (*loc. cit.*). From the mean percentages of dioxide thus obtained, the atomic weight of tellurium in the α -fractions was calculated to be 126.53, 126.64, and 126.31 respectively, giving a mean of 126.49. From the β -fractions the calculated atomic weights were 128.97, 128.77, and 128.81, the mean being 128.85.

Two portions of tellurium dioxide from each fraction, prepared by the ignition of the basic nitrates, were dissolved in equal amounts of hydrochloric acid, and treated with equal amounts of boiling distilled water. The results obtained indicated different degrees of hydrolytic susceptibility on the part of the tetrachloride prepared from these fractions.

The material used in the above experiments was carefully examined for impurities, but such were not found. There is therefore no explanation of the differences observed other than the complexity of the original substance.

T. S. P.

Compounds of Ammonia and Water. ANDREAS SMITS and S. POSTMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 186—188).—In connexion with the question of the form in which ammonia is present in its aqueous solutions, the authors have determined what compounds are deposited when various mixtures of ammonia and water are cooled. The freezing-point curves indicate that the two compounds $\text{NH}_3 \cdot \text{H}_2\text{O}$ and $2\text{NH}_3 \cdot \text{H}_2\text{O}$ are formed; these melt at -77° and -78° respectively.

H. M. D.

Formation of Nitric Oxide in the Carbon Monoxide Flame. FRITZ HABER and JOSEPH E. COATES (*Zeitsch. physikal. Chem.*, 1909, **69**, 337—388).—The method of experiment was a modification of that described in previous papers (compare this vol., ii, 384, 801). The arrangements for working under high pressure (up to 45 atmospheres) are described in detail.

With a mixture of nitrogen and oxygen in equal volumes at the ordinary pressure, very little nitric oxide is obtained, even when the gases are previously warmed to 800° before entering the combustion chamber. The yield of nitrous products is greatly increased by increasing the pressure above 5 atmospheres. With the same mixture at 5 atmospheres, an amount of nitrous products equivalent to 4—5 mols. of nitric acid per 100 mols. of carbon dioxide is obtained without preliminary heating, and when the gases are previously heated, as much as 6 mols. of nitric acid are obtained. Increasing the pressure from 5 to 9 atmospheres increases the yield, but a further increase to 45 atmospheres has not much effect. When air is used instead of equal volumes of nitrogen and oxygen, and the gases are not previously heated, the yield is small even under pressure, but when the gases are previously heated, 3 mols. of nitric acid per 100 mols. of carbon dioxide are obtained. A considerable

increase of temperature does not greatly affect the yield, so that the temperature-coefficient of the reaction is very small under the experimental conditions.

The yield of nitric oxide is calculated on the assumption that equilibrium is established in the neighbourhood of 2400° , and that it is not displaced on cooling. A comparison appears to show that the amounts obtained are greater than the calculated values. Although this is not regarded as definitely proved, owing to the uncertainty of some of the assumptions made in the calculations, there appears to be some evidence that, apart from purely thermal effects, the occurrence of ionisation in certain regions of the flame is also of importance for the yield of nitrous products.

Nitric oxide is also formed by combination of nitrogen and oxygen in the electric arc, the electric spark, and at white-hot solid surfaces. Although in these circumstances the yields are not greater than the values calculated from the thermal effects alone, yet ionisation may play a part as well. Some support is afforded to this view by the fact that previous warming of the reacting substances greatly increases the yield of nitrous products. From purely thermal considerations, the yield must depend greatly on the prevention of decomposition of the products by cooling them as rapidly as possible, and this would not be favoured by previous warming of the reacting substances.

G. S.

Dynamic Allotropy of Phosphorus. ERNST COHEN and J. OLIE, Jun. (*Chem. Weekblad*, 1909, 6, 821—848. Compare Hittorf, *Ann. Phys. Chem.*, 1865, 126, 193; Lemoine, this Journ., 1871, 24, 1157; Troost and Hautefeuille, *Abstr.*, 1874, 769; Arctowski, *Abstr.*, 1896, ii, 559; Chapman, *Trans.*, 1899, 75, 734; Noelting and Feuerstein, *Abstr.*, 1900, ii, 722; Giran, *Abstr.*, 1903, ii, 362; Schenck, *Abstr.*, 1905, ii, 244; Siemens, *Abstr.*, 1906, ii, 847; Böeseken, *Abstr.*, 1907, ii, 343, 760; and Colson, *Abstr.*, 1908, ii, 273).—From experiments on the specific gravity, heat of combustion, fusion, and vapour pressure of samples of red phosphorus, the authors conclude that only two allotropic modifications of phosphorus exist: white phosphorus and Hittorf's metallic phosphorus. They are to be regarded as dynamic allotropes. Red phosphorus is a solid solution of white phosphorus in the metallic modification, its composition depending on the temperature of formation and other factors. Since the physical constants for red phosphorus given in the literature are not those of an individual substance, they are without scientific significance.

A. J. W.

Solubilities of Orthophosphoric Acid and its Hydrates. A New Hydrate. ALEXANDER SMITH and ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1909, 31, 1183—1191).—This investigation was undertaken with the object of studying the hydrates of orthophosphoric acid. The method employed consisted in making a series of determinations of the concentrations of saturated solutions in stable equilibrium with the solid phase between -16.3° and 42.3° (the m. p. of orthophosphoric acid). The results show that only two hydrates exist,

namely, Joly's hydrate, $2\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (Abstr., 1885, 483), and a new hydrate, $10\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$. The solubility curves of these hydrates have been constructed. The m. p.'s of Joly's hydrate and orthophosphoric acid have been re-determined, and found to be 29.35° and 42.30° respectively. The vapour pressure of Joly's hydrate is 0.85 mm. at 25° .

The author criticises Giran's work (Abstr., 1908, ii, 685), in which an attempt was made to determine the hydrates formed by the phosphoric acids by measuring the initial f. p.'s of mixtures of water with each acid. It is stated that Giran's failure to discover the new hydrate was due to his method being insufficiently refined. E. G.

Electrical Conductivity and Viscosity of Concentrated Solutions of Orthophosphoric Acid. ALEXANDER SMITH and ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1909, 31, 1191—1194).—Of the three hydrates of sulphuric acid, only one influences the electrical conductivity. The present work was undertaken to ascertain whether the conductivity of phosphoric acid solutions is similarly related to one or both of the hydrates. The conductivity has been determined at concentrations between 89.7% and 98.8% at 29.30° . The results are tabulated and plotted as a curve, which does not show any tendency to bend at concentrations corresponding with the compositions of the hydrates. Orthophosphoric acid therefore differs from sulphuric acid in this respect. The relative viscosities of solutions of phosphoric acid of concentrations varying from 90.6% to 98.1% were determined at 25° . The curve obtained from the results does not show any marked bend. E. G.

Solubility and Hydrates of Boric Acid. RAFFAELLO NASINI and I. AGENO (*Zeitsch. physikal. Chem.*, 1909, 69, 482—485).—The solubility of boric acid in water has been determined between 0° and 120° . Some of the results, in grams H_3BO_3 in 100 grams of the solution, are as follows: 2.59 at 0° , 4.90 at 21° , 8.02 at 40° , 12.90 at 60° , 19.11 at 80° , 28.10 at 99.5° , 52.4 at 120° . Concordant results could not be obtained at higher temperatures (in sealed tubes) owing to the action of boric acid on glass.

The molecular weight of boric acid in water, as determined by the ebullioscopic method, is normal up to a concentration of 30%.

The formation of lower hydrates of boric acid on heating has been investigated by the dilatometer method. At 107 — 108° , metaboric acid is formed, and at 138 — 140° , pyroboric acid. The formation of the former acid has been confirmed by a molecular weight determination by the ebullioscopic method in anhydrous acetic acid; observed value = 38.3, theoretical value 44. G. S.

The Decolorising Properties of Amorphous Carbon. LOUIS PELET-JOLIVET and C. MAZZOLI (*Bull. Soc. chim.*, 1909 [iv], 5, 1011—1019).—It has been shown previously (Freundlich and Losev, Abstr., 1907, ii, 534, and Pelet and Grand, *Rev. gen. Mat. Col.*, 1907, 11, 225) that the absorption of colouring matters by charcoal is analogous to the absorption of dyes by textile fabrics and follows the same law.

Glassner and Suida (Abstr., 1907, ii, 932) have suggested that the absorption by charcoal is due to the presence of substances containing cyanogen groups.

In the present investigation, sixteen commercial charcoals of animal and vegetable origin have been compared as regards their decolorising powers for methylene-blue and ponceau dyes, and it was found that there was no relation between the decolorising power of a charcoal and its nitrogen content. Further, purification of the charcoal in various ways made little difference to its decolorising power, due allowance being made for experimental error. T. A. H.

Diamonds in Iron. BERNHARD NEUMANN (*Zeitsch. Elektrochem.*, 1909, 15, 817—820).—An historical account of the investigations concerning the occurrence of diamond in meteoric and technical iron. The "diamonds" which have been observed in the latter are now proved by the work of Otto Johannsen (*Stahl und Eisen*, 1908, 29, 348) to be crystals of corundum. T. E.

Transformation of Diamond into Graphite. RUDOLF VOGEL and GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1909, 69, 598—602).—The experiments were undertaken with the object of finding at what temperature diamond changes to graphite. Most of the observations were made with splinters of Cape diamonds, which were placed in glazed, sealed porcelain tubes, and heated in an electric furnace. At 1000°, the change is exceedingly slow, and may not occur at all; at 1200° a considerable transformation takes place within twenty-four hours, and at 1500° is relatively rapid. A piece of diamond, which was heated at 1600° in fused calcium silicate, so as to exclude air, was also superficially changed to graphite. G. S.

Apparatus for Separating the Inactive Gases from Mixtures by means of the Electric Flame. FERDINAND HENRICH (*Zeitsch. Elektrochem.*, 1909, 15, 749—751).—The current from an induction coil (supplied with alternating current at 110 volts and 4 amperes) is passed between thick platinum wire electrodes in a glass tube 3.5 cm. wide. The essential feature of the apparatus is that the tube is drawn out to a conical shape just above the arc, and sealed to a narrow tube through which a solution of sodium hydroxide is continuously supplied. This spreads over the glass in a thin film, cooling it and absorbing the nitrogen peroxide. The solution flows off continuously through a lute at the bottom of the tube. T. E.

Existence of Double Salts, in particular of Carnallite and Schoenite, in Aqueous Solution. ROBERT KREMANN (*Jahrb. K. K. Geol. Reichsanstalt*, 1908, 58, 71—78).—The question as to whether the double salts, carnallite and schoenite, are present in aqueous solutions of the respective component simple salts has been examined. In the case of carnallite, the concentrations of solutions of potassium chloride and of sodium chloride were determined, which, according to conductivity measurements, are isohydric with various solutions of

magnesium chloride. The fact that the isohydric solutions of potassium chloride are more concentrated than those of sodium chloride is regarded as evidence in favour of the existence of undecomposed carnallite in the more concentrated potassium magnesium chloride solutions. In more dilute solutions, no essential difference between the concentrations of the isohydric potassium and sodium chloride solution is found, indicating that the double salt molecules are more or less completely decomposed.

Similar differences are found when solutions of magnesium and of zinc sulphate are compared with reference to potassium sulphate solutions. The differences in question indicate that the corresponding double salts are unequally stable in aqueous solutions of the same molar concentration.

H. M. D.

Monoclinic Modification of Potassium Dichromate. OTTO HAUSER and H. HERZFELD (*Zeitsch. physikal. Chem.*, 1909, **68**, 175—176).—When hot concentrated solutions of potassium dichromate and of potassium thiocyanate are mixed, the dichromate crystallises on cooling in yellowish-brown, doubly-refracting, monoclinic plates. The density of this form is 2.10, whereas that of the ordinary triclinic variety is 2.67. The monoclinic dichromate is unstable, and is transformed into the triclinic salt when kept in contact with its saturated solution or in moist air. It seems probable that the new form of the potassium salt is isomorphous with monoclinic ammonium dichromate.

H. M. D.

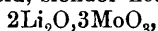
Monoclinic Variety of Sodium Alums. N. I. SURGUNOFF (*Bull. Acad. Sci. St. Pétersbourg*, 1909, 1057—1065).—A solution of sodium alum, which is supersaturated at 20° or some lower temperature, deposits crystals of the cubic system, but if supersaturation occurs at a temperature higher than 20°, monoclinic crystals,

$$a:b:c = 2.5101:1:0.9078; \beta = 109^{\circ}1',$$

are deposited. The composition of the monoclinic crystals is found to correspond almost exactly with the formula: $\text{Na}_2\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$.

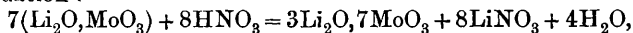
T. H. P.

Lithium Molybdates. FRITZ EPHRAIM and MAX BRAND (*Zeitsch. anorg. Chem.*, 1909, **64**, 258—262).—The only lithium molybdate hitherto known, $\text{Li}_2\text{O} \cdot \text{MoO}_3$, forms white, anhydrous, monoclinic needles, readily soluble in water to an alkaline solution. It does not form isomorphous mixtures with ammonium molybdate. With a slight excess of molybdic acid, slender needles of the salt,

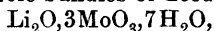


are obtained, and may be recrystallised from water, in which it is rather sparingly soluble. With hydrochloric acid, groups of needles of the salt, $\text{Li}_2\text{O} \cdot 2\text{MoO}_3 \cdot 5\text{H}_2\text{O}$, are obtained, readily soluble in hot water. It loses one-third of its water of crystallisation at 120°, the remainder only at a red heat.

Lithium paramolybdate, $3\text{Li}_2\text{O} \cdot 7\text{MoO}_3 \cdot 28\text{H}_2\text{O}$, prepared according to the equation:

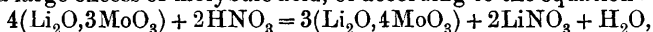


crystallises in readily soluble bundles of needles. The salt,



obtained by evaporating a solution of the next salt, removing crystals of molybdic acid, and concentrating further, forms long, slender needles. If fused and ignited in hydrogen, a dark violet, lustrous solid is obtained, resembling the alkali tungsten bronzes.

The salt, $\text{Li}_2\text{O}, 4\text{MoO}_3, 7\text{H}_2\text{O}$, obtained by boiling lithium carbonate with a large excess of molybdic acid, or according to the equation:



forms an amorphous, yellow mass, gradually becoming hard and brittle. Salts containing larger quantities of molybdenum could not be obtained.

C. H. D.

Isomorphism of Sulphates, Selenates, and Tellurates.

GIOVANNI PELLINI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 279—282).—From solutions containing various proportions and amounts of rubidium hydrogen selenate and rubidium hydrogen tellurate, the author has obtained mixed crystals containing from 51.55 to 67.46% (mol.) of the selenate. With solutions still richer in the selenate, crystals containing proportions up to 100% of the latter can be obtained. There exists, however, a limit to the proportion of the tellurate in the mixed crystals, since all solutions containing more than about 50% (mol.) of the tellurate deposit the latter in a pure state. The solubility isotherm exhibits all the characters indicative of isodimorphous salts, but no crystallographic measurements have as yet been made of the two salts and the mixed crystals.

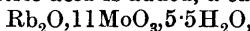
With mixed solutions of rubidium hydrogen sulphate and rubidium hydrogen tellurate, most of the results obtained can be interpreted by assuming the formation of a double salt, $\text{RbHTeO}_4, \text{RbHSO}_4$, but indications are given of a tendency to form mixed crystals.

T. H. P.

Rubidium and Cæsium Hydrogen Carbonates. ROBERT DE FORCRAND (*Compt rend.*, 1909, 149, 719—721. Compare this vol., ii, 730).—Hydrogen carbonates of rubidium and cæsium are prepared from concentrated solutions of the normal carbonates by saturating them with carbon dioxide and drying over phosphoric oxide in an atmosphere of carbon dioxide. The anhydrous hydrogen carbonates are obtained as monoclinic prisms, or, occasionally, in the case of the rubidium salt, long needles. These salts, which are not hygroscopic, are very soluble in water, the rubidium salt requiring 7.02 equivalents of water, and the cæsium salt 5.13 equivalents, for solution at 20°. They are also soluble to the extent of 2% or more in alcohol, in which potassium hydrogen carbonate is nearly insoluble. Rubidium and cæsium hydrogen carbonates, which are more stable than the potassium salt, are unaffected at 125°, and only converted into normal carbonates at 175° in a current of inert gas. The heats of dissolution at 15° are as follows: KHCO_3 - 5.320 Cal., RbHCO_3 - 4.731 Cal., CsHCO_3 - 4.317 Cal. The heats of neutralisation and of formation from the elements are remarkably similar for potassium, rubidium, and cæsium hydrogen carbonates, whereas the sodium salt gives distinctly smaller values.

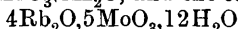
R. J. C.

Rubidium and Cæsium Molybdates. FRITZ EPHRAIM and HEINRICH HERSCHFINKEL (*Zeitsch. anorg. Chem.*, 1909, 64, 263—272. Compare this vol., ii, 1001).—*Rubidium molybdate*, $\text{Rb}_2\text{O}, \text{MoO}_3$, prepared by dissolving molybdenum trioxide in a warm solution of rubidium hydroxide, evaporating, and washing the deliquescent mass with alcohol, forms white crusts. The salt, $\text{Rb}_2\text{O}, 2\text{MoO}_3, 2\text{H}_2\text{O}$, obtained on evaporating solutions containing nitric acid, forms readily soluble prisms or plates. A corresponding potassium salt is not known. With a slight excess of nitric acid, a white precipitate of the salt, $\text{Rb}_2\text{O}, 4\text{MoO}_3, 2\cdot5\text{H}_2\text{O}$, insoluble in water, is obtained. If four times the quantity of nitric acid is added, a salt,



is obtained in pale yellow, microscopic needles on heating. With still larger quantities of nitric acid, the yellow salts, $\text{Rb}_2\text{O}, 13\text{MoO}_3, 4\text{H}_2\text{O}$ and $\text{Rb}_2\text{O}, 18\text{MoO}_3$, are obtained.

By boiling rubidium molybdate with molybdic acid, and crystallising the solution, crystals of the salt, $\text{Rb}_2\text{O}, 4\text{MoO}_3, 0\cdot5\text{H}_2\text{O}$, the *paramolybdate*, $3\text{Rb}_2\text{O}, 7\text{MoO}_3, 4\text{H}_2\text{O}$, and the salts,



and $5\text{Rb}_2\text{O}, 7\text{MoO}_3, 14\text{H}_2\text{O}$, which may be isomorphous mixtures, are obtained. The paramolybdate is partly decomposed by hot water, giving salts of the approximate composition: $3\text{Rb}_2\text{O}, 8\text{MoO}_3, 6\text{H}_2\text{O}$ and $\text{Rb}_2\text{O}, 3\text{MoO}_3, 6\cdot5\text{H}_2\text{O}$.

Similar cæsium molybdates are obtained, having the formulæ: $\text{Cs}_2\text{O}, 5\text{MoO}_3, 3\text{H}_2\text{O}$; $\text{Cs}_2\text{O}, 3\text{MoO}_3, \text{H}_2\text{O}$ (or $3\text{Cs}_2\text{O}, 10\text{MoO}_3, 3\text{H}_2\text{O}$); $2\text{Cs}_2\text{O}, 5\text{MoO}_3, 5\text{H}_2\text{O}$, and $\text{Cs}_2\text{O}, 16\text{MoO}_3, 8\text{H}_2\text{O}$. C. H. D.

The Action of Ozone on Metals and the Cause of Passivity. WILHELM MANCHOT (*Ber.*, 1909, 42, 3942—3948. Compare Manchot and Kampschulte, *Abstr.*, 1907, ii, 616).—The author's previous investigations have shown that silver only reacts with ozone in the cold when a small quantity of oxide, either chemically deposited or mechanically attached, is present. The action of cold 3% ozone is a sensitive means of detecting a film of oxide in silver and other metals. Silver is shown to form a thin film of oxide in air at 200° . A plate of silver, heated in this way or dipped in concentrated nitric acid and washed, is anodic to clean untreated silver.

Passivity is due to the formation of a thin film of oxide. The gradual spontaneous disappearance of the passivity, which has been considered to be inconsistent with the oxide hypothesis, is due to the mechanical flaking-off of the film. This process can be observed in the case of mercury at 55° .

Cadmium, iron, copper, and zinc react with oxygen at a temperature only slightly above that at which they react with ozone. Tin reacts readily with ozone at 500° , and nickel at 415° . Lead at 227° reacts like silver at 240° . Lead and iron, rendered passive by immersion in nitric acid and well washed, react almost instantaneously with ozone in the cold, and the same is observed with iron rendered passive by being made the anode in dilute sulphuric acid.

C. H. D.

Solubility of Hydrogen and Oxygen in Solid and Fused Silver. ADOLF SIEVERTS and JOH. HAGENACKER (*Zeitsch. physikal. Chem.*, 1909, 68, 115—128. Compare Abstr., 1907, ii, 741).—The measurements were made in an apparatus consisting essentially of a porcelain tube (containing the silver) connected to a manometer and to a tube for removing or admitting gases; the porcelain tube was electrically heated when necessary.

Hydrogen is not absorbed either by solid or fused silver.

Solid silver absorbs very little oxygen, but when the metal is fused, absorption is rapid, and equilibrium is reached in about fifteen minutes. One volume of silver absorbs 20.3 volumes of oxygen at 973° under 760 mm. oxygen pressure, and 17.56 volumes at 1125°, the amount diminishing regularly with increased temperature. As regards the relationship between the pressure, p , and the amount, m , of oxygen absorbed, the equation $\sqrt{p}/m = \text{constant}$ holds approximately. Henry's law, therefore, does not apply to the solubility of oxygen in fused silver; when the pressure is reduced to one-fourth of its value, the amount of gas absorbed is reduced to one-half. G. S.

Action of Heat on Silver Sulphite and its Alkali Double Sulphites. Formation of a Dithionate. HENRI BAUBIGNY (*Compt. rend.*, 1909, 149, 735—737).—Silver sulphite is said to be decomposed by boiling water into silver sulphate, sulphur dioxide, and metallic silver, but in presence of excess of alkali sulphite, the whole of the silver is precipitated. The author shows that only a small proportion of the silver sulphite is decomposed in this way, more than 80% being converted into dithionate: $2\text{Ag}_2\text{SO}_3 \rightarrow \text{Ag}_2\text{S}_2\text{O}_6 + 2\text{Ag}$, and it is only at a much higher temperature that sulphate and sulphur dioxide are produced from the dithionate. Double sulphites are converted almost quantitatively (95%) into dithionates: $2\text{AgNaSO}_3 \rightarrow \text{Na}_2\text{S}_2\text{O}_6 + 2\text{Ag}$, and the whole of the silver is precipitated. After precipitating any excess of alkali sulphite by barium chloride, only a slight odour of sulphur dioxide can be detected, but the solution then contains barium dithionate.

The formation of dithionates from sulphites is analogous to the formation of trithionates from the double thiosulphates of alkali and heavy metals (Spring, this Journ., 1875, 129). R. J. C.

Volatility of the Bromides of Radium, Barium, Strontium, and Calcium. ALFRED STOCK and HANS HEYNEMANN (*Ber.*, 1909, 42, 4088—4093).—Experiments have been made to see if radium bromide could be conveniently separated from barium bromide by fractional sublimation. The substance to be investigated was gradually heated in a quartz tube, and the temperature noticed at which a definite deposit was formed on the cold part of the tube. These sublimation temperatures could be sharply determined in the case of the bromides of calcium, strontium, and barium; they were respectively 720°, 770°, and 820°. Barium bromides containing 1/1000, 1/100, and 6% respectively of radium bromide were then investigated; the sublimate formed were collected while the tube

was heated to about 900° for some hours. A first and smaller sublimate was generally collected, and then a second larger one.

It was found (1) that radium bromide is less volatile than barium bromide; (2) that by fractional sublimation the residue becomes richer in radium. The radium concentrations in the residue and sublimate are all the more different the smaller the quantity of the latter.

T. S. P.

Preparation of Compounds containing Active Oxygen.

EMANUEL MERCK (D.R.-P. 213457).—When the alkali hydrogen sulphates, or hydrogen carbonates, are treated in aqueous solution with the alkaline earth peroxides, or perhydroxides, the corresponding *peroxysulphates* or *peroxycarbonates* are formed, as represented by the equation: $\text{Ba(OH)}_4 + 2\text{NaHCO}_3 = \text{BaCO}_3 + \text{Na}_2\text{CO}_4 + 3\text{H}_2\text{O}$.

F. M. G. M.

Loss [of Weight] of Heavy Spar on Heating. WILHELM VAUBEL (*Chem. Zeit.*, 1909, 33, 1121—1122).—Barium sulphate shows a loss of weight when heated for an hour in the Bunsen flame. The resulting product is alkaline, and contains an appreciable quantity of barium sulphide. It has been found that certain heavy spars lose from 0.5 to 0.7% in weight on heating, and a portion of this has been traced to the evolution of carbon dioxide.

H. M. D.

Solutions of Lime and Silica in Fused Calcium Chloride.

KURT ARNDT and WILLI LOEWENSTEIN (*Zeitsch. Elektrochem.*, 1909, 15, 784—790).—Between 860° and 940°, 100 grams of calcium chloride dissolve 16.2 grams of calcium oxide. Silica dissolves slowly, chlorine being evolved and calcium orthosilicate formed. The percentages of silica in the saturated solutions are at 800°, 2.5; 850°, 3.8; 900°, 5.4; 950°, 7.6. When a solution of lime in calcium chloride is fused in a porcelain tube, it dissolves nearly one molecule of silica for two molecules of lime in solution. The conductivities of several solutions of this kind are measured; the results are in harmony with the view that the calcium orthosilicate and lime in solution diminish the conductivity of the calcium chloride independently and in proportion to their quantity. From the measurements, the specific conductivity of pure calcium chloride is extrapolated; it is at 800°, 2.10; 850°, 2.27; 900°, 2.40; 950°, 2.51. The densities of solutions of lime in calcium chloride are also determined; the density increases by 0.009 for each 1% of dissolved calcium oxide; the density of pure calcium chloride is at 800°, 2.048; 850°, 2.026; 900°, 2.002. One per cent. of calcium orthosilicate increases the density by 0.012. The equivalent conductivity of calcium chloride is calculated from these data.

T. E.

Permeability of Glass to Vapours. HANS LANDOLT (*Zeitsch. physikal. Chem.*, 1909, 68, 169—174).—On the basis of experiments which appeared to indicate that many gases and vapours can pass through glass at the ordinary temperature, Zengelis (this vol., ii, 134) has suggested that Landolt's experiments, relating to the total weight

of substances before and after chemical reaction, afford evidence of a real loss of weight in certain cases. To test the possibility of the correctness of this view, the author has made experiments with solutions of silver sulphate and ferrous sulphate, and with solutions of hydriodic and iodic acids, under conditions similar to those employed by Zengelis. Samples of the same glass as that used in the weight experiments were employed, but entirely negative results were obtained. With sealed vessels of thinner glass, the results were also negative. As a result of these measurements, the explanation previously given (Abstr., 1908, ii, 366) of the observed small changes in weight of the above-mentioned substances on reaction requires no modification. The fact that the changes were found to be smaller in vessels which were covered on the inside with a layer of paraffin, is attributed to the low thermal conductivity of the paraffin layer.

H. M. D.

Zinc Alloys. B. E. CURRY (*J. Physical Chem.*, 1909, 13, 589—605).—The work of Mönkemeyer (Abstr., 1905, ii, 171) and Schemtschuschny (Abstr., 1906, ii, 549) on the freezing-point curve of zinc-antimony alloys indicated the existence of two compounds, ZnSb and Zn_3Sb_2 , and of three eutectic mixtures. An inversion point was noticed in the cooling curves of all alloys between Zn_3Sb_2 and pure Zn. This point, about 321° in Mönkemeyer's experiments, was supposed to indicate an allotropic form of zinc, but Schemtschuschny showed that the inversion was in the alloy Zn_3Sb_2 . It is now shown that considerable errors due to supercooling were present in the experiments referred to. The author's experiments were made on the heating, instead of cooling, curves of well annealed ingots.

The curve obtained exhibits only one maximum and two eutectics. The compound ZnSb (35% Zn) is confirmed. Both microscopical and thermal data disprove the formation of a compound Zn_3Sb_2 . A solid solution of the alloy ZnSb and zinc begins to appear above 35% zinc. Alloys from 40% to 45% of zinc are homogeneous whether chill cast or annealed, and consist of crystals of solid solution. Beyond 45% the solid solution crystals are mixed with crystals of zinc. The solid solution shows a maximum melting point, 565° , at 45%.

The heating curves of all alloys containing the solid solution exhibit, not one, but two inversion temperatures. The solid solution therefore exists in three forms: α , β , and γ . In presence of zinc, that is, in alloys containing more than 45% of zinc, γ is transformed into β at 405° , and β into α at 437° . In presence of the compound SbZn , that is, in alloys containing 35—40% of zinc, the transformation temperatures are 485° and 500° respectively. In solid solutions containing 40—45% of zinc, crystallising homogeneously, the transformation temperatures are intermediate and vary with the composition. The one inversion point noticed by Mönkemeyer and Schemtschuschny is more than 70° too low, owing to supercooling. The freezing-point curve cuts the transformation curve of β into α (437°) at 95% of zinc, so that between 95% and 100% of zinc no α is formed from the melt.

The eutectic mixture at 97.5% of zinc, solidifying at 411° , that is, above the transformation temperature of γ into β , consists of β and

pure zinc. No microscopic difference can be detected between α , β , and γ , the evidence for which is entirely thermal. The compound ZnSb does not form solid solutions with antimony.

Alloys of zinc with tin contain no compounds, the only two phases being pure zinc and a solid solution of zinc in tin containing up to 5% of zinc if chill cast or 7% after annealing at 180° .

Zinc cadmium alloys give a similar curve, but the phases are two series of solid solutions of zinc in cadmium and of cadmium in zinc, containing upwards of 4% and 5% of solute respectively after annealing at 217° .

The miscibility of zinc with lead and of zinc with bismuth is very slight. Practically pure lead and zinc separate from all mixtures of the two, distinct layers being formed. The liquid phases become more miscible as the temperature rises, until near 920° the liquid is homogeneous.

Mixtures of zinc and bismuth deposit two phases, namely, pure zinc and a solid solution of zinc in bismuth, containing upwards of 4%. The melted mixture becomes homogeneous at 820° . R. J. C.

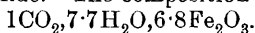
Action of Carbon and Silicon on Zinc Sulphide at High Temperatures. WALTER FRAENKEL (*Metallurgie*, 1909, 6, 682—688).—Mixtures of zinc sulphide and carbon are known to volatilise at high temperatures. When the mixture is heated in a quartz vessel to 1300 — 1400° in an atmosphere of nitrogen, a volatile product is obtained, containing zinc, carbon, and sulphur, which reacts with the silica of the enclosing vessel. The product is also volatile, and corresponds approximately with the composition ZnSSi . Using a carbon lining to the tube, the vapours nevertheless penetrate to the quartz, and introduce silicon into the mixture.

The compound, ZnSSi , is also obtained by heating zinc sulphide to 1300° with silicon. It condenses to hard, brown crusts. With acids the sulphur is evolved quantitatively as hydrogen sulphide, and with aqueous alkalis, hydrogen is evolved. It may be polished like a metal, and is microscopically homogeneous. The electrical conductivity is less than that of silicon. C. H. D.

Carbonates of Some Heavy Metals. KARL FEIST (*Arch. Pharm.*, 1909, 247, 439—447).—The preparation of pure basic carbonates of metals such as zinc is a very tedious operation, owing to the difficulty of washing the voluminous precipitates produced when solutions of the salts are precipitated with sodium carbonate. This difficulty is met by grinding the crystalline salt of the heavy metal with a slight excess of crystallised sodium carbonate until no more carbon dioxide is evolved and the whole mass has become liquid. Water is then added, the precipitate washed by decantation, since it readily settles, and dried.

Zinc sulphate gave a basic carbonate having the composition $1\text{H}_2\text{O}, 1.03\text{CO}_2, 2.15\text{ZnO}$, which agrees approximately with the formula $\text{ZnCO}_3 \cdot \text{Zn}(\text{OH})_2$. In only one case was a good result obtained with copper sulphate, the precipitate generally retaining basic sulphate. With lead nitrate or acetate a basic carbonate intermediate in

composition between that of the normal carbonate and that of white lead was produced. Aluminium sulphate gave a precipitate which contained a basic sulphate and also a basic carbonate, which could not be removed by washing. With ferric chloride ($\text{FeCl}_3, 12\text{H}_2\text{O}$) a neutral dark brown powder was obtained, which dissolved in acids with evolution of carbon dioxide. The composition was



Continued washing with water gradually removed the basic carbonate, because of hydrolysis, and then the precipitate no longer settled rapidly.

T. S. P.

Metastability of the Metallic World. ERNST COHEN and KATSUJI INOUE (*Chem. Weekblad*, 1909, 6, 881—892. Compare Cohen, Abstr., 1908, ii, 858).—Metals in ordinary use are in a metastable condition, and can be changed into a more stable state, not only by rise of temperature, but also by inoculation. When a strip of lead having a cross etched on its surface by the action of 50% nitric acid for thirty minutes, is kept in contact under pressure with a similar unetched lead strip at 180° for seventeen hours, the cross is found to be developed on the second strip. Similar results can be obtained by inoculating zinc with zinc, brass with brass and copper, copper with copper, and bismuth with bismuth, the extent of the inoculation depending on the nature of the metallic substances and the experimental conditions. The temperatures employed by the authors were 100° and 180° , and the duration of the experiments varied between seventeen and forty-eight hours. Contact under pressure at ordinary temperatures does not induce the inoculation. All the metals and alloys employed in the experiments had been rolled out in strips, and therefore had been submitted to severe mechanical strain.

The decay of lamp reservoirs made of rolled brass, stamped out to the required form, as well as that of door handles and other metallic objects, is attributed by the authors to a tendency to pass into a more stable condition. The appearance of the corroded parts, viewed through the microscope, is similar to that of the metal after etching, whilst that of the sound portions resembles the appearance of freshly-rolled brass.

A. J. W.

New Method for Determining the Composition of Mixed Crystals Deposited by Alloys at Different Temperatures. DOMENICO MAZZOTTO (*Nuovo Cim.*, 1909, [v], 18, ii, 180—196).—This method, which is based on a knowledge of the heats of fusion developed when the mixed crystals solidify, may be used for determining the compositions of the mixed crystals separating, not only at the eutectic point, but also at higher temperatures. If an alloy of two metals, *A* and *B*, having the composition *a*, begins to solidify at the temperature *t*, higher than the eutectic temperature, and if also the concentration *a*₁ corresponds with some lower temperature *t*₁, and *p* be the weight of the crystals deposited between the temperatures *t* and *t*₁, then unit weight of the alloy may be divided into two parts: (1) a weight *p* of crystals of unknown composition *a*₂, and (2) a weight $1 - p$ of liquid alloy of composition *a*₁. The weight of the component *A* contained in

the crystals (1) will be pa_2 , and in the liquid portion $(1-p)a_1$, so that $pa_2 + (1-p)a_1 = a$ or $a_2 = (a - a_1)/p + a_1$. The value of p is given by the formula $p = Q/c$, where Q represents the number of calories developed in the partial solidification occurring between the temperatures t and t_1 and c the mean heat of fusion of the solid deposited, which can be determined by the formula $c = (c_2 - Q_1)/(1 - Q_1/c_1)$, Q_1 being the heat developed by solidification of the alloy down to the eutectic point, c_1 the heat of fusion of the eutectic alloy, and c_2 the total heat of fusion of the alloy. If a_2 is found to have the value 0, it is evident that the component B is deposited in the pure state from alloys which, with respect to the eutectic, have an excess of B , whilst if $a_2 = 1$, the pure component A is deposited from alloys containing excess of A . In the case in which the alloy solidifies completely above the eutectic point, Q would have the value zero and $c = c_2$. The case when t_1 corresponds with the eutectic temperature is discussed with the help of a construction similar to that employed by Tammann (Abstr., 1904, ii, 113; 1905, ii, 444) in the thermal analysis of crystallised chemical compounds, the ordinates representing, not the duration of the arrest of the thermometer at the eutectic point, but the heats developed by the solidification of the separate alloys down to the eutectic point.

The method is applied to the following binary alloys: (1) Lead and tin; the results obtained are in good agreement with those of Rosenhain and Tucker (Abstr., 1908, ii, 1038). (2) Tin and zinc.—Here the values of c for alloys containing excess of tin ($a = 0.952$ or 0.941) or excess of zinc are higher than the respective heats of fusion of pure tin and zinc; this phenomenon is probably connected with the large amount of heat absorbed in the formation of these alloys. The alloys rich in zinc deposit pure zinc, and those rich in tin, pure tin. (3) Tin and bismuth.—The results here indicate that the mixed crystals at the eutectic point contain 16% of bismuth. Alloys with excess of bismuth (a for tin = 0.200 and 0.111) deposit either pure bismuth or crystals containing a very small proportion of tin. (4). Bismuth and lead.—In this case the values of c for alloys containing excess of bismuth differ little from the heat of fusion of this metal, but for other alloys, for instance, the eutectic, the values of c are very low compared with those for the two components; this behaviour is doubtless related to the large amount of heat developed in the formation of these alloys. The alloys with excess of bismuth deposit this metal in a sensibly pure state, but with those containing excess of lead, mixed crystals containing proportions of bismuth varying up to a maximum of 38–39% are deposited.

T. H. P.

Two Lead Silicates. HERMON C. COOPER, L. I. SHAW, and N. E. LOOMIS (*Ber.*, 1909, 42, 3991–3993; *Amer. Chem. J.*, 1909, 42, 461–473. Compare this vol., ii, 890).—A number of mixtures of lead oxide and finely-powdered quartz, in which the proportions varied from 100 to 43 equivalents % of lead oxide, have been investigated. In order to obtain an uniform composition, the mixtures were melted, then cooled, and the solid finely-powdered, again melted,

slowly cooled, and powdered; the resulting powder could then be used for the investigation proper. This method of procedure was necessary, since no conclusions could be drawn from the cooling curves owing to the large amount of supercooling. The heating curves were therefore taken, and the results obtained point to the existence of two lead silicates, namely, the ortho-silicate, Pb_2SiO_4 , melting at 746° , and the meta-silicate, PbSiO_3 , melting at 766° . Lead oxide was found to melt at 888° .

When quickly cooled, all fusions containing less than 80 equivalents % of lead oxide give clear, coloured glasses. When slowly cooled, all fusions containing more than 60 equivalents % of lead oxide crystallise completely; those which are richer in silica crystallise only in part, but if the resulting solid is finely powdered and heated for several hours to a temperature which is $10\text{--}100^\circ$ lower than the melting point, a sintered, crystalline mass is obtained.

T. S. P.

Co-precipitation of Thallium Sulphide with other Sulphides.

LUDWIK BRUNER and J. ZAWADSKI (*Bull. Acad. Sci. Cracow*, 1909, 312—321).—If thallium is precipitated as sulphide from solutions containing other metals, the value of the constant $k = [\text{Ti}']^2[\text{H}_2\text{S}]/[\text{H}']^2$ will be affected if sulphides of the other metals are precipitated along with the thallium. The relation between the value of the constant and the molar composition of the precipitate will give information as to the nature of the precipitate.

Qualitative experiments showed that besides the sulphides of the arsenic sub-group, the sulphides of mercury and copper are thrown down together with thallium from acid solutions; lead and cadmium sulphides do not carry down thallium sulphide with them. Quantitative experiments were made in the presence of arsenic and copper salts, the equilibria being determined from both sides as follows: Solutions containing thallium sulphate and either arsenious oxide or copper sulphate were treated at 25° with hydrogen sulphide, or else the precipitate so obtained was treated with sulphuric acid in a current of hydrogen sulphide. Equilibrium is attained only after a very long time, in some cases only after two or three months.

Arsenious sulphide forms a series of solid solutions with thallium sulphide from pure arsenious sulphide to 73.5 mols. % of thallium sulphide. Above 73.5 mols. % the normal value for the equilibrium constant is obtained, and the precipitate can be seen to contain two phases, namely, black, crystalline thallium sulphide and a brown, solid solution of arsenious and thallium sulphides.

Cupric sulphide forms a compound, $\text{Tl}_2\text{S}_4\text{CuS}$, with thallium sulphide, and over the interval 20—36 mols. % of thallium sulphide it forms a series of solid solutions which are best explained as being solutions of $\text{Tl}_2\text{S}_2\text{CuS}$ in $\text{Tl}_2\text{S}_4\text{CuS}$, and of Tl_2S in $\text{Tl}_2\text{S}_2\text{CuS}$. At concentrations of more than 36 mols. %, normal values of the equilibrium constant are obtained; there are then two solid phases, consisting of thallium sulphide and probably a solid solution of thallium sulphide in the compound $\text{Tl}_2\text{S}_2\text{CuS}$.

T. S. P.

The Occurrence of Copper in the Stassfurt Potash Deposits. WILHELM BILTZ and E. MARCUS (*Zeitsch. anorg. Chem.*, 1909, 64, 236—244).—The samples of potash deposits recently examined for the presence of ammonia and nitrates (this vol., ii, 571) have now been tested for copper, which has been proved to exist in sea-water.

Copper sulphide is soluble in concentrated solutions of sodium chloride. For rock-salt specimens, therefore, 200 grams are dissolved in 650 c.c. of water, and the bulk of the salt precipitated by hydrogen chloride; the copper is precipitated from the filtrate by hydrogen sulphide, reprecipitated, and ultimately estimated colorimetrically with potassium ferricyanide. Carnallite may be precipitated directly with hydrogen sulphide, as it does not retain copper sulphide in solution. Salt-clay and anhydrite must be extracted with a mixture of one part hydrochloric acid and 5 parts nitric acid. The clay probably contains copper as sulphide.

The quantity of copper ranges from 0.10 mg. in 200 grams rock salt to 1.32 mg. in salt-clay. The anhydrite veins are slightly richer than the neighbouring salt.

The adsorption of copper sulphate by salt-clay and fire-clay has been measured. The former has three times as great a capacity for adsorbing copper as the latter.

C. H. D.

Transformation Points of Copper-Aluminium Alloys.

Variation of Electrical Resistance with Temperature. MAURICE BARRÉE (*Compt. rend.*, 1909, 149, 678—681. Compare Guillet, *Abstr.*, 1905, ii, 712).—The tempering of aluminium bronzes containing 8 to 16% of aluminium has been shown to depend on transformations which occur at about 500° and 750°, although there is some disagreement as to the actual temperatures. The author has measured the electrical resistance of thick bars of two alloys containing 9% and 12% of aluminium. The bars were heated in an Heraeus resistance furnace, a vacuum being maintained to prevent oxidation, and the temperature being measured by a Le Chatelier couple. Transition points were found at roughly 200°, 500°, and 750°. The alloys were not uniform in composition, and the impurities such as iron, silicon, etc., were irregularly distributed, so that the transition points in every sample were different. The changes are reversible, but in every case the retransformation on cooling takes place at a lower temperature. Continual heating and cooling do not alter the transformation temperatures, but render them sharper, owing to the increase in homogeneity which occurs. Liquation is also an important factor.

R. J. C.

Ammoniacal Solutions of Cupric Hydroxide. HARRY M. DAWSON (*Zeitsch. physikal. Chem.*, 1909, 69, 110—122).—The nature of the complex present in ammoniacal solutions of cupric hydroxide has been investigated by solubility and distribution measurements, as well as by electrical conductivity measurements. The results appear to indicate that the copper is present in the form of the compound $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$, a moderately strong base.

The cupric hydroxide was prepared by adding ammonia to a boiling solution of cupric sulphate until the supernatant liquid begins to turn blue; the precipitated basic salt, after washing, is treated with sodium hydroxide, and the resulting bright blue, crystalline hydroxide washed and dried. The product thus obtained appears to be a definite modification of the hydroxide. Solubility measurements were made at 18° in solutions containing from 0.20 to 10 mols. of ammonia per litre. A formula for calculating the results is deduced, and good constants are obtained for solutions containing 1 to 8 mols. of ammonia per litre on the assumption that the copper is associated with 4NH_3 . The "constants" in very dilute and very concentrated solutions are somewhat smaller than the normal value on the above assumption as to the nature of the complex, but for this plausible explanations have been found. The experimental results are not in agreement with those of Bonsdorff (Abstr., 1904, ii, 733), and it is suggested that the solutions used by the latter were supersaturated.

The variation of the electrical conductivity of ammoniacal cupric hydroxide solutions with the ammonia concentration has been measured and compared with the results obtained for ammoniacal solutions of barium hydroxide, piperidinium hydroxide, copper sulphate, and sodium sulphate in equivalent concentration. All the curves in which the conductivities are plotted as ordinates against the ammonia concentrations as abscissæ show maxima at different ammonia concentrations in each case. No very definite conclusions can be drawn from the results; they are not incompatible with the assumption that the ammoniacal cupric hydroxide solution contains one and the same base, independent of the ammonia concentration.

Measurements of the distribution of ammonia between the solutions in question and chloroform have been made at 18° , but the results are not very conclusive, owing to the fact that the ratio of total ammonia to copper is of the order 100 : 1, and that the correction to be applied for the salting-out effect of the cuprammonia hydroxide on the ammonia is somewhat uncertain. On the whole, the results support the view that the ratio of combined ammonia to copper is 4 : 1.

G. S.

The System Cu_2S -FeS. KARL BORNEMANN and F. SCHREYER (*Metallurgie*, 1909, 6, 619—630).—Mixtures of the synthetic sulphides are heated in a fire-clay crucible with a thin lining of Marquardt mass in an atmosphere of nitrogen. In most cases some copper is set free during cooling. The freezing-point curve is complicated, and is considered to indicate the existence of three compounds, $2\text{Cu}_2\text{S}, \text{FeS}$, $3\text{Cu}_2\text{S}, 2\text{FeS}$, and $2\text{Cu}_2\text{S}, 5\text{FeS}$, the formula of the last being uncertain. Only the first of these is stable at all temperatures below the freezing point. The compound $2\text{Cu}_2\text{S}, 5\text{FeS}$ undergoes a transformation at 915° , and breaks up between 500° and 600° into $2\text{Cu}_2\text{S}, \text{FeS}$ and FeS. The compound $3\text{Cu}_2\text{S}, 2\text{FeS}$ undergoes a change at 180 — 230° , metallic copper being set free, the other product of the reaction being a compound rich in sulphur, probably FeS_2 , forming solid solutions with the undecomposed compound. Attempts to inhibit the reactions by quenching failed in all cases.

Both the microscopical and thermal methods of investigation were used.
C. H. D.

Cuprous Sulphites of Étard and of Rogojski. LUDWIG RAMBERG (*Zeitsch. physikal. Chem.*, 1909, **69**, 512—522).—As there is some difference of opinion as to the purity and even the existence of the cuprous sulphites described by Étard (Abstr., 1882, 1165) and Rogojski (*J. pr. Chem.*, 1851, **53**, 409) respectively, these salts have been prepared and examined by the author.

Étard's salt was prepared by boiling 50 c.c. of a 65% solution of acetic acid with powdered copper acetate until the solution is saturated; the clear liquid is decanted, and a brisk stream of sulphur dioxide passed through it for five to seven minutes in a special apparatus kept in boiling water. The liquid quickly becomes deep blue and the sulphite separates in the form of small, lustrous, light amber-coloured plates; formula, $\text{Cu}_2\text{SO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$. The yield is about 90% of the calculated value.

Cuprous acetate, first prepared pure by Péchard (Abstr., 1903, ii, 293), has also been obtained by the action of sulphur dioxide on the solution of cupric acetate in acetic acid prepared as above.

Rogojski's salt was prepared by adding 5 grams of ammonium cuprous sulphite, $\text{Cu}_2(\text{NH}_4)_2(\text{SO}_3)_2$ to an almost saturated, aqueous solution of sulphurous acid, and then passing a slow stream of sulphur dioxide through the solution. After six hours, the colourless crystals at first obtained are completely changed to red, prismatic crystals of the composition $\text{Cu}_2\text{SO}_3 \cdot \text{H}_2\text{O}$. The salt obtained in this way is not quite pure, but is obtained pure by digesting Étard's salt with an aqueous solution of sulphurous acid in the absence of air.

The constitution of the two salts has not yet been elucidated.

G. S.

Atomic Weight of Mercury. C. W. EASLEY (*J. Amer. Chem. Soc.*, 1909, **31**, 1207—1218).—The atomic weight of mercury has been determined by the analysis of pure mercuric chloride. In order to determine the ratio $\text{HgCl}_2 : \text{Hg}$, the mercury was estimated in the following manner. A known weight of mercuric chloride was dissolved in water, sodium hydroxide was added in slight excess of the amount required to precipitate the mercuric oxide, and hydrogen peroxide was gradually added until all the oxide had been reduced to the metal. On applying heat, the mercury collected into a globule with the exception of a small quantity which remained in a finely divided state. The globule of mercury was washed repeatedly with water and afterwards with acetone, and dried in a current of air. The finely divided mercury was collected on a small filter, which was afterwards treated with nitric acid and heated on the steam-bath, bromine being added to ensure the complete conversion of the mercury into mercuric salt. The solution was then diluted and boiled to eliminate the excess of bromine, and was treated with hydrogen sulphide in order to precipitate the mercury as mercuric sulphide. The sulphide was collected on a small filter, and the latter was placed in a platinum crucible and covered with water acidified with hydro-

chloric acid. By the use of a cathode of gold foil, the mercury was deposited and could be weighed, the weight thus obtained being added to that of the mercury globule. From the results of four experiments, the average value for the atomic weight of mercury was found to be 200.48 ($\text{Cl} = 35.46$).

In estimating the chlorine in mercuric chloride, the mercury was first removed by the method already described. The filtrate and washings containing the chlorine were acidified with nitric acid. A weighed amount of pure silver was dissolved in nitric acid, and, after being heated to expel nitrous fumes, was diluted to about $N/10$ concentration and added to the solution containing the chlorine. The silver chloride was carefully collected and washed, and the small quantity dissolved in the filtrate and washings was estimated by means of the nephelometer. The average of six experiments gave the atomic weight of mercury, calculated from the ratio $\text{HgCl}_2 : 2\text{AgCl}$, as 200.62 ($\text{Cl} = 35.46$, $\text{Ag} = 107.88$). This value is regarded as more accurate than that obtained from the first series of experiments, and is 0.3 higher than the value at present accepted. E. G.

Potassium Mercuri-iodide. J. HÖFLE and G. VERVUERT (*Centr. Min.*, 1909, 554—555).—The following alteration in Goldschmidt's method for preparing Thoulet's solution is described. Mercuric iodide and the minimum necessary quantity of water are triturated to a thick paste, care being taken to avoid the formation of lumps. The requisite quantity of powdered potassium iodide is then added in small quantities at a time, stirring meanwhile. Solution takes place rapidly, and a clear liquid is obtained, from which the excess of water is removed by evaporation on the water-bath to incipient crystallisation. The resulting solution has a density greater than 3.220, but it does not remain constant; it may be taken as 3.22, however. The potassium mercuri-iodide can be obtained from the solution in the form of yellow crystals. When heated with water, mercuric iodide is deposited at first, but it readily dissolves in the resulting solution.

T. S. P.

Compounds of Selenium and of Tellurium with Mercury. GIOVANNI PELLINI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 211—217).—[With R. SACERDOTI].—At the ordinary pressure, combination of mercury and selenium under the action of heat takes place slowly, the presence of excess of selenium being requisite; this can only be separated from the crystalline compound, HgSe , by slow fractional distillation. When the two elements are mixed in atomic proportions, complete combination occurs only in a sealed tube, the whole of which must be heated at 550—600° for some time. The pasty, amalgam-like masses obtained on triturating mercury and selenium in a mortar consist of mixtures of mercury and mercuric selenides. At 500—550°, a mixture of the two elements containing 98, 95, 90, 80, or 70 atom % of selenium undergoes partial fusion, and on cooling the mass the thermometer exhibits, in all cases, one resting stage at 132—139°. The fusion curves for the same mixtures show a thermometric stoppage at 216—218°, the m. p. of pure selenium being 220°. The conclusion

is drawn that mercuric selenide dissolves very slightly in selenium, even at a high temperature. The temperature halt of the fusion curves corresponds with the eutectic $\text{Se} + \text{HgSe}$, whilst that of the freezing curves is due to the rapid transformation of the superfused selenium into the stable, grey modification.

[With C. AUREGGI.]—Mixtures of mercury and powdered tellurium react readily on heating with development of a considerable amount of heat. When 66 atom % or more of tellurium is present, the mixture fuses completely, whilst mixtures less rich in tellurium decompose at a high temperature with liberation of mercury. The solidification curves of mixtures containing from 60 to 95 atom % of tellurium exhibit a eutectic temperature halt at about 410° . The form of the curves indicates the existence of a mercuric telluride, HgTe , which, however, melts with decomposition at the ordinary pressure, its upper limit of stability being about 550° . The eutectic $\text{Te} + \text{HgTe}$ corresponds with 87 atom % of tellurium, and has a distinctly crystalline appearance. Tellurium dissolves only slightly in mercury. When triturated in a mortar at the ordinary temperature, mercury and tellurium yield a greyish-white paste with a metallic lustre, from which, after a long time, or by gently heating, the compound HgTe may be isolated.

T. H. P.

Solubility of Aluminium Hydroxide in Solutions of Aluminium Sulphate and Artificial Production of Alumian. ROBERT KREMAN and K. HÜTTINGER (*Jahrb. K. K. Reichsanstalt*, 1908, 58, 637—658).—Aluminium hydroxide is only slightly soluble in very concentrated solutions of aluminium sulphate. As the concentration of this diminishes, the solubility increases, and attains a maximum, which at 20° , 40° , and 60° corresponds respectively with solutions containing 32, 28, and 38% of aluminium sulphate. With further diminution of the concentration of the sulphate, the solubility of the hydroxide decreases. The solubility curve shows a break at points corresponding with 8.5% aluminium sulphate at 20° , and with 7.5% at 40° and 60° .

Crystallisation experiments have shown that the solid phases which correspond with the three parts of the solubility curve are respectively : $\text{Al}_2(\text{SO}_4)_3, 16\text{H}_2\text{O}$; alumian, $\text{Al}_2\text{O}(\text{SO}_4)_2, 12\text{H}_2\text{O}$, and in the case of the more dilute aluminium sulphate solutions, a salt more basic than alumian.

From observations of the rate of decomposition of methyl acetate in corresponding solutions of normal aluminium sulphate and the basic salt alumian, it appears that the latter is hydrolysed to a greater extent than the former.

Measurements of the vapour tension of the partly dehydrated normal and basic salts indicate that normal aluminium sulphate forms hydrates with $2\text{H}_2\text{O}$ and $12\text{H}_2\text{O}$, as well as with $16\text{H}_2\text{O}$ and $18\text{H}_2\text{O}$, and that the basic salt forms hydrates with $10\text{H}_2\text{O}$ and $11\text{H}_2\text{O}$, as well as with $12\text{H}_2\text{O}$.

H. M. D.

Binary Systems of Alumina with Silica, Lime, and Magnesia. EARNEST S. SHEPHERD, GEORGE A. RANKIN, and FRED. EUGENE WRIGHT (*Amer. J. Sci.*, 1909, [iv], 28, 293—333).—Only one

compound of alumina and silica is stable in contact with the fused mass; this is the mineral sillimanite, Al_2SiO_5 . The minerals andalusite and cyanite of this same composition were not produced artificially; they pass slowly into sillimanite when heated above 1300° .

Of lime and alumina there are four definite compounds:

$3\text{CaO}, \text{Al}_2\text{O}_3$ (m. p. $< 1550^\circ$); $5\text{CaO}, 3\text{Al}_2\text{O}_3$ (m. p. 1387°);

$\text{CaO}, \text{Al}_2\text{O}_3$ (m. p. 1587°); $3\text{CaO}, 5\text{Al}_2\text{O}_3$ (m. p. $< 1725^\circ$).

The first and last of these have no true m. p., but they are completely liquid at the temperatures quoted. A second unstable form of each of the compounds $5\text{CaO}, 3\text{Al}_2\text{O}_3$ and $3\text{CaO}, 5\text{Al}_2\text{O}_3$ is recognised.

There is only one compound of magnesia and alumina, namely, $\text{MgO}, \text{Al}_2\text{O}_3$ (artificial spinel).

The system $\text{MgO}-\text{CaO}$ appears to be a eutectic series with no compound and little, if any, solid solution. Here the temperature ranges are too high for satisfactory investigation.

The optical characters of the above-mentioned compounds, and also those of lime and alumina (artificial corundum), are described in detail. The products are in all cases extremely fine grained. L. J. S.

Hydrolysis of Salts of the Cations Al^{+++} and Cr^{+++} . G. POVARIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1014—1033).—The author has devised an apparatus for determining the degree of hydrolysis of a salt in solution by measuring the p. d. in an element consisting of the salt solution, with and without the addition of the anion of the salt, hydrogen-platinum electrodes being employed. The salts used in the experiments described were aluminium, chromic, and sodium sulphates and sodium chloride. The results of the measurements made lead to the following conclusions.

The retardation of the hydrolysis of aluminium and chromic sulphates produced by the ion SO_4^{--} is greater than that caused by 2Cl^- . Hence these sulphates, in presence of the ions of an univalent metal (Na^+), are hydrolysed to a less degree than are the corresponding chlorides. In general, chromic sulphate is somewhat more strongly dehydrolysed by the ions SO_4^{--} and Cl^- than is aluminium sulphate. For the concentrations $v_{33}-v_{51}$, chromic sulphate is hydrolysed to less extent than aluminium sulphate, which is opposed to what was found for the chlorides of these metals at the concentration v_{32} by Bjerrum (*Abstr.*, 1907, ii, 554) and Denham (*Trans.*, 1908, 93, 41); it is possible that for other concentrations this relation is reversed. Alcohol and formaldehyde lower the extent of hydrolysis of aluminium and chromic sulphates, whilst sucrose is without influence.

T. H. P.

Passivity of Iron. WOLF J. MÜLLER and JOHANNES KÖNIGSBERGER (*Zeitsch. Elektrochem.*, 1909, 15, 742—746).—The authors reply to Krassa's criticism of their observations of the reflecting power of active and passive iron (this vol., ii, 738). They consider that they have proved definitely that iron may be passive when there is no film of oxide on it. Krassa's argument in favour of the oxide theory may be expressed thus: in many cases in which iron is passive, a skin of

oxide can be seen on it; the skin will therefore exist in cases in which it is not visible. This is an inadmissible extrapolation of optical observations (compare also Manchot, this vol., ii, 1003). T. E.

Metallographic Observations in a Vacuum at High Temperatures. P. OBERHOFFER (*Metallurgie*, 1909, 6, 554—567).—A modification of Le Chatelier's microscope is described, by means of which a metal surface may be examined at temperatures from 0° to 1000° in a vacuum. The vacuum furnace is made of quartz, heated by a platinum resistance wound on quartz.

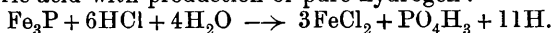
The formation of temper carbon when a steel containing 2.5% C and 1.7% Si is annealed has been observed in this apparatus, and it is shown that the formation of temper carbon takes place in the cementite and proceeds with increasing rapidity. C. H. D.

The Equilibrium Diagram of Iron-Carbon Alloys. FRIEDRICH WUST [with N. GUTOWSKY] (*Metallurgie*, 1909, 6, 512—529).—The solidus curve of the iron-carbon series between 0 and 4.2% C has been determined by quenching experiments. The saturation point of the solid solution lies near 1.8% C. Carbon separates from the solutions only in the form of cementite, Fe_3C , the production of graphite being always due to a secondary decomposition of the cementite. The presence of silicon is not necessary for the liberation of graphite. The evidence on these points is provided by photo-micrographs of the alloys under various conditions of quenching. C. H. D.

Iron Phosphides. HENRI LE CHATELIER and S. WOŁODZINE (*Compt. rend.*, 1909, 149, 709—714).—Although nine different phosphides of iron have been described, the authors have been unable to prepare five of these. Four compounds, Fe_3P , Fe_2P , FeP , and Fe_2P_3 , certainly exist, although the composition of the last two is not absolutely established.

Fused mixtures of phosphorus and iron containing more than 84.4% of iron were found to consist of crystals of Fe_3P embedded in a eutectic mixture of this phosphide with iron. The mass was powdered, and the more magnetic particles, separated by the magnet, had the composition Fe_3P . This phosphide may also be prepared by fusing copper phosphide with a sufficient quantity of iron, when almost pure Fe_3P rises to the top as a separate phase. This is also purified by removing non-magnetic impurities.

The *phosphide*, Fe_3P , has D 6.74, m. p. 1110°, and magnetic transformation point 445—435°. At the ordinary temperature its permeability is one-third that of pure iron. It dissolves in concentrated hydrochloric acid with production of pure hydrogen:



The next member of the series, Fe_2P , is insoluble in acids, except *aqua regia*. Mixtures of Fe_3P and Fe_2P form no eutectic, and the compound Fe_5P_2 , described by Boblique, does not exist.

The *phosphide*, Fe_2P , is obtained by fusing excess of copper phosphide with iron. On dissolving the mass in nitric acid, beautiful crystalline needles, apparently hexagonal, remain. Reduction of phosphates by

the aluminothermic method sometimes gives pure Fe_2P , which may also be obtained by fusing phosphorus with iron and separating the more magnetic impurities. Fe_2P has $D_{6.56}$, m. p. 1290° , magnetic transformation point 80° , and permeability about $1/50$ th that of Fe_3P .

The *phosphide*, FeP , is obtained by passing phosphorus vapour over Fe_2P at red heat until no further increase in weight occurs. It is slightly more magnetic than Fe_2P , $D_{5.76}$; magnetic transformation point 48° .

The *compound*, Fe_2P_3 , has been prepared by the authors by the action of phosphorus iodide vapour on reduced iron. A variable mass is obtained, but on the edges steel-grey crystals of a non-magnetic character are found, which have a constant composition. It has $D_{4.5}$, and its magnetic permeability, $1/75$ th that of the phosphide FeP , is only thirty times that of distilled water. The permeability increases slowly as the temperature falls to -50° , but no magnetic transformation point could be found.

R. J. C.

Reactions in Non-aqueous Solutions. IV. In Methyl Acetate. ALEXANDER NAUMANN [with JEAN RILL and FERDINAND BEZOLD] (*Ber.*, 1909, 42, 3789—3796. Compare Abstr., 1904, ii, 819).—The anhydrous methyl acetate used distilled between 56.8° and 57.6° , and had $D_4^{18} = 0.935$. For the majority of the experiments, half-saturated solutions were used. A lengthy list is given of salts which are soluble or insoluble in methyl acetate.

A solution of potassium thiocyanate reacts with solutions of sodium iodide and lithium nitrate, giving precipitates of potassium iodide and potassium nitrate respectively. Ammonium thiocyanate and lithium nitrate give a precipitate of ammonium nitrate.

At 18° the saturated solution of cobalt chloride in methyl acetate, $D_4^{18} = 0.938$, contains 1 part of solute to 271 parts of solvent. With potassium thiocyanate a white precipitate of potassium chloride is formed; with lithium nitrate the precipitation of lithium chloride is incomplete. On passing ammonia into the saturated solution, dark rose-red crystals, having the composition $\text{CoCl}_2 \cdot 6\text{NH}_3$, were obtained.

Cobalt bromide dissolves in methyl acetate to the extent of 1 part in 9.74 at 18° ; $D_4^{18} = 1.013$. With potassium thiocyanate the solution gives a precipitate of potassium bromide. On treatment with ammonia, pale rose-red crystals, $\text{CoBr}_2 \cdot 6\text{NH}_3$, were obtained; these crystals lose ammonia on heating, and at 120° they have the composition $\text{CoBr}_2 \cdot 2\text{NH}_3$, their colour then being blue. Hydrogen sulphide produces only a slight cloudiness in the solution of cobalt bromide; the further addition of ammonia gives a precipitate of cobalt sulphide.

At 18° a saturated solution of cupric chloride, $D_4^{18} = 0.939$, contains 1 part of that salt to 181 parts of methyl acetate. With stannous chloride a precipitate of cuprous chloride is produced. Ammonia produces a blue precipitate of the composition $\text{CuCl}_2 \cdot 6\text{NH}_3$; at 135° these crystals lose ammonia and become green, their formula then being $\text{CuCl}_2 \cdot 2\text{NH}_3$. With hydrogen sulphide a precipitate of cupric sulphide is formed.

A saturated solution of mercuric chloride, $D_4^{18} = 1.251$, contains

1 part mercuric chloride to 2.35 parts methyl acetate at 18° . With potassium thiocyanate, ammonium thiocyanate, barium iodide, and potassium mercuri-iodide, it gives precipitates of potassium chloride, ammonium chloride, barium chloride, and potassium chloride respectively. Ammonia gives the compound $\text{HgCl}_2 \cdot 2\text{NH}_3$. With hydrogen sulphide a yellow compound, $\text{HgCl}_2 \cdot 2\text{HgS}$, is produced, whereas with ammonia and hydrogen sulphide, mercuric sulphide is formed. Stannous chloride gives mercurous chloride when present in small amount, but when in excess mercury is precipitated.

Mercuric bromide dissolves in methyl acetate to the extent of 1 part in 4.56 at 18° . The solution has $D_4^{18} = 1.090$. Ammonia gives the compound $\text{HgBr}_2 \cdot 2\text{NH}_3$, and hydrogen sulphide the yellow compound $\text{HgBr}_2 \cdot 2\text{HgS}$. Ammonia and hydrogen sulphide together give rise to mercuric sulphide.

Calcium nitrate dissolves in methyl acetate to the extent of 1 part in 1.44 at 18° ; $D_4^{18} = 1.313$. Hydrogen chloride produces a precipitate of the double compound, $\text{CaCl}_2 \cdot \text{CH}_3 \cdot \text{CO}_2 \text{Me}$. This compound was also obtained when methyl acetate was dried with calcium chloride. Mercuric, stannous, zinc, cupric, and cobalt chlorides have no action.

T. S. P.

Phosphorus Compounds of Cobalt. S. F. SCHEMTSCHUSCHNY and J. SCHEPELEFF (*Zeitsch. anorg. Chem.*, 1909, **64**, 245—257).—Phosphides of metals of high melting point are conveniently prepared by making pellets of the metal with red phosphorus, heating in a crucible, then covering with barium chloride, and raising the temperature to the melting point. More metal is then added, and red phosphorus, enclosed in an asbestos tube, is introduced. A saturated alloy is obtained in this way, which may be re-melted with more metal. Alloys melting near 1500° must be melted in a magnesia crucible without protecting layer, barium chloride being volatile. A granulated carbon resistance furnace is used.

Cobalt phosphide, Co_2P , melts at 1386° , causing a maximum on the freezing-point curve. The eutectic point is at 1022° and 19.85 atomic % P. The compound undergoes a polymorphic change at 920° . Its hardness is 6, D 6.3—6.6, and the magnetic properties are much weaker than those of alloys containing free cobalt.

Microscopically, the phosphide forms sharply-defined crystals, whilst cobalt forms rounded crystal skeletons.

C. H. D.

Preparation of Anhydrous Nitrates of Manganese, Copper, Nickel, and Cobalt. ANTOINE GUNTZ and MARTIN (*Bull. Soc. chim.*, 1909, [iv], 5, 1004—1011. Compare Ditte, *Abstr.*, 1880, 154).—The anhydrous nitrates are prepared by the action of nitric anhydride, or a solution of this in nitric acid, on hydrated salts of the metals. The reactions are carried out in a special apparatus figured in the original.

Manganese nitrate monohydrate is obtained by melting the hexahydrate in its water of crystallisation, and evaporating with the continuous addition of nitric acid drop by drop. The cooled mass on solution in nitric acid deposits pale pink, deliquescent crystals of the

monohydrate. On warming, the latter melts, begins to decompose at 140° , and is completely decomposed at 190 – 200° . When fused with nitric anhydride, it yields the *anhydrous* salt; the latter occurs in colourless crystals with a faint pink tint, has heat of solution 12.93 cal., and is completely decomposed at 200° .

Anhydrous copper nitrate is a white powder, with a faint blue tinge, has heat of solution 10.47 cal., is very deliquescent, and begins to decompose at 155 – 160° .

Anhydrous nickel nitrate is a pale greenish-yellow powder, has heat of solution 11.82 cal., and begins to evolve nitrous fumes at 105 – 110° .

Anhydrous cobalt nitrate is a slightly pink powder, has heat of solution 11.88 cal., and begins to decompose at 100 – 105° .

T. A. H.

Reduction of $\text{Cr}_2\text{O}_7''$ by Thiosulphate. G. POVARNIN and CHITRIN (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1033–1042).—The authors have investigated the course of the reaction between potassium dichromate, sodium thiosulphate, and hydrochloric acid in varying proportions and concentrations at 17 – 18° (compare Luther and Rutter, *Abstr.*, 1907, ii, 555; Jabłczyński, *Abstr.*, 1908, ii, 935).

In concentrated solutions, the oxidation of the thiosulphate ion by dichromate proceeds most readily in absence of excess of acid, that is, when the solution contains not more than 8H^+ per 2Cr ; when such excess of acid is present, increase of the concentration is accompanied by an increase in the proportion of thiosulphate ions decomposed. In no case did more than 4.2 mols. of sodium thiosulphate per 1 mol. $\text{K}_2\text{Cr}_2\text{O}_7$ take part in the first stage of the reaction.

The proportion of sulphur separated increases with the concentration of the hydrogen ions; in neutral solutions no sulphur is formed, the reaction proceeding according to the equation: $2\text{Cr}_2\text{O}_7'' + \text{S}_2\text{O}_3'' = \text{CrO}_4'' + 2\text{SO}_3'' + 3\text{CrO}_2$.

When the proportion of hydrogen ions is increased from 8 to 14 (per 2Cr), there occurs a small change in the amount of thiosulphate used up, but an increase in the quantity of sulphur separated; these results indicate that when the concentration of hydrogen ions is low, the reaction of formation of $\text{S}_4\text{O}_6''$ takes place, decomposition of $\text{S}_4\text{O}_6''$ occurring when the concentration of hydrogen ions is high.

T. H. P.

Anodic Behaviour of Tungsten. MAX LE BLANC and HORACE G. BYERS (*Zeitsch. physikal. Chem.*, 1909, **69**, 19–25).—As anode a commercial specimen of tungsten, containing 98 – 99% of the pure metal, and in some experiments a pure fused specimen were used; the cathode was usually of platinum, and a number of electrolytes were employed in the course of the experiments. The anode was weighed before and after an experiment, and from the loss in weight and the results of simultaneous measurements with a copper coulometer the valency with which tungsten dissolves could be calculated. Further, on the assumption that tungsten dissolves as a sexavalent metal, the efficiency of the current in dissolving tungsten could be determined.

When sulphuric, hydrochloric, and nitric acids in normal solutions are used as electrolytes, tungsten is practically unattacked. In solutions of phosphoric acid and of sodium hydrogen phosphate at high temperatures, it dissolves in the sexavalent form; at low temperatures, however, the current efficiency is smaller. In oxalic acid with small currents and at high temperatures, the current efficiency reaches the theoretical value, but is much less with relatively large currents at room temperature. The current efficiency also approximates to the theoretical value in normal solutions of potassium hydroxide and of ammonium sulphide.

The change from the active to the passive (relatively insoluble) form of the metal is favoured by increasing the current density and by lowering the temperature. It is improbable that the passivity is conditioned by the formation of a layer on the surface of the metal; it is more likely connected with a change in the reaction velocity.

G. S.

Physico-chemical Researches on Tin. VIII. ERNST COHEN (*Zeitsch. physikal. Chem.*, 1909, 68, 214—231. Compare Abstr., 1908, ii, 858).—The change in the structure of tin, described by Hasslinger (Abstr., 1908, ii, 953) as a new form of "tin plague," has been further investigated. It is shown that the change in question is exhibited by all forms of tin which have been subjected to mechanical treatment (rolled tin, tin-plate, tin-foil). It takes place both above and below the temperature at which tetragonal tin is transformed into the rhombic form (161°), and is induced by simple contact with material which has already undergone the change in structure. With rise of temperature, the velocity with which the change takes place increases rapidly.

The observations indicate that the structural change of the worked metal consists in a recrystallisation process, the result of which is the formation of larger tin crystals from smaller ones. On the basis of this view, it follows that the various forms of mechanically worked tin are in a metastable condition with reference to unstrained tetragonal tin above 18° , and also with reference to grey tin below 18° . The so-called "Moiré metallique," which results when tin-plate is etched by means of hydrochloric acid and potassium chlorate, corresponds with the "recrystallised" tin. It is shown that this can be used to start the change in other samples of tin-plate.

H. M. D.

Ammonia-Additive Products of the Iodides of Tin. FRITZ EPHRAIM and THEODOR SCHMIDT (*Ber.*, 1909, 42, 3856—3857).—If ammonia is led into a solution of tin tetraiodide in carbon disulphide, and at the same time the solvent is allowed to evaporate, a white substance having the composition $\text{SnI}_4 \cdot 8\text{NH}_3$ is left; it is insoluble in water, and gives stannic acid with nitric acid. It can also be produced by passing ammonia over tin tetraiodide, a solvent being unnecessary.

Stannous iodide on treatment with dry ammonia gives a yellow compound having the composition $\text{SnI}_2 \cdot 2\text{NH}_3$.

T. S. P.

Equilibrium Diagrams of Tin with Sulphur, Selenium, and Tellurium. WILHELM BILTZ and WERNER MECKLENBURG (*Zeitsch. anorg. Chem.*, 1909, **64**, 226—235. Compare Pélabon, Abstr., 1906, ii, 454).—Mixtures of tin and sulphur can only be investigated as far as 23·4% S, further quantities of sulphur being lost by volatilisation. The compound SnS melts at 881° , and the eutectic mixture consists of almost pure tin. The passage of the molten sulphide into a viscous condition towards 950° , again becoming liquid at 1100° , was observed in a few instances, and has been recorded by other observers, but the conditions for a repetition of the experiment have not been found.

Sulphur and selenium form a compound, SnSe , melting at 861° , and another, either Sn_2Se_3 or SnSe_2 , which melts near 650° , only the first being marked by a maximum on the freezing-point curve. The two eutectics consist of almost pure tin and selenium respectively.

The tin-tellurium mixtures are more readily investigated, owing to the lesser volatility of tellurium. There is a well-marked maximum at 800° , corresponding with the compound SnTe , the eutectics being tin and a mixture containing 85% Te and melting at 404° respectively.

[With W. GOLDBECK.]—The microscopical investigation of the mixtures shows that the compounds SnS , SnSe , and SnTe crystallise well, but leaves the existence of a second selenide uncertain.

C. H. D.

Preparation of Vanadium and other Metals by the Thermite Method. WILHELM PRANDTL and BENNO BLEYER (*Zeitsch. anorg. Chem.*, 1909, **64**, 217—224).—Former attempts to reduce vanadium oxide by means of aluminium have either failed (see Koppel and Kaufmann, Abstr., 1905, ii, 593) or have yielded an impure metal (Vogel and Tammann, Abstr., 1908, ii, 502). A product containing 91—93% V has been obtained by reduction with a mixture of metals of the cerium group (Muthmann, Abstr., 1904, ii, 410; 1907, ii, 781).

Calcium reduces vanadium oxide vigorously, but owing to the absence of a fusible slag, the metal remains in isolated particles. A mixture of calcium (3 atoms) and aluminium (2 atoms) acts readily, and yields a fusible, crystalline slag and a homogeneous regulus. If large quantities are used, it is advisable to moderate the violence of the reaction by dilution with slag or previously prepared metal.

Vanadium, prepared in this manner, is a hard, steel-grey metal, taking a high polish. It is hard enough to scratch quartz. The content of vanadium does not exceed 94·5%, owing to the introduction of carbon, silicon, and iron from the calcium and aluminium. Crucibles of magnesia, or with a lining of magnesia, are required, or temporary crucibles which resist the temperature well may be made by ramming fluorite or magnesia into a tinned iron vessel round a cylindrical core.

C. H. D.

The Preparation of Vanadium by the Aluminothermic Method. RUDOLF VOGEL and GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1909, **64**, 225. Compare preceding abstract).—Vanadium, containing 99·07% of the metal, may be obtained by reducing vanadium

pentoxide with aluminium in a crucible lined with magnesia. Nearly 1% of silicon is present, but the product is free from aluminium. Occasionally, under undetermined conditions, a product containing much oxide is obtained.
C. H. D.

Compounds of Antimony Pentachloride with Antimony Pentafluoride. A Contribution to the Theory of Valency. OTTO RUFF [with J. ZEDNER, KNOCH, and GRAF] (*Ber.*, 1909, 42, 4021—4044).—An investigation of the freezing-point curves of mixtures of antimony pentafluoride and antimony pentachloride shows the following compounds to exist: $3\text{SbF}_5, \text{SbCl}_5$; $2\text{SbF}_5, \text{SbCl}_5$; $\text{SbF}_5, \text{SbCl}_5$; $2\text{SbF}_5, 3\text{SbCl}_5$; $\text{SbF}_5, 2\text{SbCl}_5$, and $\text{SbF}_5, 3\text{SbCl}_5$. The compounds $\text{SbF}_5, \text{SbCl}_5$, $2\text{SbF}_5, 3\text{SbCl}_5$, and $\text{SbF}_5, 3\text{SbCl}_5$ were isolated from the fusions and analysed; the compound $2\text{SbF}_5, \text{SbCl}_5$ was obtained in the pure form by extracting with liquid chlorine the solid obtained from fusions containing 60—66.7 mol. % SbF_5 . The compound $\text{SbF}_5, 2\text{SbCl}_5$ has a distinctly different crystalline form from those of its immediate neighbours. No indications were obtained of a compound $3\text{SbF}_5, 2\text{SbCl}_5$. On fusion, all the compounds are to a very great extent split up into their components. Their behaviour on volatilisation depends on the external pressure. In a very good vacuum the only compounds which are primarily deposited from the vapour are $\text{SbF}_5, 3\text{SbCl}_5$ and $3\text{SbF}_5, \text{SbCl}_5$.

Molecular weight determinations in sulphuryl chloride solution showed that $2\text{SbF}_5, \text{SbCl}_5$ behaves normally in 10% solution; in diluter solutions it is dissociated. $2\text{SbF}_5, 3\text{SbCl}_5$ and $\text{SbF}_5, 3\text{SbCl}_5$ give values which are only about one-third of the theoretical molecular weight, even in concentrated solution.

The following densities, D_0^{20} , were obtained: $2\text{SbF}_5, \text{SbCl}_5$, 3.08; $2\text{SbF}_5, 3\text{SbCl}_5$, 2.79; $\text{SbF}_5, 2\text{SbCl}_5$, 2.82, and $\text{SbF}_5, 3\text{SbCl}_5$, 2.73. The respective molecular volumes are 236, 473, 287, and 406. When the compounds are formed from their constituents there is a considerable decrease in volume.

The chemical behaviour of these compounds, except in so far as their behaviour towards bromine and a mixture of arsenic trifluoride and bromine is concerned, is similar to what one would expect from a mixture of antimony pentachloride and antimony pentafluoride in the given proportions. When bromine is mixed with twice its weight of $3\text{SbF}_5, \text{SbCl}_5$ or $2\text{SbF}_5, \text{SbCl}_5$, there is a slight development of heat, and some of the compound dissolves in the bromine; on mixing with $2\text{SbF}_5, 3\text{SbCl}_5$, $\text{SbF}_5, 2\text{SbCl}_5$, or $\text{SbF}_5, 3\text{SbCl}_5$, however, there is a considerable absorption of heat, and the mixture becomes liquid. The mixture of arsenic trifluoride and bromine does not give arsenic pentafluoride with any of the above compounds.

The isolation and properties of the individual compounds are described in detail.

As regards the affinity of the valencies which are used to form these compounds, the negative affinity of the antimony pentafluoride molecule is considered to lie between those of elementary fluorine and chlorine, whereas the affinity of the antimony pentachloride molecule is more negative than that of the iodine molecule, and about

as strong as that of the bromine molecule. In the light of Werner's theory, the maximum co-ordination number of the antimony pentahalogenides is 8.
T. S. P.

The Decomposition of Platinous Hydroxide into Platinum Dioxide and Metal. LOTHAR WÖHLER and FRIEDRICH MARTIN (*Zeitsch. Elektrochem.*, 1909, 15, 791—792).—When platinous chloride or platinous hydroxide is dissolved in hydrochloric acid a little platinum and hydrochloroplatinic acid are always formed. Platinous hydroxide may be heated at 160° with water without decomposition; hydrochloroplatinous acid is also stable in hydrochloric acid solution at 120°. If, however, a nearly neutral solution of hydrochloroplatinous acid (obtained by reducing a solution of platinichloride with sulphur dioxide), or a solution of platinous chloride, is heated at 120°, quantitative decomposition into metal and a salt of quadrivalent platinum takes place.
T. E.

Tervalent Platinum. LOTHAR WÖHLER and FRIEDRICH MARTIN (*Ber.*, 1909, 42, 3958—3965. Compare Blondel, *Abstr.*, 1905, ii, 720).—*Platinum trichloride*, PtCl_3 , may be prepared by heating platinic chloride in pure, dry chlorine at 390°. After ten hours, the mass is completely converted into the trichloride, a dark green, nearly black, powder, dissolving slightly in cold water only after several days. It dissolves in boiling water to a reddish-brown acid solution. Hot concentrated hydrochloric acid decomposes it, forming the dichloride and tetrachloride. Like the dichloride, it dissolves readily in potassium iodide solution.

Hydrated *platinum sesquioxide*, $\text{Pt}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, is prepared by adding the solid trichloride to a hot solution of sodium carbonate, or by dissolving in potassium hydroxide solution (1 : 1) and precipitating with acetic acid. The latter method yields a product containing some of the higher oxide. It is not possible to prepare it by the oxidation of moist platinous hydroxide by heating in air (compare this vol., ii, 322).

The colour of the hydrated oxide is brown, the shade being darker if precipitated hot. It is not oxidised by boiling with water through which a current of oxygen is passed. When dehydrated in a vacuum, decomposition takes place, and the oxide Pt_2O_3 has not been isolated. The hydroxide dissolves in concentrated alkali hydroxides, and in concentrated sulphuric acid. In its chemical behaviour it occupies an intermediate position between platinous and platinic hydroxides.
C. H. D.

Tervalent Platinum. II. LOTHAR WÖHLER and FRIEDRICH MARTIN (*Ber.*, 1909, 42, 4100—4108. Compare preceding abstracts).—When potassium platinosochloride is oxidised with chlorine water at 0°, only the platinichloride is obtained, and the rubidium salt gives a similar result; but a cold solution of caesium platinosochloride gives with chlorine water a green, crystalline precipitate of *caesium platinoseschloride*, Cs_2PtCl_5 . This salt forms regular crystals, and may also be obtained by dissolving platinum trihydroxide in hydrochloric acid containing caesium chloride. For analysis, on account of the volatility of

cæsium chloride, the salt is heated with oxalic acid in hydrogen, the temperature of decomposition being thus lowered. An impure product is obtained by adding cæsium chloride to platinum trichloride. Sunlight accelerates the decomposition into the higher and lower chlorides.

The free acid, H_2PtCl_5 , has not been isolated, but on passing a little chlorine into a solution of the acid H_2PtCl_4 , the presence of tervalent platinum may be recognised by precipitation as the green cæsium salt, but decomposition sets in rapidly.

The stability of tervalent platinum in simple and complex compounds is compared with that of similar derivatives of other metals.

C. H. D.

Iridium. ALEXANDER GUTBIER and M. RIESS (*Ber.*, 1909, 42, 3905—3912).—Freshly precipitated iridium hydroxide dissolves in hydrobromic acid to a deep blue solution, which decomposes when warmed or evaporated, liberating bromine. It has not been found possible to isolate the compounds IrBr_4 or H_2IrBr_6 , but the presence of the latter in the blue solution is proved by the action of alkali bromides, which precipitate the iridibromides. The same salts are obtained on adding alkali bromide to a solution of iridium chloride on the water-bath.

The iridibromides may be recrystallised from hot dilute hydrobromic acid containing a little bromine. They form small, bluish-black crystals, yielding a dark blue powder and blue solutions. They are more soluble than the corresponding chloro-compounds. They readily lose bromine in solution or when warmed.

Ammonium iridibromide, $(\text{NH}_4)_2\text{IrBr}_6$, and the *potassium, rubidium*, and *cæsium* salts of the same composition, form dark blue octahedra. The sodium salt has not been obtained in a sufficiently pure state for analysis.

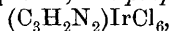
By the addition of a cold saturated solution of an alkali bromide to an excess of iridium chloride containing hydrochloric acid, the iridichlorides are precipitated as brownish-red crystals, identical with those prepared by other methods (compare following abstract). C. H. D.

Hexachloro-Iridium Compounds. ALEXANDER GUTBIER [with F. LINDNER] (*Zeitsch. physikal. Chem.*, 1909, 69, 304—314. Compare Rimbach and Korten, *Abstr.*, 1907, ii, 276).—Iridium tetrachloride, IrCl_4 , has been prepared pure by Vauquelin's method, depending on the decomposition of ammonium iridium chloride, $(\text{NH}_4)_2\text{IrCl}_6$, by gaseous chlorine. From the tetrachloride the double salts with alkali chlorides of the type M_2IrCl_6 have been prepared by mixing hot aqueous solutions of the components; they have already been described by previous observers.

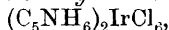
The remaining double salts described in the paper were prepared by mixing hot solutions of iridium chloride and the other chloride, and were recrystallised from hot dilute hydrochloric acid. *Methylammonium iridichloride*, $(\text{NH}_3\text{Me})_2\text{IrCl}_6$, occurs in dark reddish-brown, lustrous, hexagonal plates; the corresponding *dimethylamine* compound, $(\text{NH}_2\text{Me}_2)_2\text{IrCl}_6$, in small, reddish-brown needles, and the *trimethylamine* compound, $(\text{NMe}_3)_2\text{IrCl}_6$, in red, rhombic plates. *Ethylammonium*

iridichloride, $(\text{NH}_3\text{Et})_2\text{IrCl}_6$, occurs in dark reddish-brown, hexagonal crystals; the corresponding *diethylamine* compound, $(\text{NH}_2\text{Et}_2)_2\text{IrCl}_6$, in red, highly refracting plates, and the *triethylamine* compound, $(\text{NHEt}_3)_2\text{IrCl}_6$, in reddish-brown leaflets. *Propylammonium iridichloride*, $(\text{NH}_3\text{Pr})_2\text{IrCl}_6$, occurs in very dark-coloured, highly refracting needles; the *dipropylamine* compound, $(\text{NH}_2\text{Pr}_2)_2\text{IrCl}_6$, in brown, monoclinic, highly refractive crystals, and the *isopropylamine* compound, $(\text{NH}_3\text{Pi}^\beta)_2\text{IrCl}_6$, in red, highly refracting needles. *Butylammonium iridichloride*, $(\text{NH}_3\text{C}_4\text{H}_9)_2\text{IrCl}_6$, occurs in brownish-red, highly refracting plates; the *isobutylamine* compound in reddish-brown leaflets.

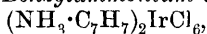
Ethylenediammonium iridichloride, $(\text{C}_2\text{H}_{10}\text{N}_2)\text{IrCl}_6$, forms black, highly refracting, rhombic plates; the *propylene* compound,



also forms almost black plates. *Pyridinium iridichloride*,



and the corresponding α -picoline compound, $(\text{C}_5\text{NH}_5\text{Me})_2\text{IrCl}_6$, form large, red needles; the quinoline compound, $(\text{C}_9\text{NH}_8)_2\text{IrCl}_6$, in small, red, monoclinic needles. *Benzylammonium iridichloride*,



the *dibenzylamine* compound, $[\text{NH}_2(\text{C}_7\text{H}_7)_2]\text{IrCl}_6$, and the *benzylethylamine* compound, $(\text{NH}_2\text{Et} \cdot \text{C}_7\text{H}_7)_2\text{IrCl}_6$, all form reddish-brown, rhombic needles.

G. S.

Mineralogical Chemistry.

Spectrographic Analysis of Blende. GEORGES URBAIN (*Compt. rend.*, 1909, 149, 602—603).—The arc spectra of sixty-four samples of blendes have been examined between wave-lengths 2663·3 and 3403·8 in the ultraviolet with the special object of finding new minerals containing germanium. Thirty-eight blendes contained germanium, which was present in appreciable amounts in the five samples emanating from Webb City (Missouri), Stolberg (near Aix-la-Chapelle), European Turkey, Raibl (Corinth), and Mexico respectively.

Nearly all the blendes contained gallium, silver, copper, cadmium, and lead, whereas indium was present chiefly in those which contained little or no germanium. Samples from Zinnwald, Wirtzborn, and Scharfenberg were particularly rich in indium. Tin was found in thirty-two specimens, antimony in twenty-six, cobalt in fourteen, bismuth in ten, arsenic in nine, molybdenum in five. Iron and manganese were also very frequent.

These results indicate only the relative rarity of the elements in question, since by chemical concentration nearly all can be detected in every blende. R. J. C.

Arizonite : Ferric Metatitanate. CHASE PALMER (*Amer. J. Sci.*, 1909, [iv], 28, 353—356).—The new mineral occurs as irregular masses together with gadolinite, which it somewhat resembles in external appearance, in a pegmatite-vein near Hackberry, in Arizona. Its fracture is sub-conchoidal, with a dark steel-grey colour and

metallic to sub-metallic lustre; the streak is brown. The mineral is opaque, but under the microscope very thin splinters are deep red by transmitted light. One indistinctly developed crystal was found; this is described doubtfully as monoclinic. The mineral is brittle; H 5—6, D 4·25. Analysis I agrees closely with the formula $\text{Fe}_2\text{O}_3, 3\text{TiO}_2$, that is, ferric metatitanate. The mineral is thus distinct from ilmenite, which is essentially ferrous titanate, FeO, TiO_2 ; iserine is possibly a mixture of the two.

	TiO_2	FeO	Fe_2O_3	H_2O	Total.*
I.	58·26	0·70	38·38	1·20†	100·12

* Including portion insoluble in hot concentrated sulphuric acid, consisting of TiO_2 , 0·56; SiO_2 , 1·02.

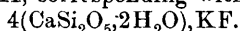
† Of this amount, 0·18 per cent. is expelled below 110°.

The gadolinite gave the partial results under II :

	SiO_2	Y_2O_3 , &c.	Ce_2O_3 , &c.	GfO	FeO	Total.	Sp. gr.
II.	24·41	36·86	11·50	11·50	11·56	95·83	4·28

L. J. S.

Errors in the Determination of Water in Zeolites. STANISLAUS J. THUGUTT (*Centr. Min.*, 1909, 677—686).—The amount of water held by zeolites is a function of the size of the particles of the material (that is, dependent on the surface energy), the tension of aqueous vapour in the surrounding atmosphere, and the period of time that the material remains in contact with this atmosphere. Zeolites in a finely-powdered condition (the particles measuring 1—10 μ across) gave on ignition more water than when the material was more coarsely powdered (grains 0·1—0·5 mm. diameter); in the twenty-four minerals so examined, there were differences of from 0·41% to 4·88% between the two determinations for each mineral. Apophyllite, on the other hand, loses some of its water on being finely powdered. More detailed experiments were made with natrolite from Leitmeritz, Bohemia, and with apophyllite from Guanajuato, Mexico. The natrolite consisted of perfectly clear, prismatic crystals of some size, and they appeared to be perfectly pure, but microchemical coloration tests proved the presence of traces of diasporite, hydrargillite, calcite, and chalybite. Analysis gave the results under I, agreeing closely, after deducting the slight amount of impurities, with the formula $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_{10}, 2\text{H}_2\text{O}$. The water determination (9·77% loss on ignition, including 0·20% CO_2 present as calcium, iron, and magnesium carbonates) was made with the coarsely-powdered material (0·1—0·5 mm.); the same sample when finely powdered (1—3 μ) lost on ignition 12·31%. Colourless crystals of apophyllite when coarsely powdered gave analysis II, corresponding with the formula



The same sample of material when finely powdered contained 15·87% H_2O (the amount required by the above formula is 15·84%).

	SiO_2	Al_2O_3	FeO	CaO	MgO	K_2O	Na_2O	F.	H_2O	Total, less O for F.	Sp. gr.
I.	47·34	26·84	0·11	0·11	0·04	0·14	15·96	—	9·77	100·31	2·25
II.	53·01	—	—	23·76	0·48	3·62	0·37	1·91	16·78	99·13	2·352

L. J. S.

Stellerite, a New Zeolite. JÓZEF A. MOROZEWICZ (*Bull. Acad. Sci. Cracow*, 1909, 344—359).—A new zeolite, stellerite, has been found at the N. W. Cape of Copper Island, one of the Komandorski islands in the Aleutian Group of Islands.

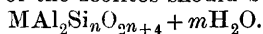
Analysis gave the following composition :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	Na ₂ O.	H ₂ O.
59·23	14·41	0·22	8·23	—	18·15

It is a calcium aluminosilicate, $\text{CaAl}_2\text{Si}_7\text{O}_{18} \cdot 7\text{H}_2\text{O}$, and crystallises in the rhombic system, $a:b:c = 0.98:1:0.761$; $D = 2.124$, and the hardness is $3\frac{1}{2}$ —4. On treatment with hot 2*N*-hydrochloric acid, crystalline, doubly refracting skeleton-crystals of silica are left, possessing a definite optical orientation.

The behaviour of the zeolites towards hydrochloric acid depends on the number of atoms of silicon to the molecule. Only when there are more than 5 such atoms of silicon is a doubly refracting skeleton-crystal of silica left.

The general formula of the zeolites should be written

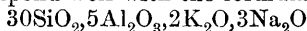


T. S. P.

Chemical Investigation of Mosandrite and Wöhlerite, occurring together, and of Certain Minerals of the Matrix. G. P. TSCHERNIK (*Bull. Acad. Sci. St. Pétersbourg*, 1909, 903—925).—The author has examined the various constituents of a Norwegian ore (probably from the shores of the Langesund fjord), the principal one consisting of pale grey plates of feldspar, $D^{17} 2.626$, having the composition :

SiO ₂ .	Al ₂ O ₃ .	K ₂ O.	Na ₂ O.	Fe ₂ O ₃ .	CaO.	MgO.	TiO ₂	FeO.
66·02	18·79	6·94	6·85	0·14	0·26	0·06	Trace	Trace
		F.	CO ₂ .	Loss at red heat.		Total.		
		Trace	Trace	0·42		99·48		

These figures correspond well with the formula

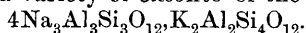


or $2\text{K}_2\text{Al}_2\text{Si}_6\text{O}_{16}, 3\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$.

Next to the feldspar, the most abundant constituent is one which occurs in large pieces varying in colour from greenish-blue to reddish-brown, and exhibiting traces of crystalline faces. The greenish-blue form, $D^{17} 2.606$, hardness 5, has the composition :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	F.	Total.
44·41	32·27	0·96	0·29	0·08	3·95	17·01	0·84	Trace	99·81

this mineral is hence a variety of elaeolite of the formula,



One of the reddish-brown specimens (I), $D^{17} 2.509$, and another darker one (II), $D^{17} 2.494$, give on analysis the following results :

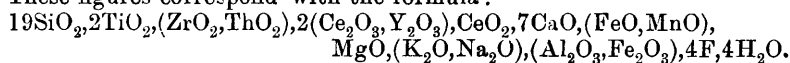
	SiO ₂ .	Al ₂ O ₃ .	Na ₂ O.	K ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	H ₂ O.	F.	Total.
I.	42·96	31·99	14·36	2·94	0·25	0·05	0·78	5·79	Trace	99·12
II.	41·39	31·87	12·73	1·95	0·22	0·05	0·74	10·36	Trace	99·31

These figures do not correspond in either case with any simple formula, and the three varieties, greenish-blue, reddish-brown, and dark reddish-brown, certainly represent one and the same mineral in different stages of efflorescence; the molecules of water present in the three cases are in the proportion 1·0129 : 7·217 : 13·399.

The next mineral examined consisted of thin, pale yellow plates with a brown tinge, D^{16} 2·986, hardness 4—5, having the composition :

SiO ₂ .	TiO ₂ .	ZrO ₂ .	ThO ₂ .	Ce ₂ O ₃ .	Y ₂ O ₃ .	CeO ₂ .	CaO.	FeO ₂ .	MnO.	MgO.
37·19	5·13	3·82	0·70	20·80	0·79	5·58	12·75	2·22	0·22	1·32
Na ₂ O.	K ₂ O.	Al ₂ O ₃ .	Fe ₂ O ₃ .	H ₂ O.	F.	Total (less O = 2F).				
1·92	0·21	3·25	0·25	2·32	2·45	99·89				

These figures correspond with the formula :

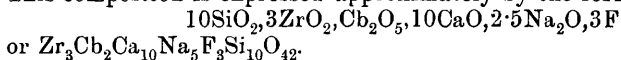


The mineral is allied to those of the mosandrite group.

A specimen of woehlerite occurring in the same ore in large, yellow prisms, D 3·45, hardness greater than 5, was found to have the composition :

SiO ₂ .	Ce ₂ O ₃ .	ZrO ₂ .	Cb ₂ O ₅ .	CaO.	FeO.	MnO.	MgO.	Al ₂ O ₃ and Fe ₂ O ₃ .
30·11	Trace	18·25	12·80	26·78	0·70	0·57	0·16	Traces
Na ₂ O.	F.	H ₂ O.	Total (less O = 2F).					
7·67	2·80	0·26	98·92					

This composition is expressed approximately by the formula



T. H. P.

Physiological Chemistry.

The Influence of Training on the Output of Carbon Dioxide in Isometric Muscular Work. A. F. HELLSTEN (*Skand. Archiv. Physiol.*, 1909, 22, 1—22).—The experiments were carried out by a form of ergograph (Johansson's) in which the contractions are isometric, and their net results show that with training the output of carbon dioxide is diminished for the same amount of work. The amount of the decrease varies in individuals. W. D. H.

"Accessory Breathing" in Animal Tissues. FR. BATTELLI and LINA STERN (*Biochem. Zeitsch.*, 1909, 21, 487—509).—The experiments on animals recorded lead to the conclusion that the respiratory process consists of two, probably distinct, parts, main respiration and accessory respiration; the former falls off, and then vanishes after death; the latter continues (especially in the liver) constant for a long time after death. Phein, a hypothetical substance previously described

by the authors, which can be extracted with water from several tissues (muscle, liver, etc.), does not influence accessory breathing. The respiratory quotient in this form of breathing is very low. The influence of various factors is described at length, and among these temperature may be mentioned, the optimum being 50—55°.

W. D. H.

Passage of Calcium Ions through the Blood-corpuscles. HARTOG J. HAMBURGER (*Zeitsch. physikal. Chem.*, 1909, 69, 663—685).—The view generally held that blood-corpuscles do not contain calcium is erroneous. When defibrinated ox-blood is subjected to centrifugal action to remove the serum, and the corpuscles, after washing several times with a solution of sucrose to remove every trace of calcium and chlorine, are placed in dilute sodium chloride solution, calcium can be detected in the solution after a time.

When a little calcium chloride is added to blood, it is found after a time that only part of it is present in the serum, showing that the corpuscles are permeable for Ca^{++} ions. When serum mixed with sodium chloride or water is added to blood, calcium passes from the serum into the corpuscles. The increased proportion of calcium which has entered the corpuscles can be washed out by treating the latter with normal serum, so that Ca^{++} ions can pass in either direction through the walls of the corpuscles.

As regards the conditions for the transference of Ca^{++} ions inside the cells, this appears to occur only when an exchange is possible with equivalent or non-equivalent ions on the other side. Differences of osmotic pressure are very important in this connexion.

G. S.

Modifications in the Chemico-physical Properties of Blood-serum by Heating at 55—60°. G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 217—222).—In blood-serum, which has been heated at 55—60° and then submitted to dialysis, the globulins are precipitated more slowly than in the original serum, the retardation increasing with the duration of heating. The heated and dialysed blood-serum behaves towards the ordinary reagents like strongly alkaline proteins. The electrical conductivity of the serum, even after heating at 55—60° for several days, does not differ appreciably from that of normal serum, but the viscosity is augmented by an amount increasing with the duration of heating. When the heating is continued for not less than twelve days, the serum gradually gelatinises at the ordinary temperature (22—23°). The velocity of thermal coagulation of the heated serum is notably inferior to that of normal serum.

These observations are explained as due to the transformation of the proteins of the serum, by the prolonged action of gentle heating, into alkali proteins (meta-proteins); part of the carbon dioxide is expelled by the heating, so that the alkalinity increases, the alkalis normally existent in the serum being sufficient to effect the transformation mentioned above.

T. H. P.

Estimation of Antipepsin in Serum. Y. OGURO (*Biochem. Zeitsch.*, 1909, 22, 266—277).—Horse's serum is more antipeptic

than the serum of rabbit and man. In disease in man, very little variation was found, but this aspect of the subject is to be continued. The peptic activity is determined by the carmine-fibrin method, also by the time taken to dissolve gelatin, or render a solution of ricin clear.

W. D. H.

An Anti-Substance to Globin. CARL H. BROWNING and G. HASWELL WILSON (*J. Path. Bact.*, 1909, 14, 174—183).—A full account of a research previously published (this vol, ii., 817).

W. D. H.

The Influence of Pepsin and the Amount of Hydrochloric Acid on the Intensity of Digestion, Especially in the Absence of Free Hydrochloric Acid. JULIUS SCHÜTZ (*Biochem. Zeitsch.*, 1909, 22, 33—44).—Casein and egg-white undergo marked peptic digestion when the hydrochloric acid is deficient; the presence of hydrogen ions is not necessary, but digestion begins when a very small amount of hydrochloric acid united to the protein is present. The digestive activity on egg-white increases as more acid is added, and within certain limits this increase is proportional to the square root of the amount of acid. The square root rule also holds for peptic action in the absence of "free" acid.

W. D. H.

The Relationship between the Proteolytic Power, the Nitrogen, and the Total Solids of the Pancreatic Juice. B. P. BABKIN and N. P. TICHOMIROFF (*Zeitsch. physiol. Chem.*, 1909, 62, 468—491).—A parallelism exists between the proteolytic activity of pancreatic juice (dog) as measured by Mett's method and the nitrogenous constituents, especially protein, of the juice. If the protein percentage is taken as the measure of the amount of trypsin present, the results of digestive activity come out very closely according to the Schütz-Borissow law of square roots.

W. D. H.

Chemistry of Digestion and Absorption in the Animal Body. XXXIV. Further Methods. E. S. LONDON. XXXV. Digestion and Absorption in the Stomach of the Dog. E. S. LONDON and W. W. POLOWZOWA. XXXVI. The Behaviour of Nucleo-protein in the Alimentary Canal. E. S. LONDON. XXXVII. The Intestinal Digestion of Proteins. E. S. LONDON and F. RIVOSCH-SANDBERG. XXXVIII. The Relation between Digestion Time and Absorption. E. S. LONDON and W. W. POLOWZOWA (*Zeitsch. physiol. Chem.*, 1909, 62, 443—445, 446—450, 451—454, 455—461, 462—464).—XXXIV. These methods deal with details of operative procedure.

XXXV. If gliadin is administered to dogs, the glutamic acid is not absorbed in the stomach, but is present in the unabsorbed material, not free, but in combination with other constituents of the protein molecule.

XXXVI. In the stomach about two-thirds of the nucleo-protein given passes into solution, and the dissolved substance gives the reactions of nucleic acid. In the duodenum an excess of nitrogen

and phosphorus are present, which originate from the juice secreted there. The cleavage of the nucleo-protein molecule occurs in the intestine, due to the action of the succus entericus.

XXXVII. The "formaldehyde method" can be applied with good results for the determination of the amount of amino-acids in the intestinal contents. The proteoses and peptones which leave the stomach undergo further cleavage in the intestine, and this is the main duty of the pancreatic juice.

XXXVIII. A parallelism is shown to exist between the time occupied and the amount of digestion and absorption which take place. W. D. H.

Does Absorption depend on the Surface Tension of the Absorbed Fluid? GIUSEPPE BUGLIA (*Biochem. Zeitsch.*, 1909, 22, 1—23).—From experiments *in vitro* and *in vivo* (with intestinal loops), in which the surface tension of solutions of salts and Witte's peptone was reduced by bile and other substances, the conclusion is reached that such procedure does not favour absorption, and therefore that Traube's views on the importance of surface tension are incorrect.

W. D. H.

Action of Lead Hydrosol and Lead Acetate on Metabolism. LUIGI PRETI (*Biochem. Zeitsch.*, 1909, 21, 551—561).—The administration of lead hydrosol and acetate to dogs in non-toxic quantities furthers nitrogenous catabolism, leading to a deficit of nitrogen in the body. This persists for days subsequently. The urea is much increased; the effect on uric acid is not so decided.

W. D. H.

The Biological Action of Salts. II. Influence of Salts on Metabolism. ERNST SCHLOSS (*Biochem. Zeitsch.*, 1909, 22, 283—289. Compare this vol., ii, 598).—The salts employed lead to retention of water in the body; sodium chloride acts in this way more strongly than the bromide, and that more strongly than the iodide; the chlorides of potassium and calcium are also the most powerful salts in this direction. Large doses, except in the case of sodium chloride, lead later to loss of water and of body weight. It is believed that the action of salts has a simple chemico-physical explanation, which is postponed until the next paper on the subject.

W. D. H.

Influence of Carbohydrates and Fats on Protein Metabolism. E. PROVAN CATHCART (*J. Physiol.*, 1909, 39, 311—330).—From experiments on man, it was found that the urinary nitrogen falls on a pure carbohydrate diet, but it rises markedly on a pure fat diet. During inanition, the urine always contains creatine, but its amount is lessened on taking carbohydrate alone, and is increased by taking fat alone. The amount excreted during the fat period is not markedly reduced by adding protein to the food. The hypothesis is put forward that carbohydrates are absolutely essential for endo-cellular synthetic processes in connexion with protein metabolism, and it is probable that food stuffs should be valued, as Chauveau suggested, more on account of their isoglycogenic than their isodynamic value.

W. D. H.

The Value of Protein-cleavage Products in the Human Organism. EMIL ABDERHALDEN, FRANZ FRANK, and ALFRED SCHITTENHELM (*Zeitsch. physiol. Chem.*, 1909, 63, 215—221. Compare this vol., ii, 817).—An experiment was carried out on a boy (with stricture of the œsophagus, and who was fed by rectum) similar to those previously conducted on animals. For fifteen days he was fed on the abiuretic products of meat which had been subjected to lengthy pancreatic digestion. Full details are given, the net result of which was that the boy remained in nitrogenous equilibrium and even put on flesh, whilst his general condition improved. W. D. H.

Nuclein Synthesis in the Animal Body. ELMER V. MCCOLLUM (*Amer. J. Physiol.*, 1909, 25, 120—141).—Without palatability a ration may possess all the necessary food ingredients and yet fail to properly nourish an animal. This factor has in the past been much neglected in attempts to study the action of pure food principles. Very young animals, however, adapt themselves to a low degree of palatability more readily than adults. All the phosphorus needed for skeleton, nuclein, and phosphatide formation can be drawn from inorganic phosphates. An animal has the power to synthesise the purine bases necessary for nuclein formation from complexes contained in protein molecules, and does not necessarily use purine bases of exogenous origin for the purpose. W. D. H.

Disappearance of Pentosans from the Digestive Tract of the Cow. ELMER V. MCCOLLUM and W. A. BRANNON (*J. Amer. Chem. Soc.*, 1909, 31, 1252—1260).—This investigation was carried out with the object of comparing the relative ease with which the pentosans from different sources disappear from the digestive tract, and to ascertain the behaviour of methylpentosans under the same conditions. Cows were fed exclusively on plants of a single kind, either maize, wheat, or oats, and in each case the excreta were collected and the pentosans estimated. The results show that the pentosans of the maize plant are more easily attacked and disappear from the digestive tract to a greater extent than those of the wheat and oat plants, and that the methylpentosans of these three plants are less resistant to the agencies operating in the digestive tract than the simple pentosans. In order to study the action of the intestinal bacteria on the pentosans, fermentation experiments were carried out with maize fodder, wheat straw, and oat straw respectively, and it was found that the pentosans of the maize plant are less resistant than those of the oat plant, and that the latter are less resistant than those of the wheat plant, these results being in accord with those observed in the feeding experiments. E. G.

Rôle of Inorganic Phosphorus in the Nutrition of Animals. EDWIN B. HART, ELMER V. MCCOLLUM, and J. G. FULLER (*Univ. Wisconsin Agric. Exper. Stat. Research Bul.*, 1909, 1).—Pigs fed on a ration very deficient in phosphorus gained in weight as much as when receiving abundance of phosphorus up to a certain point (70 to 100 lbs.), after which there was a loss of weight, followed by collapse.

When calcium phosphates were added to rations otherwise deficient in phosphorus, development was normal, and the results equal to those obtained with phosphorus wholly in organic forms.

Determinations of calcium and phosphorus in the principal organs and tissues of pigs fed with low amounts of phosphorus showed results similar to those obtained with normally fed pigs. In the bones, however, the percentage of ash was reduced to about one-half.

A growing pig (50 lbs.) should receive 4—5 grams of phosphorus per day.

N. H. J. M.

Enzymes of the Placenta. WALTHER LÖB and SHIGEJI HIGUCHI. **Ash Constituents of the Placenta.** SHIGEJI HIGUCHI (*Biochem. Zeitsch.*, 1909, 22, 316—336, 341—344. Compare this vol., ii, 76).—The blood-free placenta, whether fresh or dried, contains catalase, oxydase, and a diastase which acts on starch and glycogen. Inulase, lactase, invertase, glycolytic and lipolytic enzymes are present in fresh, but not in dry, placenta. The same is true for a pepsin-like enzyme, but enzymes of the type of erepsin, urease, and de-amidases are absent.

The various mineral constituents were estimated and the results given in a table. Sodium salts are the most abundant. Calcium salts show great variations. By washing out the blood, the yield of iron is lessened from 0.07 to 0.014%.

W. D. H.

Purines and Purine Metabolism of the Human Fœtus and Placenta. H. GIDEON WELLS and HARRY J. COOPER (*J. Biol. Chem.*, 1909, 6, 469—482. Compare this vol., ii, 749).—Guanase appears at the third month of fœtal life, and adenase at the fifth month. The liver at the fifth month contains both enzymes, thus differing from the pig and dog's livers. Xantho-oxydase is demonstrable in the liver and combined viscera at full term, but not in muscle, intestines, kidney, spleen, or thymus. It appears at or after the sixth month. It is an enzyme which is easily destroyed. The uricolytic enzyme is absent throughout. Fœtal tissues contain more guanine than adenine, for, after autolysis, twice as much xanthine as hypoxanthine is found. The presence of xantho-oxydase or uricase could not be demonstrated in mature placenta. The placenta contains 14% of nitrogen (dry weight), and about 2.1% of this is purine nitrogen; of this, 45% is guanine, 40% is adenine, and 15% hypoxanthine. Xanthine occurs in traces only.

W. D. H.

Trypsinogen and Enterokinase in the New-born Child and in the Human Embryo. JUSSUF IBRAHIM (*Biochem. Zeitsch.*, 1909, 22, 24—32).—The various proteolytic enzymes of the human alimentary canal are present at birth. They appear almost simultaneously during fœtal life; pepsin appears at the beginning of the fourth month, trypsin during the same month, enterokinase at the same time or a little later, and erepsin in the fifth month.

W. D. H.

Chemical Composition of the Dog's Body. J. STOCKHAUSEN (*Biochem. Zeitsch.*, 1909, 22, 244—265).—Statistical tables of the

weight, percentage of nitrogen, and other details of the tissues and organs of four dogs. Two of these were fed on protein-poor and two on protein-rich diet; in the latter, the nitrogen of liver and muscles was increased.

W. D. H.

The Physiology of the Glands. XIV. The Influence of Proteins and Protein Degradation Products on the Activity of the Liver. LEON ASHER and DIMITRI PLETNEW (*Biochem. Zeitsch.*, 1909, 21, 355—380).—The method of investigation consisted in adding to dogs' diets sugar in quantities just insufficient to produce alimentary glycosuria, and then superimposing on these diets proteins, or peptones, or amino-acids. These additions caused glycosuria, and as sugar output is regulated by the liver, the conclusion was drawn from the results that this organ takes part in the metabolism of protein and protein degradation products, the addition of such products taxing the capacity of the liver beyond its physiological limits. This conclusion is also fortified by the fact that bile pigments also appear in the urine. The sugar output lasts until the day after the administration of the extra protein or protein degradation products.

S. B. S.

The Part Played by the Liver in Creatinine Metabolism. E. S. LONDON and N. BOLJARSKI (*Zeitsch. physiol. Chem.*, 1906, 62, 465—467).—From experiments on two dogs, in which the liver was thrown out of gear by an Eck's fistula, the following conclusions are drawn. The amount of creatine excreted is greatest on days when no food is given. The admixture of creatinine with the food does not increase the amount found in the urine; admixture of the food with creatine caused no increase in the excretion of that substance, but raised the output of creatinine. Sodium nucleate produces no marked result.

W. D. H.

Autolysis. T. KIKKOJI. **Autolysis and Preservatives.** ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1909, 63, 109—135, 136—142).—The first paper relates to the action of chloroform water, toluene, and mixtures of these reagents in varying proportions, also to the action of formaldehyde and benzoic acid on the course of autolysis. The optimum concentration of each is determined, but autolysis runs a quicker course when the optimum concentration of some preservatives is used than it does for others, for instance, it is more rapid for benzoic acid in comparison with chloroform. The second paper is mainly critical, and emphasises the point that the antiseptic selected is not immaterial, and neglect to recognise this will explain divergent results hitherto published.

W. D. H.

The Non-dependence of Autolytic Protein-cleavage on the Presence of Blood. ERNST BLOCH (*Biochem. Zeitsch.*, 1909, 21, 519—522).—The autolytic enzymes which produce protein-cleavage in the dog's liver are really tissue-enzymes, and bring about autolysis when the organ is entirely freed from blood.

W. D. H.

The Hæmolytically Acting Organ Extracts. JULIUS MORGENROTH and P. SCHÄFER (*Biochem. Zeitsch.*, 1909, 21, 305—320).—The extracts of organs which act hæmolytically owe this property, not to substances in solution, but to substances in suspension. Experiments were carried out with alcoholic extracts of pancreas (made by extracting the organ with alcohol diluted with physiological saline) to determine the conditions under which the most active preparations could be obtained. It was found that the extracts made from organs of well-fed animals were more active if the organs had been previously allowed to autolyse for some hours at room temperature. The extracts from fresh organs of fasting animals were more active than those from well-fed animals; there was not the corresponding increase in activity in this case after autolysis. It was also shown that the matter causing hæmolysis can be taken up by suspended matter, as experiments made with particles of coagulated serum proteins with sodium oleate solutions showed. The particles of protein which had taken up the oleate were capable of acting hæmolytically. S. B. S.

Action of Extracts of the Pituitary Body. HENRY H. DALE (*Bio-Chem. J.*, 1909, 4, 427—447).—Extracts of the posterior lobe of the pituitary directly stimulate all kinds of involuntary muscle without any relation to innervation. The action is nearly allied to that of digitalis, but the pituitary substance acts less powerfully on the heart, and more powerfully on plain muscle, than the members of the digitalis group. The active principle is excreted in the urine. Repeated injections produce no true immunity in the sense that immune substances are developed. The evidence adduced by Schäfer and Herring, that the extract contains separate pressor and diuretic substances, is considered inadequate. W. D. H.

Chemico-physical Investigations on the Crystalline Lens. G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 288—294. Compare Bottazzi and Scalinci, this vol., ii, 502).—The author has studied the velocity of coagulation of the crystalline lens at 65° in 0.9% sodium chloride solution, with and without the addition of various proportions of sodium hydroxide.

With 0.9% sodium chloride solution at 65°, the ratio of the surface of the lens in sq. cm. to the time occupied in coagulation in minutes has the constant value 0.0186, so that the true measure of the velocity of coagulation of a solid is given by the area of the surface which coagulates in unit time.

In presence of sodium hydroxide, the velocity of coagulation diminishes with, but not proportionally to, the concentration of the alkali. The curve connecting the velocity with concentration of sodium hydroxide resembles a logarithmic curve, and is apparently asymptotic to the concentration axis. The imbibition of the lens in alkali or acid solution is not augmented or diminished by decrease or increase of the osmotic pressure of the solution in which the lens is immersed. T. H. P.

Diastases. III. The Behaviour of the Diastase in the Blood. JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1909, 21, 381—422).—The

diastatic power was estimated by the author's method, by determining the smallest quantity of the ferment which is capable of degrading 5 c.c. of a 1% starch solution to dextrin in a given time (twenty-four hours), using iodine solution to determine this factor. It was found that the starch degradation products under these conditions caused no inhibition of the ferment action. The diastatic power of serum is the same as that of plasma. Treatment of the serum with fibrin does not diminish its diastatic capacity. The diastatic capacity remains unchanged on keeping the serum (under aseptic conditions) for several months. The diastatic concentration of serum from all the superficial blood-vessels is the same. The smallest amounts of diastase are found in human blood, ox, and goat; somewhat more is found in the blood of rabbits, and the largest quantities in the blood of guinea-pigs and dogs. The blood of a fasting dog contains as much ferment as that of a well-fed animal. The quality of the diet has no influence on the amount; neither have specific excitants of the pancreas, such as secretin and hydrochloric acid. The ligaturing of the pancreatic ducts increases the amount largely. The increase commences after three to four hours, reaches its maximum in twenty-four hours, at which it remains for several days (generally six to eight), after which the quantity gradually returns to the normal. The increase also occurs when the animal is kept without food after the operation. Increase also occurs even after ligature of a single duct. It occurs, too, after partial extirpation of the pancreas. Adrenaline-glycosuria, phloridzin, and phloretin diabetes have no influence on the quantity of diastase. Asphyxia does not increase the amount. The pancreas is not the sole source of the diastase of the blood.

S. B. S.

Diastases. IV. The Question of the Internal Secretion of the Pancreas. R. EHLMANN and JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1909, 21, 423—431).—The quantity of diastase from the blood taken from the vena pancreatico-duodenalis was compared with that of the blood taken from a femoral artery. In only one case (several experiments were carried out under different conditions of nutrition) could an increased quantity from the former vein be detected, and this was only very slight. Care was taken that none of the blood came into contact with any of the gland substance.

S. B. S.

Diastases. V. The Behaviour of the Diastase of the Urine. JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1909, 21, 432—446).—The acidity or alkalinity of the natural urine is without marked effect on the diastatic action. The urine of males contains more diastase than that of females. In fasting condition, the urine contains the most diastase; the quantity sinks after ingestion of food, and reaches a minimum in three to four hours, afterwards it rises again. Similar results were obtained with rabbits' urine. The amount of diastase in dogs' urine is small. In cases of nephritis and diabetes, the amount was smaller than the normal. In dogs with ligatured pancreatic ducts, the amount of diastase ran parallel with that found in the blood (see preceding abstract). A high diastase-

concentration was also found at times in the urine of human patients with obstructed pancreatic duct. In dogs with obstructed bile ducts, an increase in the diastase in the urine was only observed after several days. This increase is probably due to a disturbance in the pancreatic duct as a result of the operation, and not a direct consequence of the ligation of the bile duct. If the latter is ligated in animals in which the pancreatic duct had been previously obstructed, no increase of diastase in the urine was observed. S. B. S.

Diastases. VI. The Influence of the Bile on Diastases. JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1909, 21, 447—459).—Bile alone has little diastatic power. It has, however, the power of increasing the diastatic action of other plant and animal diastases (diastases of saliva, serum, pancreas, etc.). The activating action is probably due, not to a ferment, but to a heat-stable, dialysable substance which is soluble in alcohol. S. B. S.

Diastases. VII. The Diastase Content of Different Organs of the Rabbit under Normal and Pathological Conditions. A Contribution to the Subject of the Nature of Phloridzin Diabetes. JULIUS WOHLGEMUTH and J. BENZUR (*Biochem. Zeitsch.*, 1909, 21, 460—475).—The kidneys contain the largest amount of diastase; the muscles contain less, and the liver less still. Phloridzin increases the amount of diastase in the kidneys, and, in two out of four cases, the amount in the liver. It had no effect on the diastase-content of the blood. The action of phloretin was similar. No increase in the amount of liver diastase was observed after administration of adrenaline. The authors discuss the bearing of their results on the question of phloridzin diabetes. S. B. S.

Diastases. VIII. The Influence of Radium Emanations on the Action of the Diastatic Ferment. S. LOEWENTHAL and JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1909, 21, 476—483).—Radium emanations favour the action of the diastatic ferment of the blood, liver, saliva, and pancreas. The action is not immediate, for in the first twenty-four hours an inhibition is observed. This passes off, and finally there is an increased action. In certain cases, however, only the inhibitory action was observed. S. B. S.

Oxidation Products of Cholesterol in the Animal Organism. IV. ISAAC LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1909, 63, 222—234. Compare this vol., ii, 77).—The oxycholesterols of the blood-fat, which are almost completely absent in the liver cells, are believed to be transformed by the liver into acid compounds in the bile. Although found in certain organs, they are not only absent from the liver, but also in the bile and faeces of the animals investigated (ox and horse). The paper contains a discussion of the probable rôle of cholesterol in the body, and among the functions attributed to it is that of assisting emulsification in the upper part of the intestine. W. D. H.

The Biological Significance of Lecithin. III. The Lecithin and Iron Content of Human Milk and Cow's Milk. W. GLIKIN (*Biochem. Zeitsch.*, 1909, 21, 348—354).—When the fats are separated

from milk, practically all the lecithin (as determined by phosphorus estimations in the whole milk and the cream) goes into the cream. The total lecithin iron was also determined, and it was found that the higher the lecithin content of a given sample, the higher was the iron content. S. B. S.

Pentoses in the Urine of Men and Animals. Utilisation of Pentoses in the Animal Organism. LUIGI COMINOTTI (*Biochem. Zeitsch.*, 1909, 22, 106—119).—Herbivora and pigs on an abundant diet excrete pentoses in their urine, but only in small quantities as compared with the pentosans in the food. The greater part of the pentosans is therefore utilised in the body. Pentose is absent from the urine of dogs on bread and meat diet, and of men on a meat diet, but human urine always contains pentose if the diet is a mixed one. In the fasting horse, pentose disappears from the urine, but on prolonged inanition it reappears in small quantities; this is probably due to the catabolism of certain organs which yield pentose. W. D. H.

The Question of the Existence of Glycine in Normal Human Urine. G. OEHLER (*Biochem. Zeitsch.*, 1909, 21, 484—486).—The glycine was isolated in the form of the β -naphthalenesulphonyl chloride derivative. The urines of twelve healthy workers of the Pathological Institute of Berlin were examined. In eleven cases the quantity of the derivative isolated was too small to determine gravimetrically, and in a twelfth case 0.054 gram was obtained. S. B. S.

The Aromatic Compounds in Urine. W. MOOSER (*Zeitsch. physiol. Chem.*, 1909, 63, 155—200).—In estimating phenol and *p*-cresol in urine by Kossler and Penny's method (*Abstr.*, 1893, ii, 100), several difficulties have been met with. The method of distillation with sulphuric acid in order to hydrolyse phenylsulphuric acids and subsequent titration gives low results for *p*-cresol. This can be overcome by using phosphoric acid in place of the sulphuric. It is also shown that when phenols are distilled with calcium carbonate and water, evolution of carbon dioxide occurs, and a portion of the phenol remains in the distillation flask as a calcium phenoxide. This is overcome by passing a stream of carbon dioxide through the flask during the distillation. The following is the general method for estimating phenols in urine recommended. A weighed quantity (250—500 grams) of the urine is made faintly alkaline, and evaporated to one-fifth of its volume on the water-bath. It is transferred to a distillation flask fitted with a condenser and receiver. Syrupy phosphoric acid is run in (about one-fifth of the original volume of urine), and the whole well shaken and distilled to about 100 c.c.; 50. c.c. of water are added, and the distillation continued. These operations are repeated until a drop of the distillate no longer gives the Millon test. An excess of calcium carbonate is added to the distillate in a capacious flask, and the distillation repeated whilst a stream of pure carbon dioxide is led through the apparatus. Water is added, and the distillation continued until all the phenol has passed over, when the distillate is titrated by Kossler and Penny's method.

The results obtained show that 1 litre of fresh cow's urine contains 0.5—0.77 gram of combined *p*-cresol during winter feeding and 0.25—0.46 gram during summer feeding. When the urine (winter feeding) is allowed to undergo decomposition, the amount of *p*-cresol increases, as a rule, to an appreciable extent (1.13 grams per litre), and a small part of this is in the free, but the greater proportion is still in the combined, state.

The average amount of combined *p*-cresol in human urine is 0.036—0.053 gram per diem.

In estimating benzoic acid in decomposed urine, the authors add sulphuric acid and extract with light petroleum (b. p. 40°) in a Katz apparatus, and titrate with standard alkali, using litmus as indicator. The results show some 8.5 grams of benzoic acid per litre of decomposed urine.

The results of an investigation as to the phenols present in cow's urine indicate that phenol itself is absent, and that the chief substance is *p*-cresol, with probably a small amount of the meta-compound.

Städeler's oil, *urogon* (*Annalen*, 1851, 77, 17), has been examined. It was separated from the alkaline solution of phenols by extraction with light petroleum. Its analyses agree fairly well with the formula C_7H_8O . It has b. p. 199.9° (corr.), as determined by Schliermacher's method, mol.-wt. 130, D^{15}_4 1.0201, and n^{24}_D 1.5289. It is insoluble in water, and is decomposed when warmed with alkalis; with dilute alkalis it gives a hydrocarbon, *urogene*, and when fused with potassium hydroxide yields a phenol (*urogol*). Dilute chromic acid has no action on the oil, and permanganate yields no definite products. The oil forms additive compounds with bromine and iodine.

Urogene, $C_{21}H_{42}$, crystallises in slender needles, has m. p. 59.9—60°, and b. p. 140°/high vacuum (green light). It does not combine with bromine even in sunlight. It is possible that *rogene* is identical with Willstätter's phytene (*Abstr.*, 1907, i, 784).

Urogol, C_7H_8O , has b. p. 207.6° (corr.), n^{26}_D 1.53054, and gives the ordinary phenolic reactions. It yields an iodo-derivative of a grass-green colour.

J. J. S.

Chemistry of Cancer. S. YOSHIMOTO (*Biochem. Zeitsch.*, 1909, 22, 299—308).—During autolysis of the cancerous liver and still more of the cancerous breast, proteolysis is much more energetic than in normal tissues, and this depends not on the tumour itself, but on the portions of the organ which are still approximately normal. The partition of nitrogen in the autolysed fluid differs in liver cancer from that obtained from the normal organ in two points, namely, in a lessening of the purine nitrogen, and an increase in the nitrogen of diamino-acids, ammonia, and peptone.

W. D. H.

Chemical Composition of Milk from Tuberculous Cows. A. MONVOISIN (*Compt. rend.*, 1909, 149, 644—645).—The author gives in tabular form the results of analyses of milk from cows in various stages of tuberculosis. The fats, lactose, and casein diminish with the progress of the malady, whilst the total nitrogen

increases, owing to increased infiltration of proteins. The ash increases, especially the sodium chloride. The refractive index of the serum diminishes, whilst its electrical conductivity increases. In the more advanced stages of tuberculosis, the composition of the milk approximates to that of blood-serum. W. O. W.

The Physiological Effects of Selenium Compounds with Relation to their Action on Glycogen and Sugar Derivatives in the Tissues. CHARLES O. JONES (*Bio-Chem. J.*, 1909, 4, 405—419).—In the body, selenate is reduced to selenite; a small quantity is excreted in the urine, and the remainder is carried to the spleen and liver, where it is reduced by dextrose to selenium; when dextrose furnished from the glycogen is becoming exhausted, fat is called on. There is a retention of chlorides, a disappearance of hydrochloric acid, and a great relish for sodium chloride. This is interpreted as meaning that the salt raises the sugar in the blood to satisfy the selenite, and so protect the cells from toxic effects.

It is suggested that dextrose is possibly the means by which all reduction processes in the body are brought about. W. D. H.

The Action of Thorium on the Normal and on the Fatty-Degenerated Heart. S. TUVERI (*Arch. Farm. speriment.*, 1909, 8, 297—306).—The thorium salts act exactly in the same way as the caesium salts on the excised frog's heart both when in normal condition and after fatty degeneration. S. B. S.

The Fate of Lactic Acid in Normal Animals, and in those Poisoned with Phosphorus. E. NEUBAUER (*Arch. exp. Path. Pharm.*, 1909, 61, 387—400).—If sodium lactate is given to normal rabbits, it is not completely burnt in the body, but it partly leaves the body in the urine as lactic acid, and in the form of other acids soluble in ether. In rabbits poisoned with phosphorus, exactly the same occurs. The administration of sugar or alanine does not increase the urinary acids which are soluble in ether, in either class of animals. W. D. H.

The Behaviour of 3:5-Di-iodo-*l*-tyrosine and 3:5-Di-iodo-*r*-tyrosine in the Animal Organism. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1909, 62, 399—403).—The two substances were administered to dogs and rabbits, and the excreta examined. From the urine, the major part of the iodine was recovered, and in the case of the *l*-compound, about 46% was present in ionised form; in the case of the *r*-compound, about 50%. The compounds, in which the remainder of the iodine occurred, are not yet fully identified.

W. D. H.

Physiological Behaviour of *l*- and *d*-Suprarenine. V. EMIL ABDERHALDEN, KARL KAUTZSCH, and FRANZ MÜLLER (*Zeitsch. physiol. Chem.*, 1909, 62, 404—409. Compare this vol., ii, 751).—In dogs, the previous administration of *d*-suprarenine does not modify the effect produced on blood-pressure by the injection of *d*- and *l*-suprarenine.

W. D. H.

The Varying Activity of *apoMorphine* Preparations and the Pharmacological Behaviour of *apoMorphine* Derivatives (Euporphine, etc.). ERICH HARNACK and HERMANN HILDEBRANDT (*Arch. exp. Path. Pharm.*, 1909, 61, 343—362).—There are doubtless several *apomorphines* related closely to one another, but differing in their action on frogs; their paralyzing action on the central nervous system and on striped muscles is about equal. The amorphous varieties show actions differing qualitatively on warm-blooded animals. Bergell and Pschorr's dibenzoyl*apomorphine*, in which the hydroxyl groups are no longer intact, is not an emetic. The euporphine (*apomorphine* methobromide) of the same authors is a very feeble emetic, although the hydroxyls are intact; it has a curare-like action. A combination of the ammonium base of euporphine with *apomorphine* raises the paralyzing action on the frog. Commercial euporphine contains 8% of *apomorphine*, and acts as an emetic.
W. D. H.

The Behaviour of Synthetic Muscarine in the Animal Body. II. HERMANN FÜHNER [and, in part, E. ROSENOW] (*Arch. exp. Path. Pharm.*, 1909, 61, 283—296. Compare Abstr., 1908, ii, 1061).—The estimation of synthetic muscarine may be carried out biologically on the isolated frog's heart. Rabbits fed on muscarine pass it in their urine in small quantities, but if the drug is given subcutaneously, much more is present. The urine of rabbits on a mixed diet has a slight muscarine-like action. If muscarine is given in lethal doses, it can be detected in the blood, but not when it is given in non-lethal doses. Similar experiments were made on cats.
W. D. H.

Action of Poisons on Tissue Respiration. HORACE M. VERNON (*J. Physiol.*, 1909, 39, 149—183).—Freshly excised rabbits' kidneys were perfused with saline solution containing the poison for half an hour, and then with oxygenated saline for ten hours. The oxygen absorbed and carbon dioxide produced were estimated. Various poisons were found to depress the respiratory activity in different degrees. A theory is propounded that the tissues can absorb oxygen by means of a substance present which forms an organic peroxide, and this by the help of a peroxidase can transfer the oxygen to amino-acids and carbohydrates in the tissues. Some poisons (hydrocyanic acid, sodium fluoride, etc.) paralyse respiration by uniting with aldehyde groupings, and others (formaldehyde, acids, and alkalis) paralyse the power of forming carbon dioxide by destroying the peroxidase.
W. D. H.

Poisoning with Inorganic and Organic Acids. ALEXANDER SZILI (*Pflüger's Archiv*, 1909, 130, 134—135).—By means of experiments on animals, it has been deduced that the toxic action of inorganic acids is dependent, as a rule, on their strength, that is, the amount of their dissociation; this, however, is not always the case, sulphuric acid being, for instance, much more lethal than nitric acid. In the case of organic acids, the dissociation constants bear no relation whatever to their toxicity; the physiological action is due not

alone to the dissociated hydrogen ions, but also, and in a greater degree, to the undissociated parts of the molecule. W. D. H.

Toxicology of Tin with Special Reference to the Metallic Contamination of Canned Foods. SAMUEL B. SCHRYVER (*J. Hygiene*, 1909, 9, 253—263).—Quantities of tin approximating two grains to the pound are unusual and unnecessary, and any food stuff containing such quantities should be regarded with suspicion as likely to cause irritant poisoning. A summary is given of a large number of analyses of canned foods contaminated by metal, most of which had been in tins for years. Experiments showed that the ingestion of such foods was very unlikely to be followed by chronic tin poisoning. A method is described by means of which tin can be rapidly estimated colorimetrically. W. D. H.

The Abolition of Oxalic Acid Poisoning in the Frog, and the Cause of Oxalic Acid Action. HANS JANUSCHKE (*Arch. exp. Patt. Pharm.*, 1909, 61, 363—375).—The frog's heart, paralysed by oxalic acid, begins to beat again on the injection of calcium chloride. The toxic action of the acid on other organs is similarly antagonised by calcium salts and also by strontium salts. This does not depend on the removal of oxalic acid from the poisoned cells, but on the restoration of the constituents of the cells which are lost. Paralysis of the frog's heart by barium is antagonised by sodium sulphate. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Chemical and Biological Investigations on Slime-Producing Lactic Acid Bacteria. ROBERT BURRI and O. ALLEMANN (*Zeitsch. Nahr. Genussm.*, 1909, 18, 449—461).—Experiments are described in which sterilised milk was inoculated with the ordinary and the slime-producing forms of Freudenreich's *Bact. Güntheri*, and Jensen's acid *Streptococcus*, *Bacillus casei*- ϵ , and *B. casei*- δ . The soluble nitrogen, the nitrogen not precipitated by phosphotungstic acid, the nitrogen as ammonia, the volatile acids, the total acidity, and the lactose were determined. The results indicate that the two forms of the lactic acid bacteria are identical as regards the chemical effects produced.

The slime produced by the bacteria resembles chitin in its composition and reactions. N. H. J. M.

The Formation and Consumption of Nitrous Oxide by Bacteria. MARTINUS W. BEYERINCK and D. C. J. MINKMAN (*Centr. Bakt. Par.*, 1909, ii, 25, 30—63).—Nitrates are reduced by certain soil organisms in presence of organic matter and absence of air to

form nitrous oxide, nitrogen, and ammonia. Two organisms were observed by Gayon and Dupetit to bring about this change, and were designated α and β ; they are now identified by the author as *Bacillus pyocyaneus* and *B. Stutzeri* (= *B. nitrogenus*) respectively. The author has also isolated and described two other powerful nitrate-reducers, *Bacillus nitroxus*, a polymorphic spore former, which is probably the chief nitrate destroyer in the soil, and *Micrococcus denitrificans*. So vigorous is the process that, under favourable conditions, a stream of gas can be obtained containing 80% of nitrous oxide, and rekindling a glowing splint; this happens, for instance, when soil is inoculated with bouillon containing 5 to 12% of nitrate, and the mixture kept at 20—37°. If less nitrate is present, the gases contain more free nitrogen and less nitrous oxide. The chief agent is *B. nitroxus*. Of the other organisms examined, *B. pyocyaneus*, grown in bouillon with 1% of nitrate at 37°, evolved a gas containing 65—72% of nitrous oxide; *B. Stutzeri* evolved gas containing 10%, and *Micrococcus denitrificans* evolved gas containing 20% of nitrous oxide and 42% of nitrogen.

There can be little doubt that nitrous oxide is produced in the soil, and also that it is destroyed in some way. Experiments showed that the denitrifying organisms, especially *B. Stutzeri*, could decompose it, forming nitrogen and carbon dioxide; it also acts as the oxygen source for a *Spirillum*.

The author has added one more instance to the remarkable list of "chemosyntheses," namely, syntheses of complex cell-substances from carbon dioxide by living organisms without the aid of chlorophyll or sunlight. The necessary energy was obtained by the organism simultaneously absorbing, or else determining the action between, hydrogen and nitrous oxide mixed in equal proportions. The organism is somewhat like *B. Saussurei*, which also synthesises its organic matter from carbonates, but derives the energy from the union of hydrogen and oxygen that it can in some way bring about.

The culture solution consists of tap-water, 100 parts, dipotassium phosphate, 0.02 part, ammonium chloride, 0.02 part, and sodium hydrogen carbonate, 0.01 part. No organic matter is supplied. After inoculation, the whole is placed in an atmosphere of nitrous oxide and hydrogen, which is slowly brought into reaction as the organism develops.

E. J. R.

Biochemistry of Micro-organisms. I. Quantitative Estimation of Nitrate Fermentation. HARTWIG FRANZEN and E. LÖHMANN (*Zeitsch. physiol. Chem.*, 1909, 63, 52—102).—The amounts of nitrogen as nitrates and nitrites were estimated at intervals of twenty-four hours in broth cultures of different organisms containing 1.0119 gram of potassium nitrate (in 95 c.c.). The following numbers indicate (1) the amounts of nitrogen as nitrites, and (2) the losses as free (or ammoniacal) nitrogen, as percentages of the initial nitrogen.

The results show that *Bacillus Plymouthensis*, *B. prodigiosus*, *B. Kiliense*, *Proteus vulgaris*, *B. coli commune*, and *B. typhi murium* convert nitrates into nitrites without much further change; and that *B. pyocyaneus* not only reduces nitrates to nitrites, but at once

Days.		<i>Bacillus Plymouth- ensis.</i>	<i>B. pro- digiosus.</i>	<i>B. Kiliense.</i>	<i>B. pyo- cyaneus.</i>	<i>Proteus vulgaris.</i>	<i>B. coli commune.</i>	<i>B. typhi murium.</i>
1	{ 1.	25.59	42.39	29.59	1.73	32.04	32.18	21.83
	{ 2.	8.80	2.04	4.02	5.13	3.40	3.72	14.98
2	{ 1.	—	53.91	56.73	0.36	44.84	59.01	67.23
	{ 2.	—	2.07	6.15	15.14	4.36	6.80	5.44
3	{ 1.	56.24	54.44	58.51	0.33	47.19	67.83	92.07
	{ 2.	8.20	1.63	5.18	22.31	4.81	5.12	6.15
4	{ 1.	60.41	53.46	62.24	1.29	50.21	63.44	95.63
	{ 2.	8.26	2.30	3.69	28.69	4.14	3.84	4.37
5	{ 1.	69.38	53.35	—	1.42	52.39	63.16	94.90
	{ 2.	7.91	2.54	—	32.41	3.83	3.97	5.19

converts the nitrites into non-oxidised nitrogen. *B. fluorescens*
liquefaciens had no action on nitrates. N. H. J. M.

Enzymes which Produce Cleavage of Polysaccharides in the Expressed Juice of Fungi. HANS PRINGSHEIM and GÉZA ZEMPLÉN. Studies on the Amount of Oxydases in the Same. HANS PRINGSHEIM (*Zeitsch. physiol. Chem.*, 1909, 62, 367—385, 386—389).—The juices expressed from thirteen varieties of fungus (*Aspergillus*, *Mucor*, etc.) were tested with five disaccharides and one trisaccharide (raffinose); considerable variations exist between the different fungi as to the kind of sugar they are able to decompose; these are stated in detail.

The opportunity was also taken to test the juices for catalase, oxydase, and peroxydase; and, again, the results obtained differ with the various fungi. W. D. H.

The Theory of Disinfection. I. The Disinfecting Action of Phenol. HEINRICH REICHEL (*Biochem. Zeitsch.*, 1909, 22, 149—176, 177—199).—I. The partition of phenol between an oily and aqueous phase was investigated, and also the influence of the addition of sodium chloride on this distribution. The phenol was estimated in the water before and after the addition of the oil. From the numbers obtained, the author shows how the factor of distribution of the phenol between the two phases can be calculated when the contractions on mixture of phenol-water, phenol-oil, and other constants have been ascertained.

II. The coefficient of partition between phenol and the phases coagulated protein and water, both in presence and absence of varying quantities of sodium chloride, was investigated. The methods employed were similar to those described in the previous section. Coagulated egg-white and serum-albumen were employed and also *Bacterium pyocyaneus*. S. B. S.

A Comparison of the Germicidal Power of a Disinfectant in Solution and in the Emulsified State. R. E. MASSEY (*J. Hygiene*, 1909, 9, 341—346).—Martin and Chick's experiments (this vol., ii, 171) are considered invalid, because they failed to take into account the

influence of alcohol in decreasing germicidal activity. The present experiments with "tricrosol," however, confirm their conclusions regarding the superiority of a disinfectant in the emulsified state.

W. D. H.

Influence of Aluminium Salts on Protoplasm. M. FLURI (*Bied. Zentr.*, 1909, 38, 670—672; from *Flora*, 1908, 99, 81—126).—Cells of *Spirogyra* in presence of light are deprived of starch by dilute solutions of aluminium salts (0.003—0.01%); when the threads are afterwards placed in tap water, starch is again produced. Lanthanum and yttrium nitrates produce the same results as aluminium salts. The shortest time of the action of aluminium salts is two days with 0.01% solutions. No effect is produced in presence of dextrose, isodulcitol, or glycerol.

The loss of starch may be due to increased diastatic activity under the influence of aluminium salts, but is more probably caused by increased permeability of the plasma. Assimilation is not interrupted during the removal of the starch.

N. H. J. M.

Are the Amines Assimilable by the Higher Plants? MARIN MOLLIARD (*Compt. rend.*, 1909, 149, 685—687).—Lutz (Abstr., 1898, ii, 530) has brought forward facts which appear to show that plants are capable of directly assimilating amines of low molecular weight, such as methylamine. The experiments described in the present communication do not support this view. Radishes have been grown under conditions precluding the intervention of micro-organisms. In one series of experiments the plants were supplied with a solution containing all the elements necessary for their nutriment, except nitrogen; in a second series, calcium nitrate was supplied in addition, whilst the nutrient solution in the other series contained ammonium chloride, or the hydrochlorides of methylamine, dimethylamine, ethylamine, and propylamine. Parallel experiments were carried out, employing solutions containing 5% of dextrose in addition. It appears from the tabular statement given, that in the latter cases the plants increased considerably in weight when treated with calcium nitrate or ammonium chloride. The amines, however, showed a distinctly inhibitory influence on their growth.

W. O. W.

Fermentative Ammonia Cleavage in Higher Plants. WL. BUTKEWITSCH (*Zeitsch. physiol. Chem.*, 1909, 63, 102).—A reply to Kiesel (this vol., ii, 694).

N. H. J. M.

Origin and Physiological Function of Pentosans in Plants. C. RAVENNA and O. CERESER (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 177—183).—Experiments on dwarf beans yield the following results. No marked variation of the amount of pentosans is observed during the period of activity of the chlorophyll. During the night, however, the variations are considerable, and consist sometimes of increase and sometimes of diminution. When the carbohydrate food consists wholly of dextrose, administered to the leaves, the amount of

pentosans increases greatly, especially in the light. When the function of the chlorophyll in the leaves is prevented for a somewhat prolonged period, the amount of pentosans diminishes. The conclusion is drawn that the simple sugars, more than the complex carbohydrates, exert a preponderating influence on the formation of pentosans, which function as a reserve material when the plant has exhausted the more readily utilisable foodstuffs.

T. H. P.

The Physiological Significance of Certain Glucosides. TH. WEEVERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 193—201).—Quantitative experiments with *Salix purpurea* lead to the conclusion that catechol, after hydrolysis of salicin and transport to other parts of the dextrose thus formed, remains localised in the cell and again combines to form salicin with dextrose, which is brought from elsewhere or has been formed on the spot by assimilation. The relationship of arbutin and quinol in *Vaccinium vitis idaea* was investigated on similar lines. From young shoots of *Salix purpurea* were obtained a *salicase*, identical with neither emulsin nor amygdalase, a *saligenolase*, destroyed at 85°, forming catechol from salicyl alcohol, and a thermostable *catecholase*, which does not attack salicyl alcohol, but brings about very rapidly the oxidation of catechol to a black, insoluble substance.

Populus monilifera yields an enzyme, *populase*, which splits off benzoic acid from populin. This glucoside is not hydrolysed by the mixture of enzymes from *Salix purpurea*.

G. S. W.

Distribution of Sugar, Acid, and Tannin in Apples. W. KELHOFER (*Bied. Zentr.*, 1909, 38, 678—679; from *Landw. Jahrb. Schweiz*, 1908, 745—923).—Analysis of four varieties of apples showed that the highest percentage of sugar is in the flesh; that the acidity increases from the outside towards the centre, and the tannin from the centre outwards.

During ripening, the amount of acid decreased from 9.72 to 3.95%, whilst the tannin changed only slightly, increasing from 1.57 to 1.68%. The distribution of the three chief constituents is, on the whole, the same in unripe as in ripe apples.

N. H. J. M.

Existence of a Glucoside in the Olive. BARTOLO LINO VANZETTI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 188—190. Compare Körner and Vanzetti, *Abstr.*, 1903, i, 430; Power and Tutin, *Trans.*, 1908, 891, 904).—An alcoholic extract of young branches of the olive deposits, after a long time, mannitol and a micro-crystalline substance, which resembles a paraffin, but was not investigated. When the residual extract is dissolved in water, and the tannin, extractives, and colouring matters separated by dialysis, the dialysed liquid assumes a brilliant blue fluorescence, which recalls that exhibited by *æsculin* and other derivatives of hydroxycoumarin, and is rendered more evident by making the solution alkaline. The concentrated solution reduces Fehling's solution, and, when treated with excess of phenylhydrazine yields *d*-phenylglucosazone.

T. H. P.

Physiological Function of Hydrogen Cyanide in *Sorghum vulgare*. CIRO RAVENNA and M. ZAMORANI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 283—287).—The amino-acids being, according to present-day views, regarded as the compounds from which proteins are directly synthesised in plants, the authors consider that the passage of the nitrogen from nitrates to proteins is represented by the scheme: nitrates \rightarrow hydrogen cyanide \rightarrow amino-compounds \rightarrow proteins (compare Ravenna and Peli, *Abstr.*, 1908, ii, 217). Support for this view is accorded by examination of plants of *Sorghum vulgare*, to some of which asparagine has been administered as nitrogenous food-material. It is found that these plants contain considerably less hydrogen cyanide than those to which no asparagine was supplied. The asparagine added is regarded as being utilised in the plants, which could hardly live and develop during the period of the experiments (thirty to thirty-five days) on their reserve of nitrates alone.

T. H. P.

[Constituents] of *Vebernum dentatum*. CHARLES R. BLAKE (*Chem. News*, 1909, 100, 210).—The berries contain dextrose, lævulose, protein, tannin, malic acid, and two fixed oils, the one clear, the other dark green. The latter appeared to consist mainly of laurin. The ash of the berries contains, in addition to the usual constituents, manganese and chromium sesquioxides.

T. A. H.

Rôle of Oxidation in Soil Fertility. OSWALD SCHREINER and HOWARD S. REED (*U.S. Dept. Agric. Bureau of Soils, Bul.* 1909, 56).—Roots of growing plants have an extracellular oxidising power which is most energetic in the portions of the roots provided with root-hairs. Plants growing in extracts of productive soils show a greater oxidising power than those in extracts of unproductive soils.

Oxidation is usually promoted by treating the soil extracts with an absorbing agent, and is generally accelerated by addition of nitrates. Calcium salts and phosphates are beneficial, and chlorides and sulphates are also somewhat beneficial when combined with a suitable base, such as sodium. Ammonium sulphate is less beneficial than the same amount of nitrogen in the form of nitrate. Organic toxic substances are extremely injurious to oxidation; their action is diminished by the presence of nitrates.

The process of oxidation is largely, if not entirely, due to the activity of a peroxydase produced by the roots. The enzyme is most active in neutral or slightly alkaline solutions, whilst its action may be inhibited by the presence of acid, and by conditions in which putrefaction processes occur.

N. H. J. M.

Phosphate Availability in Relation to Soil Activity. CHARLES W. STODDART (*Univ. Wisconsin Agric. Exper. Stat. Research Bul.*, 1909, No. 2, 50—60).—Acid soils were found to be deficient in available phosphorus, the phosphoric acid being combined with iron and aluminium to a greater extent than in normal soils.

Extraction with *N*/5 nitric acid for five hours at 40° was found to be very suitable for determining available phosphoric acid,

the calcium phosphate being dissolved and very little besides. The humus of acid and of non-acid soils was found to contain about the same amounts of phosphorus; the amount of humus generally decreases as the percentage of phosphorus in the humus increases. Indications were obtained that the phosphorus of humus may be unavailable to plants.

N. H. J. M.

Behaviour of Cereals towards Calcium Cyanamide. SANTE DE GRAZIA (*Bied. Zentr.*, 1909, 38, 712—713; from *Staz. sper. agrar. ital.*, 1908, 41, 657).—Experiments with wheat grown in a clayey soil showed that calcium cyanamide may be used in large amounts when applied three weeks before sowing the seed.

N. H. J. M.

Can Sodium Nitrate be Replaced by Calcium Nitrate for Sugar Beet? JULIUS STOKLASA (*Chem. Zentr.*, 1909, ii, 1489; from *Zeitsch. landw. Versuchswesen Oesterr.*, 1909, 12, 627—636).—Sodium nitrate gives higher yields of roots and of sugar than calcium nitrate. It is considered probable that sodium can partly take the place of potassium, although not in the synthesis or breaking down of carbohydrates.

N. H. J. M.

Amount and Composition of the Drainage Waters Collected During the Year 1908-9. BRYCE C. BURT (*Rep. Cawnpore Agric. Stat.*, for the year ending June 30th, 1909, 22—23. Compare this vol., ii, 261).—The total amounts of rain and drainage, and of nitrogen as nitrates in the drainage, from June 1st to October 31st were as follows:

No.	Depth of soil, inches.	Rainfall, inches.	Drainage, inches.	Nitrogen as nitrates.	
				Per million.	Lbs. per acre.
1.	72	31·53	14·154	31·96	102·38
2.	72	31·53	13·952	33·67	106·29
3.	36	31·53	15·205	18·80	64·70
4.	36	31·53	15·725	16·08	57·23

As in previous years, the soil was kept free from vegetation and was frequently hoed.

N. H. J. M.

Analytical Chemistry.

A Device for Preventing Over-Titrating. FERDINAND SCHULZ (*Chem. Zeit.*, 1909, 33, 1187).—In the liquid to be titrated is placed an open tube about 12—15 mm. in diameter, and the titration is carried out as usual whilst rotating the beaker. The column of liquid inside the tube has, however, not yet been acted on, so by using the tube as a stirrer, the two liquids mix and any over titration will be again neutralised. The last drops of the volumetric solution are then added very cautiously.

L. DE K

Porcelain Gooch Crucibles with a Layer of Spongy Platinum. HENRI J. F. DE VRIES (*Chem. Weekblad*, 1909, 6, 816—818. Compare Abstr., 1907, ii, 504, 719; 1908, ii, 430, 534; Brunck, this vol., ii, 826).—A claim for priority. The crucible described by Brunck has been employed by the author for two and a-half years. The method of preparing the platinum layer is described.
A. J. W.

Detection of Traces of Chlorides in Gelatin. LÜPPO-CRAMER (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 249—250).—The smallest trace of chloride can be detected in gelatin if a 10% solution is dried on a glass plate, and a drop of 10% silver nitrate placed thereon. Sodium chloride present to the extent of 0.001% of dry gelatin gives a white ring, 1—2 cm. in diameter, round the drop. The reaction can be used quantitatively if standards are made from chloride solutions and carefully washed gelatin. On exposing the gelatin film so treated to light, the ring turns bluish-, and the colourless space under the drop reddish-yellow. This indicates that silver chloride is present in both, but in a finer state of subdivision in the latter. The author has shown that the thickening ("reifung") of the haloid salts in a gelatin plate is due to excess of halogen, and not to excess of silver. The ring is formed where the diffusing colloidal silver chloride arrives at a region where halogen is in excess.
G. S. W.

The Presence of Iodate in Commercial Potassium Iodide. LAUNCELOT W. ANDREWS (*J. Amer. Chem. Soc.*, 1909, 31, 1039—1039).—The author states that the general belief as to the presence of iodate in commercial potassium iodide is not justified, and that if any is present its amount cannot exceed 20 parts per million. The blue colour which some samples give on adding starch paste and dilute hydrochloric acid is not necessarily due to iodate, but may be due to traces of iron oxide or cuprous oxide in presence of dissolved oxygen.

Potassium hydrogen tartrate in solutions free from air does not give the reaction with those impurities, and is therefore preferable to hydrochloric acid. A convenient arrangement for carrying out the test is described.
L. DE K.

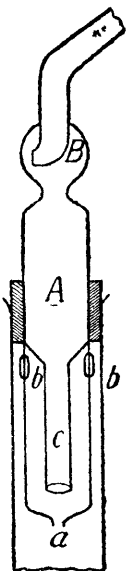
Photo-electric Measurement of Small Ozone Concentrations. Efficiency of Goldstein's Ozonisation Process at Great Dilutions. WILHELM HALLWACHS (*Ann. Physik*, 1909, [iv], 30, 602—606).—It is shown that small quantities of ozone can be estimated photo-electrically by reason of the large specific absorptive power of the gas for ultra-violet radiation of wave-length in the neighbourhood of 258μ . For such measurements the pressure of the gas in the absorption tube should be of the order of 0.01 mm. of mercury. Attempts to prepare ozone from oxygen by Goldstein's process indicated that this process is ineffective at very low pressures.
H. M. D.

Bulb Trap for Nitrogen Estimations by the Methods of Kjeldahl and Others. FR. DUDY (*Chem. Zeit.*, 1909, 33, 1158).—By using the following arrangement, all danger of any alkaline

liquid from the distilling flask getting into the standard acid is avoided.

A is a cylindrical tube of a suitable diameter. At *a* it has an opening of 1 mm., and at *b*, one of 5 mm. To the cylinder is sealed the funnel-shaped tube *c*, which has a diameter of about 5 mm. *B* is the usual bulb. On account of the great width of the tube *A*, a wide piece of rubber, not too thin, is used to connect the tube to the distilling flask.

L. DE K.



Estimation of Total Nitrogen by the Kober Method. F. W. GILL and HARRY S. GRINDLEY (*J. Amer. Chem. Soc.*, 1909, 31, 1249—1252. Compare Sebelien, Brynildsen, and Haavardsholm, this vol., ii, 757).—Kober (Abstr., 1908, ii, 776) has described a modification of the Kjeldahl method, in which the ammonia is expelled by adding excess of alkali, and passing a current of purified air through the solution. Experiments have now been carried out which show that the process is well suited to the estimation of nitrogen in organic materials, except when magnesium and phosphorus are both present in comparatively large quantities. In the latter case, the total nitrogen can be accurately estimated if the solutions are kept warm during the passage of the current of air.

E. G.

Estimation of Nitrogen in Nitrates and Nitrites. VINCENT SCHENKE (*Chem. Zeit.*, 1909, 33, 1203).—A reply to Mitscherlich (Abstr., 1909, ii, 614). Contrary to Mitscherlich's statement, the author remarks that nitrates may be completely reduced in acid solution.

L. DE K.

Detection of Nitrates in Presence of Oxidising Substances (Chlorates, Bromates) and Iodides and Bromides. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1909, 14, 413—414; *Bull. Assoc. Chim. Sucr. Dist.*, 1909, 27, 367—368).—The solution containing the above salts is introduced into a distilling flask with a large excess of sodium hydroxide. The flask is fitted with a cork, through which passes a large tube bent at right angles. (If ammonium salts should be present, the ammonia should be completely expelled by boiling.) Two or three grams of zinc dust are added, and the whole is boiled gently. The vapours are received in a conical flask containing Nessler solution, and the least trace of nitrates will then be detected by the brown coloration.

L. DE K.

Irregularities in the Titration of Arsenic after Previous Distillation. LEOPOLD BRANDT (*Chem. Zeit.*, 1909, 33, 1114—1115).—The process generally used for the estimation of arsenic in iron ores or steel (conversion into ferric sulphate by evaporation with nitric and sulphuric acids, and distilling the dry mass with fuming hydrochloric acid with addition of ferrous sulphate) is attended with a number of

slight errors, which may, however, be readily avoided. No condensing apparatus should be used, but the delivery tube, carrying a bulb and drawn out to a narrow point, dips into a large beaker containing water, which completely absorbs the acid fumes, and, consequently, the arsenic chloride; the beaker is kept cool by being placed in a larger beaker containing cold water. When distillation is finished, the contents of the beaker are neutralised with ammonia free from pyrrole; sodium hydroxide cannot be recommended on account of such frequent impurities as nitrites, chlorates, etc. After adding solution of sodium hydrogen carbonate, the arsenic is titrated with *N*/10-iodine, using 5 c.c. of a 2% freshly prepared starch solution as indicator; starch containing zinc iodide as preservative must not be used, as this causes precipitation of zinc arsenite. Pyrrole-free ammonia may be readily obtained by tinging ammonia with permanganate, and afterwards decanting from the deposit formed. L. DE K.

Electrolytic Detection of Arsenious Oxide in Presence of Arsenic Acid. ERCOLE COVELLI (*Chem. Zeit.*, 1909, 33, 1209).—Thirty c.c. of the liquid to be tested are mixed with excess of potassium hydroxide and placed in a U-tube, into the limbs of which are placed two platinum foils, which are connected with the poles of a Grove cell. In the cathode limb is suspended a strip of paper impregnated with silver nitrate, and if arsenious oxide is present, even in fractions of a mg., a decided brown coloration will be noticed in a time varying from a few minutes to an hour.

Arsenates are not affected.

L. DE K.

The Detection of Arsenic Acid in the Presence of Arsenious Acid by means of Magnesia Mixture. OSCAR LUTZ and R. SWINNE (*Zeitsch. anorg. Chem.*, 1909, 64, 298—301).—Arsenious acid has been stated to give a magnesium salt which is not readily separated from the arsenate.

Experiments with solutions of different concentrations show that a qualitative or quantitative separation is not possible, although the precipitation of the arsenite is greatly hindered by the presence of large quantities of ammonium salts. Under these conditions, however, the precipitation of the arsenate also becomes incomplete.

C. H. D.

Analysis of Orpiment. M. CAFFIN (*Collegium*, 1909, 26, 225—226).—An application of Pearce's method for estimating arsenic in minerals. The substance is fused with potassium nitrate and sodium carbonate, whereby sulphur is oxidised to sulphuric acid and arsenic to alkali arsenate. The solution is made up to a convenient volume, the arsenic precipitated and collected as silver arsenate, redissolved, and titrated with ammonium thiocyanate. Sulphur is estimated as barium sulphate in a different portion of the original solution. F. M. G. M.

Modification of the Reduction Process for Copper Spirals Used in Organic Combustions. ADRIANO OSTROGOVICH (*Chem. Zeit.*, 1909, 33, 1187).—The red-hot spirals are introduced quickly into a

long tube made of hard Jena glass open at one end. At the bottom is placed a little asbestos, which is moistened with a little methyl alcohol. A perforated cork fitted with a glass tube is inserted, and the tube connected with a pump, which is kept working until the tube has quite cooled down. The spirals will then be found to have been completely reduced.

L. DE K.

Replacement of the Platinum Capillaries in the Estimation of Carbon in Iron by the Chromic Acid Method. MAX WIDEMANN (*Chem. Zeit.*, 1909, 33, 1186).—The author dispenses with the platinum capillaries, but uses instead a silica tube 30 cm. long and 10 mm. in diameter, the walls being 1 mm. thick, which is filled with platinum cuttings. The tube is placed on an asbestos felt and heated with a Heinz burner. A complete combustion of any hydrocarbons is thus secured.

L. DE K.

Rapid Estimation of Sodium Hydrogen Carbonate in Presence of Sodium Carbonate. BERTHOLD LÖWINGER (*Chem. Zeit.*, 1909, 33, 1174).—A solution of sodium hydroxide is mixed with a little barium chloride to remove any carbonate, and the liquid is then at once standardised with hydrochloric acid, using phenolphthalein as indicator. To the solution to be examined is then added a definite volume of the standardised alkali, and the sodium carbonate formed from the acid carbonate plus that pre-existing is then precipitated by adding barium chloride. The alkalinity is then taken as before and the difference in the titrations represents the sodium hydrogen carbonate.

L. DE K.

Estimation of Calcium Oxide in Presence of Calcium Carbonate, etc. HEYER (*Chem. Zeit.*, 1909, 33, 1157—1158).—Calcium oxide may be separated from calcium carbonate by means of a 1% solution of ammonium chloride or nitrate, to 1 litre of which 48 c.c. of ammonia, D 0.910, have been added. If no free ammonia is added, a small portion of the carbonate also dissolves. The results are sufficiently accurate for technical purposes.

L. DE K.

Estimation of Magnesium Chloride in Waters. HERMANN EMDE and RICHARD SENST (*Zeitsch. angew. Chem.*, 1909, 22, 2236—2238. Compare Abstr., 1909, ii, 940).—A further series of experiments proving conclusively that, on heating magnesium salts with chlorides at 500—520°, magnesium chloride is formed, and a loss of chlorine consequently takes place. Pfeiffer's method, which is based on the decomposition of pre-existing magnesium chloride by heat, is therefore quite untrustworthy. If heated at a lower temperature, the decomposition of magnesium chloride is incomplete.

L. DE K.

Estimation of Zinc as Pyrophosphate. RALPH W. LANGLEY (*J. Amer. Chem. Soc.*, 1909, 31, 1051—1052).—A simplification of the process usually employed. To the zinc solution, which should be made neutral to litmus by means of ammonia, is added an excess of ammonium phosphate. After heating for some time on a steam-

bath, the precipitate is collected on a porcelain Gooch crucible, washed five times with cold water, and ignited to constant weight.

L. DE K.

Volumetric Estimation of Lead with Potassium Permanganate. HERMANN BOLLENBACH (*Chem. Zeit.*, 1909, 33, 1142—1143).—A slight modification of the author's previous process.

The lead solution is poured into a hot alkaline solution of potassium permanganate, standardised by means of lead nitrate, and the excess of permanganate is then titrated with the same lead solution (compare Abstr., 1908, ii, 68).

In order to cause the precipitate formed to settle more rapidly, an addition was made of some barium sulphate. This, however, has since proved to be unsatisfactory, and addition of 2 to 5 grams of potassium nitrate is now recommended.

L. DE K.

An Application of Graded Potentials to Ore Analysis. DANIEL F. CALHANE and J. C. WOODBURY (*J. Amer. Chem. Soc.*, 1909, 31, 1048—1051).—A process devised for analysis of native lead carbonate, containing also a little silver and copper, besides other impurities. Two grams of the sample are dissolved in nitric acid, and, after neutralising the liquid, 30 c.c. of nitric acid, D 1.42, are added, and the whole is diluted to 250 c.c. Twenty-five c.c. are then taken for analysis by electrolysis.

With an *E.M.F.* of exactly 1.4 volts, the silver is deposited after two hours, and may then be weighed. The electrolysis is then continued overnight at 2 volts, so as to obtain the copper and the lead, which is precipitated as peroxide on the anode. It is very important that the voltage should never exceed 2 during the operation, as otherwise the deposition of the lead peroxide and the copper is incomplete.

L. DE K.

Electrolytic Estimation of Thallium. GILBERT W. MORDEN (*J. Amer. Chem. Soc.*, 1909, 31, 1045—1048).—Thallium may be estimated electrolytically by using a mercury cathode and rotating anode, but it is advisable to use, instead of pure mercury, a very dilute zinc or cadmium amalgam. A stable non-oxidisable thallium amalgam is thus obtained.

L. DE K.

Estimation of Cuprous Oxide in Copper and its Alloys. RICHARD HENRY GREAVES (*Chem. News*, 1909, 100, 233—235).—The estimation of cuprous oxide by solution in ammonia as described in the method proposed by Coffetti (this vol., ii, 349) was found to give trustworthy results in the case of pure copper. When arsenic is present, the results are too high, but an approximate correction may be calculated from the amount of arsenic dissolved, on the assumption that it dissolves as arsenate; the same applies to antimony. Commercial copper contains, however, but little, if any, antimony or iron, and errors resulting from the presence of these two metals will be small in practice. The process may be applied to brass and bronze, but, in the case of the latter, the method is not of much use, as the

oxygen exists mainly as metastannic acid, and it is this substance which exerts the deleterious influence on the properties of the alloy. The author employs a modification of the apparatus described by Coffetti; instead of a vertical tube, a horizontal one is used. The metal is introduced through a side-tube at the middle of the main tube, this side-tube also serving as the inlet for the ammonia solution after the apparatus has been filled with hydrogen saturated with ammonia. A tube at one end of the main tube serves for the introduction of the hydrogen, whilst one at the other end acts as an outlet for the gas and liquid.

W. P. S.

Detection of Mercury in Urine according to Almén. CONRAD STICH (*Pharm. Zeit.*, 1909, 54, 833).—In Almén's process the urine is boiled with sodium hydroxide and dextrose, and the precipitate, which contains all the mercury, is then boiled with hydrochloric acid and a piece of copper or brass wire. This, on being heated in a narrow glass tube, gives a sublimate of metallic mercury, which may be recognised as such under the microscope.

The author prefers using very thin pieces of copper foil instead of the wire. These are heated afterwards on the convex part of an object glass, on which is placed another object glass to receive the mercurial sublimate. This may be further identified by placing it over another object glass, on the convex part of which a drop of tincture of iodine has been allowed to evaporate. Soon the mercury is changed to the iodide, which has a characteristic appearance under the microscope. By using "standards," an idea as to the amount of mercury present may be obtained.

L. DE K.

Estimation of Iron in Water. KLUT (*Chem. Zentr.*, 1909, ii, 1076—1077; from *Mitt. K. Prüfgs.-Anst. Wasserversorg Abwasserbeseit.*, 1909, 12, 174—182).—Five hundred to one thousand c.c. of the sample are concentrated to 150—200 c.c., and boiled with 2—3 c.c. of strong nitric acid. The iron is then precipitated with ammonia, washed, and redissolved in hydrochloric acid. It is estimated colorimetrically by means of ferrocyanide, or, preferably, thiocyanate. The process does not work well with waters charged with peaty matter; in this case, the organic matters must be got rid of by burning.

L. DE K.

Rapid Estimation of Vanadium in Ores and Technical Products. EUGENIO PIÑERÚA ALVAREZ (*Chem. Zeit.*, 1909, 33, 1149).—The finely-powdered material (about 0.5—1 gram) is fused with seven to eight times its weight of pure sodium peroxide for fifteen to twenty minutes at a red heat. When cold, the mass is treated with boiling water and the filtrate acidified with sulphuric acid. Alcohol is then added, and, without taking notice of any precipitate, a current of sulphur dioxide is passed for some time. Any undissolved matter is removed by filtration, and the liquid is freed from alcohol and excess of sulphur dioxide by heating and passing a current of carbon dioxide. If arsenic should be present, this must be removed by means of hydrogen sulphide, and, after boiling the filtrate

to expel the excess of that gas, the vanadium is titrated (in a 1% solution) with standard permanganate. This should be checked with a 1% solution of ammonium metavanadate, after first expelling the ammonia with sodium hydroxide and then reducing the solution by boiling with sulphuric acid and sulphur dioxide under similar conditions to those described.

L. DE K.

Assay of Oil of Turpentine by Bromine; Estimation of Free Bromine by Sodium Formate. MANSIER (*Ann. Chim. anal.*, 1909, 14, 417—421).—One c.c. of the sample is placed in a stoppered flask and dissolved in 5 c.c. of chloroform; 50 c.c. of 3% bromine water are then added at once, and the whole is well shaken. More bromine water is added with constant shaking until the last drop causes the chloroform to turn yellow. One c.c. of pure oil of turpentine absorbs 1.69 grams of bromine. If less is required, the presence of petroleum may be suspected and its amount calculated.

A new method is given for checking the bromine solution; 10 c.c. of sodium formate (1.6125 grams per litre) are placed in a flask, and 0.10 gram of precipitated zinc oxide is added. The bromine solution is then run in until the liquid turns yellow. One mol. of sodium formate = 2 atoms of bromine. On account of the action of bromine on zinc oxide and the amount required to colour the water, a correction of 0.018 gram must be applied.

L. DE K.

[**Estimation of Phenol and *p*-Cresol in Urine.**] W. MOOSER (*Zeitsch. physiol. Chem.*, 1909, 63, 155—200).—See this vol., ii, 1039.

Ultramicroscopical Studies. J. AMANN (*Chem. Zentr.*, 1909, ii, 1076; from *Schweiz. Woch. Chem. Pharm.*, 1909, 47, 480—483).—The reduction of Fehling's solution, observed under the ultramicroscope, is a neat and delicate reaction, it being obtainable with a solution containing 0.00001 gram of dextrose per c.c. The Fehling solution of the Swiss Pharmacopoeia, which contains glycerol, cannot, however, be used in this case; the formation of osazone by means of phenylhydrazine is also readily observed by means of the instrument.

L. DE K.

Clinical Detection of Dextrose in Urine by *o*-Nitrophenylpropionic Acid. H. BORTU (*Chem Zentr.*, 1909, ii, 1280; from *Bull. Sci. Pharmacol.*, 1909, 16, 399—401).—3.5 Grams of powdered *o*-nitrophenylpropionic acid are dissolved in 50 c.c. of 10% sodium hydroxide and diluted to 1000 c.c. Eight c.c. of the reagent are mixed in a test-tube with 20—25 drops of urine, and the upper layer is heated to boiling. Another 1 c.c. of urine is then added drop by drop. In the presence of dextrose a blue coloration and precipitate, due to indigotin, will be noticed. If the blue colour appears before the second portion of the urine is added, the amount of dextrose is sure to exceed 1%.

L. DE K.

Detection of Biliary Acids, Lævulose, Glycuronic Acid, and Pentoses in Urine. F. WITTELS and N. WELWART (*Chem. Zeit.*, 1909, 33, 1133).—An adverse criticism of Jolles's proposed modifications (compare *ibid.*, 1908, 32, 917) of the Ihl-Pechmann's process for the detection of lævulose, of Tollens's glycuronic acid test, and Bial's pentose reaction as applied to urines. The original methods are recommended.

L. DE K.

Estimation of Carbohydrates in Foods. P. C. DEN HERDER (*Pharm. Weekblad*, 1909, 46, 1306—1312).—In no case should the balance in the analysis of food products be called starch; starch should be estimated in the residue insoluble in cold water by inversion with 2% hydrochloric acid. Sugar should be inverted by Clerget's process, for, if inverted by boiling, a very serious loss (up to 30%) may occur. There is generally a deficit in the full analysis, but this may be checked to some extent by determining the portion soluble in cold water (freed from albumin) and allowing for sugars present; in a well-conducted analyses the residue should be fairly equal to the deficit in the full analysis.

For the separation of dextrin and soluble starch, it is recommended to evaporate the aqueous solution, obtained in due course, to about 10 c.c.; the dextrin, etc., is then precipitated by first adding 40 c.c. of methyl alcohol and then 160 c.c. of 95% ethyl alcohol. The alcoholic solution retains the sugars.

In these kind of analyses, it is advisable first to make a qualitative analysis; the operations may then very often be considerably shortened.

L. DE K.

Direct Detection of Formaldehyde in Leaves; Formaldehyde Reagents. THOMAS BOKORNY (*Chem. Zeit.*, 1909, 33, 1141—1142, 1150—1151).—A review of the various reagents proposed for the detection of formaldehyde, and of the attempts made up to the present to apply a direct microchemical test for that substance in leaves in which, according to recent theory, it is supposed to occur as an intermediary compound.

The author remarks that the reagents used are either too caustic or else too poisonous. The leaf, being killed, cannot go on generating formaldehyde, and the quantity already present is too small to be detected with certainty. It is also doubtful whether the distillation process yields better results.

L. DE K.

Estimation of Formic Acid. HARTWIG FRANZEN and G. GREVE (*J. pr. Chem.*, 1909, [ii], 80, 368—389).—Gravimetric methods, based on the reduction of mercuric chloride by formic acid, only yield quantitative results when the hydrochloric acid formed during the reaction is neutralised as the reduction proceeds; if this is done, the amount of mercurous chloride precipitated is equivalent to the quantity of formic acid present. The method is applicable to the estimation of formic acid in very dilute solution if the following details as to procedure are carried out. The formic acid solution, containing from 0.2 to 1.0 gram of the acid per litre, is treated with mercuric chloride

dissolved in hot water, the quantity added being fifteen times the amount required by the equation: $\text{HCO}_2\text{H} + 2\text{HgCl}_2 = \text{CO}_2 + 2\text{HCl} + \text{Hg}_2\text{Cl}_2$. The mixture is maintained at a temperature of about 100° for thirty minutes, then neutralised by the addition of sodium hydroxide solution, again heated for about thirty minutes, and once more neutralised. The neutralisation is carried to the point where mercuric oxide begins to be precipitated. When the precipitate of mercurous chloride has settled completely, 20 c.c. of concentrated hydrochloric acid are added to re-dissolve the mercuric oxide; the heating is continued for one hour, and the precipitate is then collected on a weighed filter; it is washed with hot water, dried for six to eight hours at 100° , then kept in a vacuum for about fifteen hours over sulphuric acid and potassium hydroxide, and weighed. The weight of the precipitate multiplied by 0.097726 gives the weight of the formic acid present. It is also shown that formic acid may be removed from a solution by steam-distillation in the presence of phosphoric acid. The distillation must be continued until 10 c.c. of the distillate do not require more than half a drop of *N*/10-barium hydroxide solution for neutralisation.

W. P. S.

Volumetric Estimation of Thiocyanic Acid with Permanganate; its Application to Volumetric Estimation of Copper. G. MASINO (*Chem. Zeit.*, 1909, 33, 1173—1174, 1185—1186).—An investigation of the permanganate process for the estimation of thiocyanic acid and indirect estimation of copper. The author confirms the results obtained by Klason, and by Grossmann and Hölter, which showed that thiocyanic acid is not oxidised quantitatively by permanganate, a residue being left, the amount of which increases with the dilution. If, in order to avoid this, solutions of greater concentration are used, a still greater source of error is introduced, owing to the difficulty of accurately measuring the liquids. In using this process, the standardisations and the actual analysis should, therefore, be carried out under exactly similar conditions. Hydrochloric acid solutions are preferred.

L. DE K.

Estimation of Salicylates. ATHERTON SEIDELL (*J. Amer. Chem. Soc.*, 1809, 31, 1168—1178).—After criticising unfavourably the bromate method of Freyer, and the iodine method of Messinger and Vortmann, the author proposes the following process. The salicylate is added to a known volume of standardised solution of bromine in strong hydrochloric acid, which causes the salicylic acid to be precipitated completely as a dibromo-compound, and the excess of bromine is then titrated with standard stannous chloride as usual.

L. DE K.

Silver Cyanamide. H. RUSSELL ELLIS (*Chem. News*, 1909, 100, 154—155).—In Perotti's method for the estimation of cyanamide in sodium cyanamide and in "nitrolime" (*Abstr.*, 1905, ii, 870), any sulphide, cyanide, or chloride which may be present as impurity is thrown down with the cyanamide in the precipitation with silver nitrate, and an incorrect result is obtained.

The author puts forward the following methods: 1. Estimation of cyanamide and cyanide in sodium cyanamide.—From an aqueous solution of the substance, the cyanide is precipitated by excess of silver nitrate in the presence of nitric acid. After washing the precipitate of silver cyanide, it is dissolved in nitric acid, and the silver estimated by titration with ammonium thiocyanate. The filtrate and washings from the silver cyanide are run into a slight excess of ammonium hydroxide solution and the solution warmed. A precipitate of silver cyanamide is obtained; this is dissolved in nitric acid, and the silver estimated by titration. From the silver in each case, the percentage of cyanide and cyanamide can be determined.

2. Estimation of "Nitrolime."—One to two grams of the finely powdered substance are shaken up with water, and filtered into a 500 c.c. flask, the residue being well washed until the filtrate gives no precipitate with ammoniacal silver nitrate solution. An aliquot portion of this solution is precipitated by excess of ammoniacal silver nitrate. The precipitate is well washed with warm water, and then treated with dilute nitric acid (1 : 5), in order to remove all the silver cyanamide.

The silver in the filtrate and washings is then estimated by titration. Any sulphide or chloride of silver remains on the filter paper. Any fluoride present in the cyanamide will not dissolve in water, or if any dissolves, it is not precipitated.

The above methods assume that silver cyanamide has the formula Ag_2CN_2 . To verify this, the pure salt was prepared from "nitrolime" and analysed. The percentage of silver was determined (a) by heating, and weighing the silver left, (b) by dissolving the salt in nitric acid and estimating the silver with ammonium thiocyanate. The results are in agreement with the formula Ag_2CN_2 , and not with AgHCN_2 , although the two methods do not give the same percentage of silver—84.48 in (a) and 83.3 in (b).

When silver cyanamide is heated, it explodes more or less violently. The gases formed by the explosion were found to be cyanogen and nitrogen. Quantitative estimations indicated that the decomposition occurs in accordance with the equation: $2\text{Ag}_2\text{CN}_2 = 4\text{Ag} + \text{C}_2\text{N}_2 + \text{N}_2$.
T. S. P.

The Detection and Method of Formation of Aromatic Substances in the Organism. I. Detection of Indole and Scatole. FERDINAND BLUMENTHAL, FRIEDRICH HERSCHMANN, and ERNST JACOBY (*Biochem. Zeitsch.*, 1909, 19, 521—533).—The various reactions for the identification of indole and scatole were investigated. The *p*-dimethylaminobenzaldehyde reaction can be employed to distinguish between the two substances if nitrite is added. Scatole on addition of nitrite gives a bluish colour, whereas indole gives a more orange colour. By this reaction indole and scatole can be detected in mixtures. The other reactions investigated were (a) the vanillin reaction, which is not suitable for detecting the two substances when both are present; (b) the *p*-nitrobenzaldehyde reaction, by means of which both can be detected when scatole is present in relatively high concentration; and (c) the protocatechualdehyde reaction, which is not applicable for detection of the mixtures; the heliotropin, the

safrole, cinnamaldehyde, eugenol, glyoxylic acid and other reactions were also investigated. S. B. S.

Chemistry of Urine. L. DE JAGER (*Zeitsch. physiol. Chem.*, 1909, 62, 333—346).—This paper treats of two subjects: (1) the boiling test for albumin in urine, and its fallacies, especially in relation to the reaction of the urine, and the precipitability of certain phosphates on heating, and (2) the incorrectness of ammonia estimations by the "formaldehyde method" recently introduced; as others have pointed out, amino-acids also react with the reagent.

W. D. H.

Volumetric Estimation of Caseinogen in Cow's Milk. EDWIN B. HART (*J. Biol. Chem.*, 1909, 6, 445—451).—The caseinogen is precipitated by acetic acid, washed on the filter with cold water, then returned to the flask with the filter, dissolved in *N*/10-potassium hydroxide diluted with water free from carbon dioxide, and titrated with *N*/10-acid, using phenolphthalein as indicator. A correction is made for the acidity of a blank experiment, and the amount of acid used is a measure of the quantity of caseinogen. The whole process occupies less than two hours.

W. D. H.

Employment of Hydrogen Peroxide in Investigations on Oxydases. T. KIKKOJI and CARL NEUBERG (*Biochem. Zeitsch.*, 1909, 20, 523—525).—The employment of hydrogen peroxide and iron salts for the detection of oxydases is often resorted to. The authors show that phenol and twenty-five other substances, of which a list is given, yield, in presence of iron salts with the peroxide, dark colours or precipitates. The pigmented substance from phenol was prepared in quantity, and differed from melanins in that it contained 12.60—14.32% iron.

S. B. S.

A Reaction for Acid Soils. OSCAR LOEW (*Zeitsch. landw. Versuchswesen Oesterr.*, 1909, 461—463).—The soil (10 grams) is heated on a water-bath for five to ten minutes with 10 c.c. of a 1% solution of potassium iodide. A few drops of a 1% solution of potassium nitrite are added, and then a few drops of starch solution, after which it is quickly cooled.

The blue coloration may sometimes be produced in absence of potassium nitrite with soils containing basic ferric salts (a very intense reaction was obtained with so-called colloidal ferric hydroxide which contained basic ferric chloride). The presence of basic ferric sulphate in such soils can be established by extracting several times with boiling water, digesting with ammonia, evaporating the ammoniacal filtrate, and treating with barium chloride and hydrogen chloride.

N. H. J. M. J